



Spintronics based on heterostructures of 2D and 2D ferromagnetic materials

Frederic Brunnett

► To cite this version:

Frederic Brunnett. Spintronics based on heterostructures of 2D and 2D ferromagnetic materials. Condensed Matter [cond-mat]. Université Paris-Saclay, 2025. English. ⟨NNT : 2025UPASP055⟩. ⟨tel-05702652⟩

HAL Id: tel-05702652

<https://theses.hal.science/tel-05702652v1>

Submitted on 23 Jul 2026

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Spintronics based on heterostructures of 2D and 2D ferromagnetic materials

Spintronique à base d'hétérostructures de matériaux 2D et 2D ferromagnétiques

Thèse de doctorat de l'université Paris-Saclay

École doctorale n°564, Physique en Île-de-France (PIF)

Spécialité de doctorat: Physique

Graduate School: Physique. Référent: Faculté des Sciences d'Orsay

Thèse préparée dans l'unité de recherche **Laboratoire Albert Fert (CNRS, Thales, Université Paris-Saclay)**, sous la direction de **Pierre SENEOR**, professeur à l'Université Paris-Saclay, et la co-direction de **Bruno DLUBAK**, chercheur CNRS.

Thèse soutenue à Paris-Saclay, le 16 Juillet 2025, par

Frederic BRUNETT

Composition du Jury

Membres du jury avec voix délibérative

Aurélien MANCHON

Professeur, Aix-Marseille Université,
CINaM

Président

Ilaria BERGENTI

équiv. Maître de conférence (HDR),
Università di Bologna
CNR, ISMN

Rapporteur & Examinatrice

Daniel LACOUR

Directeur de recherche, CNRS,
Université de Lorraine,
Institut Jean Lamour

Rapporteur & Examineur

Jean-Christophe LE BRETON

Chargé de Recherche, CNRS,
Université de Rennes

Examineur

Titre: Spintronique à base d'hétérostructures de matériaux 2D et 2D ferromagnétiques

Mots clés: spintronique, matériaux 2D, jonction à effet tunnel magnétique

Résumé: Les matériaux bidimensionnels (2D) ont ouvert la voie au développement de dispositifs spintroniques de nouvelle génération. Parmi eux, les 2D ferromagnétiques récemment découverts, en particulier la famille FexGeTe_2 (FGT), offrent des fonctionnalités prometteuses en raison de leur magnétisme intrinsèque contrôlable par effet de grille et de leur potentiel à atteindre des températures de Curie élevées, bien supérieures à la température ambiante. Malgré cette promesse, une caractérisation complète de leurs propriétés spintroniques, même pour le Fe_3GeTe_2 relativement bien étudié, et une compréhension plus approfondie des autres phases du FGT restent largement inexplorées.

Dans ce travail, nous présentons la première caractérisation du Fe_3GeTe_2 (à aimantation perpendiculaire) intégré dans une jonction tunnel magnétique (MTJ) conventionnelle. Ceci a été réalisé en utilisant du Fe_3GeTe_2 exfolié et une multicouche Co/Pt, comme analyseur de spin de référence avec une polarisation de spin bien définie. Un processus de fabrication dédié, réalisé dans des conditions inertes et incorporant un dépôt de couche par atomique layer deposition (ALD) pour la passivation, a été développé pour préserver l'intégrité de l'interface et assurer un comportement tunnel de haute qualité. Cette approche a permis, pour la première fois, une détermination claire du signe de la polarisation de spin de Fe_3GeTe_2 , qui s'est avéré être négatif. Ce résultat est en accord avec des calculs ab initio, menés en collaboration avec l'Université

Catholique de Louvain, qui indiquent une prédominance des canaux de spin minoritaire proche du point Γ .

Afin de répondre aux limitations de l'exfoliation et aller vers l'intégration de nouveaux dispositifs, nous avons également développé une nouvelle méthode de croissance pour FexGeTe_2 , permettant un dépôt direct sur n'importe quel substrat avec des conditions CMOS-compatible. Nous avons utilisé le dépôt par ablation laser pulsée (PLD) et son potentiel à changer facilement de cible, en tirant parti de nos développements antérieurs en matière d'hétérostructures 2D. En utilisant cette technique, nous avons réussi la première croissance grande surface de Fe_3GeTe_2 et de Fe_4GeTe_2 à des températures inférieures à 450 °C (compatible CMOS) sur SiO_2 amorphe, dans des conditions epitaxy-free. Notamment, le Fe_4GeTe_2 cristallin obtenu présente une température de Curie supérieure à 450 K, avec des cycles d'hystérésis bien définis observés bien au-delà de la température ambiante. Nous avons pu aussi retracer le magnétisme fondamental à l'aide d'une analyse par exposant critique (étayée par un calcul ab-initio) qui s'avère être de nature quasi 2D. En outre, notre approche PLD a facilité le dépôt in situ de dichalcogénures de métaux de transition (TMD) sur les films de FGT, soulignant la faisabilité d'hétérostructures complexes et marquant une étape importante vers des architectures spintroniques tout 2D.

Title: Spintronics based on heterostructures of 2D and 2D ferromagnetic materials

Keywords: spintronics, 2D materials, magnetic tunnel junction

Abstract: Two-dimensional (2D) materials have paved the way for the development of next-generation spintronic devices. Among them, recently discovered 2D ferromagnets, particularly the Fe_xGeTe_2 (FGT) family, offer promising functionalities due to their gate-tunable intrinsic magnetism and potential for high Curie temperatures, well above room temperature. Despite this promise, a comprehensive characterisation of their spintronic properties, even for the relatively well-studied Fe_3GeTe_2 , and a deeper understanding of the other phases of FGT magnetism remain largely unexplored.

In this work, we present the first characterisation of perpendicularly magnetised Fe_3GeTe_2 integrated into a conventional magnetic tunnel junction (MTJ). This was achieved using exfoliated Fe_3GeTe_2 and a Co/Pt multilayer as a reference spin analyser with well-defined spin polarisation. A customised fabrication process, performed under inert conditions and incorporating atomic layer deposition for passivation, was developed to preserve interface integrity and ensure high-quality tunnelling behaviour. This approach enabled, for the first time, a definitive determination of the spin polarisation sign in Fe_3GeTe_2 , found to be negative. This result aligns with ab initio calculations, conducted in collaboration with

the Université Catholique de Louvain, which indicate a predominance of minority-spin channels near the Γ -point.

To address the limitations of exfoliated flakes and advance toward scalable device integration, we also developed a novel growth method for Fe_xGeTe_2 , enabling direct deposition on any substrates with CMOS compatibility. We employed pulsed laser deposition (PLD), leveraging our prior experience with 2D heterostructures formed by simple target swapping. Using this technique, we successfully achieved the first large-area growth of Fe_3GeTe_2 and Fe_4GeTe_2 at temperatures below 450°C on amorphous SiO_2 , under epitaxy-free conditions. Notably, crystalline Fe_4GeTe_2 exhibited a Curie temperature exceeding 450 K , with well-defined hysteresis cycles observed well above room temperature. We were able to track down the magnetism using a critical exponent analysis supported by ab-initio calculation, to be quasi-2D by nature. Moreover, our PLD approach facilitated in-situ deposition of transition metal dichalcogenides (TMDs) atop FGT films, highlighting the feasibility of complex heterostructures and marking a significant step toward fully integrated 2D spintronic architectures.

TABLE OF CONTENTS

Part A: State of the Art

1	General Introduction.....	17
1.	Spintronics	21
1.1	Discovery of Magnetoresistance	21
1.2	Magnetic Tunnel Junctions.....	22
1.3	MRAM and beyond	27
2	2D Materials.....	31
2.1	Introduction of Graphene	31
2.2	Beyond Graphene.....	34
2.2.1	Hexagonal Boron Nitride.....	34
2.2.2	TMDs	36
2.3	MTJs with Graphene	39
2.4	MTJs beyond Graphene	41
3	Magnetism in 2D materials.....	49
3.1	Introduction	49
3.2	Main Families	53
3.3	MTJs with 2D FM electrodes	68

Part B: Results

4	MTJ with F3GT	77
4.1	Bottom spin analyser	79
4.2	Top 2D magnetic electrode.....	83
4.3	Passivation and Device contacting.....	86
4.4	Magnetotransport measurements.....	88
5	Growth of 2D FGT	95
5.1	Early stage growth of FGT	95
5.2	Towards large scale FGT	96
5.3	Potential of PLD for FGT	97
5.4	PLD-grown FGT	101
5.4.1	Fabrication.....	101
5.4.2	Parameter dependence.....	103
5.4.3	Fe ₃ GeTe ₂	107
5.4.4	Fe ₄ GeTe ₂	110
6	Conclusion and Perspective.....	127

Remerciements

I feel incredibly fortunate to have spent these past years at the Laboratoire Albert Fert, surrounded by so many inspiring people. This thesis is not the result of individual effort alone, but of the countless moments of support, help, and collaboration I have received from everyone in the lab. I would like to thank the entire Laboratoire Albert Fert for the excellent working atmosphere, which is created and carried by every single person there. I could not have wished for a better place to spend these years. Every day was filled with good energy, curiosity, competence, humor, and openness. The words I write here will inevitably fall short of doing justice to the gratitude I feel, but I would still like to take this opportunity to thank all of you who have made this journey possible and so very memorable.

Sincere thanks my jury, Aurélien Manchon, Ilaria Bergenti, Daniel Lacour and Jean-Christophe Le Breton, for accepting to evaluate my work. Thank you, Aurélien, for the honor of presiding over my jury. Many thanks to Ilaria and Daniel for being my rapporteur and to Jean-Christophe as my examiner. It was a true pleasure to discuss my work with you during the defense, and I am deeply grateful for the interest you have shown in it.

Special thanks go to my supervisors. Pierre, thank you for welcoming me into the group. Your ability to balance seriousness with joy is truly admirable. It makes coming to work not only motivating, but also uplifting. Your expertise has deeply impressed me, and I have greatly enjoyed our physics discussions. And yet you always kept an open ear for everything, scientific or not. Thank you!

Bruno, your contagious energy and enthusiasm light up the lab every single day. You were always there when I needed help, with immense knowledge and optimism. You gave me the push I needed when I felt stuck and for that, I am truly grateful.

And MB, thank you for all our many discussions, whether scientific or beyond. Talking with you has always been a great pleasure. Your openness and warmth are simply unmatched.

The true master of machines Florian. Always cheerful, always helpful, and often with a French chanson echoing through the corridors (often in duet with Etiennchen!). Thank you both for making even long measurement days memorable.

Without your technical skills Julius, many measurements would have been lost in noise. Your improvisation skills during Kerr experiments were outstanding. Beyond that, I truly enjoyed the times we shared at conferences and that you shared your knowledge with me. Hao, we walked this path together, and that means a lot. I had so much fun with you, and I'm impressed by your passion for cooking! To the new crew Samuel,

Emma, Jeremy, and Jane: I wish you all the best for the future. You already make a great team, and I'm sure you'll have a fantastic time together. I only wish I could still be around to laugh with you!

Thanks as well to Paolo and Vincent, who manage the lab with such dedication and make it the unique place it is. And, of course, to everyone working behind the scenes to keep everything running smoothly, thank you Anne, Florence, Zelia, and Ylliam. Ylliam, our time together was short but intense and always with a smile!

A big thank you to all the permanent staff who taught me so much and introduced me to the machines. Many thanks to Richard for all your help with HC and SQUID measurements. Cécile, thank you for your support, expertise, and good spirit (that there will always be water in the pool!). Sophie, thank you for pushing me to improve my French, and for taking me to see handball and basketball live for the first time. I will never forget our very first interaction during my internship with you Karim and your "warm" welcome. Finally, you don't have to see me in the lab anymore, but now you're left with Luis as the source of ciggies. Luis, what a joy it was, whether in the office, the deposition room, or the garden, the man for everything! Thank you for your kind heart and patience Faycal! And for your open nature and all your help with AFM measurements Aymeric. Dedalo, your left hand is a keyboard, your right hand is light, and what you can do with your hands is simply magic. Nicolas, Vincent, and Isabella, thank you so much for your incredible expertise and the help you gave me during measurements. Many things would not have worked out so smoothly without all of you.

So many people welcomed me into the lab and guided me, many of whom will stay there long after I've gone. Congratulations to Sarah, Sarah, Ping, and Katia – may you carry on the true non-permanent spirit! Viki, you laid the foundation I could build upon, and it was a rock-solid one. Your energy and thirst for knowledge have truly inspired me. Ollie, without you I would still not understand XRD, but even better than that are the camping and the dancing. We'll see each other soon, promise! My Brazilian brother, Sylvao may your hips always swing faster than your THz radiation. It is always a party with you! And Nicolas one day, our picture in front of the sugarloaf mountain will be a tourist poster!

I could go on forever, whether it's the "old PhD veterans" like Hugo or Dongshu, or the younger ones like Malik or Greeshmani, you all contributed so much to the great atmosphere in the lab. Sahteen Amr, one day, you will hear a full sentence of Arabic from me. Greetings also to Mainz: Sachin, with whom I shared the coldest beers after work.

And then there is Laurette. Without any doubt, the most beautiful and meaningful chapter of my PhD was meeting you. My head is full of countless moments with you,

laughing and doing Mumpitz together. At HC we probably played more songs than we measured curves, and with Sheithe we created things that went far beyond the boundaries of science. You are the best thing that happened to me during this time. Without you, I wouldn't be where I am today. I am endlessly grateful for all that lies behind us and I am even more excited for everything that is still to come <3.

My deepest gratitude also goes to my parents and my sister, who have supported me unconditionally every single day. I would never have come this far without you. Thank you for your love.

And finally, warm greetings to my friends back in Berlin, the guys and girls I missed so much during my time in Paris and special kisses to Marla!

Résumé

Le développement rapide des technologies de l'information, telles que l'intelligence artificielle, l'Internet des objets et les centres de données, a conduit à une demande croissante en efficacité énergétique et en performances de calcul élevées. Pendant des décennies, la technologie CMOS a permis de répondre à ces exigences, suivant la prédiction de Moore grâce à la miniaturisation continue des transistors, mais elle fait désormais face à des limites fondamentales liées à la dissipation thermique, aux courants de fuite et aux effets quantiques à l'échelle nanométrique. Pour surmonter ces contraintes, des paradigmes alternatifs sont activement explorés.

Dans ce contexte, la spintronique offre une voie prometteuse en exploitant le degré de liberté de spin des électrons, en plus de leur charge. En effet, le concept de magnétorésistance géante (GMR) fut le précurseur de ce domaine, menant à la production massive de disques durs haute densité. Les technologies émergentes, telles que les Magnetic Random Access Memory (MRAM), démontrent davantage le potentiel de la spintronique, non seulement pour le stockage de données classique mais aussi pour de nouveaux paradigmes de calcul comme le calcul stochastique et neuromorphique.

Parallèlement à ces développements, les matériaux bidimensionnels (2D) sont apparus comme une nouvelle plateforme matérielle. Le graphène, matériau 2D prototype, a suscité un large intérêt grâce à sa conductivité exceptionnelle et à ses grandes longueurs de diffusion de spin, le rendant très attractif pour les dispositifs logiques basés sur le spin. Plus récemment, la découverte expérimentale de ferromagnétiques intrinsèquement 2D a ouvert de nouvelles perspectives pour l'utilisation des matériaux 2D en spintronique, permettant potentiellement la réalisation de mémoires et d'architectures logiques magnétiques à l'échelle atomique, au-delà des matériaux conventionnels tels que le CoFeB utilisé dans les MRAM. Un groupe remarquable de candidats pour cette mise en œuvre est constitué des dérivés FexGeTe_2 ($x=3,4,5$), caractérisés par leur température de Curie intrinsèquement élevée et leur conductivité métallique.

Malgré ces promesses, les ferromagnétiques 2D font encore face à des défis importants. Leur grande sensibilité aux conditions environnementales et la difficulté de produire des films homogènes sur de grandes surfaces limitent actuellement leur déploiement pratique.

Cette thèse vise à répondre à certains de ces défis en explorant à la fois l'intégration dans des dispositifs et la synthèse de matériaux à grande échelle. Plus précisément, elle étudie l'utilisation de Fe_3GeTe_2 (F3GT) exfolié dans des jonctions tunnel magnétiques (MTJ). De plus, elle développe la croissance à grande échelle de films minces de F3GT et Fe_4GeTe_2 (F4GT) par dépôt laser pulsé (PLD). Les trois premiers chapitres présentent l'état de l'art : une introduction générale à la spintronique, la spintronique avec des matériaux 2D et les matériaux 2D ferromagnétiques. Le chapitre

4 décrit les méthodes de fabrication d'une jonction tunnel magnétique à base de FGT et les mesures de transport magnétique, afin de sonder les propriétés de transport de spin intrinsèques du ferromagnétique 2D. Le chapitre 5 présente la croissance à grande échelle, compatible CMOS, de films minces de F3GT et F4GT par PLD, ainsi que leur caractérisation.

Les fondements de la spintronique reposent sur le couplage entre le spin et le transport de charge des électrons. La découverte de la GMR par Fert et Grünberg a montré que la résistance électronique dépend de l'orientation relative des couches magnétiques, permettant une lecture électrique des états magnétiques. Cet effet a révolutionné les disques durs et est rapidement devenu la base des architectures de mémoire non volatile.

La jonction tunnel magnétique (MTJ), constituée de deux électrodes ferromagnétiques séparées par une fine barrière isolante, est la structure clé de la spintronique moderne. Lorsque les aimantations des électrodes sont parallèles, le courant tunnel est élevé ; lorsqu'elles sont antiparallèles, il est réduit, produisant une magnétorésistance tunnel (TMR) mesurable. Ainsi, les MTJ peuvent coder l'information sous forme d'états de résistance binaire. Les avancées dans la qualité des barrières, notamment l'utilisation de MgO cristallin, ont permis d'augmenter les valeurs de TMR de quelques dizaines de pourcents à plusieurs centaines de pourcents, ouvrant la voie à la MRAM commerciale. Aujourd'hui, la MRAM existe en deux générations principales : la MRAM commutée par champ et la MRAM à couple de transfert de spin (STT-MRAM), avec une troisième génération en développement, basée sur le couple de spin-orbite (SOT-MRAM). Ces technologies illustrent l'importance de la qualité des interfaces, de la polarisation de spin et de l'anisotropie magnétique sur les performances des dispositifs. Cependant, les matériaux conventionnels comme le CoFeB montrent des limites, ce qui motive la recherche de nouveaux matériaux avec des propriétés améliorées, tels que les matériaux 2D.

L'exfoliation du graphène en 2004 a marqué un tournant en physique de la matière condensée. Premier cristal véritablement bidimensionnel stable, le graphène a montré une conductivité exceptionnelle, une grande robustesse mécanique et de longues longueurs de diffusion de spin. Il a rapidement été intégré dans des MTJ, où il a servi à la fois de filtre de spin et de couche protectrice contre l'oxydation des électrodes. Bien que les premières valeurs de magnétorésistance mesurées aient été modestes, les améliorations obtenues grâce à la croissance par dépôt chimique en phase vapeur (CVD) et à des stratégies d'intégration propres ont démontré le potentiel du graphène comme intercouche fonctionnelle.

Au-delà du graphène, la famille des matériaux 2D s'est rapidement élargie. Le nitrure de bore hexagonal (h-BN), avec son large gap, est apparu comme une barrière tunnel idéale, offrant des surfaces atomiquement lisses et une grande stabilité chimique. Les dichalcogénures de métaux de transition (TMDs), tels que MoS₂, WS₂ et WSe₂, ont introduit des propriétés semi-conductrices avec des gaps dépendant de l'épaisseur.

Leur fort couplage spin-orbite a ouvert de nouvelles perspectives pour la spintronique et l'électronique de vallée.

L'intégration de ces matériaux dans les MTJ a révélé à la fois des opportunités et des défis. En théorie, ils pourraient offrir un filtrage de spin élevé et des propriétés électroniques adaptées, mais en pratique, des problèmes tels que la contamination des interfaces, l'oxydation et la diffusion latérale du courant ont limité leurs performances. Néanmoins, ces travaux ont établi une base cruciale pour combiner la spintronique et les matériaux 2D. Cependant, pour exploiter pleinement le potentiel des MTJ van der Waals 2D, la couche ferromagnétique doit être remplacée par un ferromagnétique 2D.

Pendant des décennies, le théorème de Mermin-Wagner suggérait que le ferromagnétisme à longue portée ne pouvait pas exister en deux dimensions sans forte anisotropie. Cette hypothèse a été remise en question en 2017, lorsque des ferromagnétiques intrinsèques 2D, tels que CrI₃ et F3GT, ont été démontrés expérimentalement. Leur découverte a suscité un énorme intérêt, car elle permet d'explorer les théories magnétiques en dimension réduite et de concevoir des dispositifs magnétiques à l'échelle atomique.

Parmi les ferromagnétiques 2D connus, la famille FexGeTe₂ est particulièrement intéressante : F3GT combine conduction métallique et forte anisotropie magnétique perpendiculaire, ce qui en fait un excellent candidat comme électrode ferromagnétique. F4GT et F5GT présentent des températures de Curie autour de la température ambiante, ce qui en fait de solides candidats pour les applications. Les propriétés magnétiques des FGT peuvent être ajustées par effet de grille électrostatique et par proximité, offrant un contrôle dynamique absent des ferromagnétiques conventionnels, et en faisant une nouvelle classe prometteuse de matériaux pour les MTJ.

Au début de cette thèse, seul F3GT avait été intégré avec succès dans des MTJ. Bien qu'un résultat pionnier ait montré une TMR élevée, il n'a pas été reproduit par d'autres groupes, soulignant la difficulté d'implémenter FGT dans des MTJ de haute qualité. De plus, la polarisation de spin de FGT n'était pas encore clairement établie, motivant mon travail sur les MTJ à base de F3GT, qui constitue le premier axe de recherche de cette thèse.

Trois défis principaux ont été identifiés pour réaliser des MTJ de haute qualité. Premièrement, la nécessité d'un matériau de grande qualité cristalline. Deuxièmement, l'utilisation d'un analyseur de spin de référence avec polarisation connue et anisotropie perpendiculaire, afin de déterminer la polarisation de spin de F3GT. Enfin, un procédé d'intégration propre pour éviter toute dégradation du ferromagnétique 2D.

Pour relever le premier défi, seuls des cristaux F3GT de haute qualité obtenus par CVD étaient disponibles au début de mon travail. Ces cristaux devaient être exfoliés avant intégration dans les MTJ. Le choix de l'analyseur de spin s'est porté sur le cobalt, dont la polarisation est bien connue. L'anisotropie perpendiculaire a été stabilisée en introduisant des couches alternées de platine. Ce matériau a été utilisé comme

électrode de référence inférieure, avec dépôt d'une barrière d'alumine au-dessus. L'anisotropie hors plan a été validée par effet Kerr magnétique optique et par magnétométrie à gradient de champ alterné. Pour répondre au défi de l'intégration, un procédé de fabrication a été développé en atmosphère inerte. Après exfoliation de F3GT, une fine couche de passivation a été déposée par dépôt de couches atomiques (ALD), assurant une protection sans dégrader la structure du matériau, et permettant la fabrication de MTJ avec un procédé peu invasif. La structure finale des MTJ était du type : F3GT/Al₂O₃/(Co/Pt)_n

Les MTJ ont été caractérisées par des courbes I(V) montrant un comportement non linéaire typique d'un transport tunnel. De plus, la courbe G(U) avait un profil parabolique, avec des pics autour de 50 meV, liés à l'état ferromagnétique 3D de F3GT, montrant que le ferromagnétique 2D participe bien au processus de tunnel. Les expériences de magnétotransport ont mis en évidence des signaux de TMR clairs, atteignant jusqu'à 130 %. De manière cruciale, les résultats ont fourni la première détermination non ambiguë du signe de la polarisation de spin de F3GT, trouvée négative. Cela indique que le transport tunnel est dominé par les canaux de spin minoritaires, une conclusion soutenue par des calculs *ab initio* réalisés en collaboration avec Simon Dubois et Jean-Christophe Charlier (Université catholique de Louvain). Ces calculs ont montré que la densité d'états près du point Γ est fortement dominée par les spins minoritaires, en accord avec l'expérience.

Ce résultat est important non seulement pour la compréhension fondamentale du ferromagnétisme 2D, mais aussi pour la conception de dispositifs. Savoir que F3GT injecte des spins minoritaires aide à guider le choix des contre-électrodes et des barrières tunnel pour optimiser les performances spintroniques.

Le deuxième axe de recherche a abordé le défi de l'évolutivité. Les feuillets exfoliés sont utiles pour les études fondamentales mais impraticables pour une fabrication à grande échelle. Pour surmonter cela, la thèse a développé une méthode de dépôt laser pulsé (PLD) pour croître directement des films minces de FGT sur des substrats technologiques pertinents.

Cela a été réalisé en explorant l'espace des paramètres de croissance du système PLD afin d'obtenir des couches minces de FGT de haute qualité. En ajustant précisément la température de croissance de 250°C pour F3GT à 350°C pour F4GT, nous avons pu contrôler la stabilisation de phase des matériaux. Plus important encore, nous avons réussi à les faire croître sans épitaxie, sur des substrats de silice amorphe. Ce procédé de croissance à grande échelle est également compatible avec les standards industriels CMOS (<450°C). L'ordre cristallin élevé de F3GT a été confirmé par diffraction des rayons X (XRD) et mesures magnétiques. Les résultats obtenus sont comparables aux cristaux exfoliés de haute qualité, confirmant l'efficacité du PLD pour la croissance de films minces de ferromagnétiques 2D.

La qualité cristalline de F4GT a été validée par XRD, MET et analyses EDX, avec une observation remarquable du comportement magnétique. Une température de Curie comprise entre 450 et 550 K a été déterminée pour F4GT, dépassant largement les

exigences de fonctionnement à température ambiante pour les dispositifs spintroniques. L'analyse des exposants critiques à travers les mesures M vs T , les graphes d'Arrott modifiés et la théorie de la renormalisation suggère que le F4GT croît par PLD se comporte comme un modèle 3D Heisenberg / 3D XY, mais avec interactions à longue portée. Ces observations sont soutenues par des calculs *ab initio* (coll. UC Louvain), révélant un fort échange intraplan entre atomes de fer et la coexistence de magnétisme localisé et itinérant, confirmant le comportement magnétique observé.

De plus, la capacité d'échange in-situ des cibles du PLD nous a permis de croître directement du MoS₂ sur FGT en une seule étape. La couche supérieure de TMD protège non seulement le FGT de la dégradation, mais sert aussi de barrière tunnel ou de grille potentielle pour de futures expériences. Cette capacité unique de croissance hétérostructurée in-situ démontre la faisabilité de construire des architectures complexes entièrement 2D.

En conclusion, cette thèse contribue à la fois à la compréhension fondamentale et au développement technologique des ferromagnétiques bidimensionnels pour la spintronique. La première partie a démontré que F3GT exfolié peut être intégré avec succès dans des MTJ, permettant une détermination directe de sa polarisation de spin. La découverte d'une polarisation négative, soutenue par des calculs théoriques (coll. UC Louvain), fournit un éclairage précieux sur la structure électronique de ce matériau et aide à clarifier son rôle dans le transport dépendant du spin.

La seconde partie a établi le dépôt laser pulsé comme une méthode viable pour croître des ferromagnétiques Fe-van der Waals pour la première fois. Cette approche a permis d'obtenir des films hautement cristallins de F3GT et F4GT sur substrats compatibles CMOS. Notamment, le F4GT croît par PLD a montré des températures de Curie supérieures à 450 K, assurant une stabilité bien au-delà de la température ambiante et un fort potentiel pour les applications. La caractérisation magnétique de F4GT a également révélé un comportement critique quasi-2D, cohérent avec la nature feuilletée du matériau, tout en montrant des interactions à longue portée typiques des ferromagnétiques itinérants (coll. UC Louvain). De plus, le procédé PLD a permis la fabrication in-situ d'hétérostructures 2D, telles que FGT combiné à MoS₂, démontrant la faisabilité de construire des architectures complexes directement lors de la croissance.

Dans l'ensemble, ces résultats montrent comment une intégration soignée des cristaux exfoliés peut révéler des propriétés intrinsèques, tandis que la croissance de films minces à grande échelle ouvre la voie à des dispositifs pratiques. L'association d'avancées fondamentales, polarisation de spin négative de F3GT, et d'avancées technologiques, premiers films FGT croissants par PLD avec haute température de Curie, cristallinité et hétérostructures in-situ marque une étape importante vers le développement de plateformes spintroniques entièrement 2D.

1 GENERAL INTRODUCTION

The rapid development of information technology, such as artificial intelligence, the Internet of Things and data centres, has led to an increasing demand for high energy efficiency and fast computational performance. For decades, CMOS technology successfully met these requirements, following Moore's prediction through the continuous downscaling of transistor dimensions. To sustain further progress new concepts are necessary that complement or go beyond conventional CMOS approaches.

Here, spintronics offers a possible path to address these challenges, by utilising the intrinsic spin degree of freedom of electrons, in addition to their charge. Indeed, the concept of giant magnetoresistance (GMR) was the forerunner of the field of spintronics, leading to the mass fabrication of high-density hard drives. Emerging technologies, including magnetic random-access memory (MRAM), further demonstrate the potential of spintronics not only for classical data storage but also for new computing paradigms such as stochastic and neuromorphic computing.

In parallel with these developments, two-dimensional (2D) materials have emerged as a new material platform. Graphene, as the prototypical 2D material, attracted widespread attention due to its exceptional electrical conductivity and long spin diffusion lengths, making it highly attractive for spin-based logic devices. More recently, the experimental discovery of intrinsic 2D ferromagnets has opened new perspectives for the 2D material platform in spintronic applications, potentially enabling atomic-scale magnetic memory and logic architectures that goes beyond conventional materials like CoFeB used in MRAMs. An outstanding group of candidates for the implementation is the Fe_xGeTe_2 ($x=3,4,5$) derivatives with their intrinsically high Curie temperature and conductivity.

Despite their promise, 2D ferromagnets still face significant challenges. Their high sensitivity to environmental conditions and the difficulty of producing large-area, uniform films currently limit their practical deployment.

This thesis aims to address some of these challenges by exploring both device integration and scalable material synthesis. Specifically, it investigates the use of exfoliated F3GT in magnetic tunnel junctions. In addition, it develops the large-area growth of F3GT and F4GT thin films using pulsed laser deposition (PLD). The first three chapters cover the state of the art, with a general introduction to spintronics, spintronics with 2D materials, and ferromagnetic 2D materials, respectively. Chapter 4 introduces the methods to fabricate an FGT-based magnetic tunnel junction (MTJ) and the magnet transport measurements, aiming to probe the intrinsic spin transport properties of the 2D ferromagnet. Chapter 5 presents the growth of large-scale,

CMOS-compatible growth of F3GT and F4GT thin films by PLD, as well as the material characterisation.

Part A: State of the Art

1. SPINTRONICS

1.1 DISCOVERY OF MAGNETORESISTANCE

The field of spintronics emerged with the discovery of giant magnetoresistance (GMR) by Albert Fert [1] and Peter Grünberg [2] in 1988. Both measured a change in the resistance of a conductor while applying an external magnetic field (Figure 1.1). This was possible because both used Fe and Co. Grünberg heterostructures, which used only three ultra-thin layers and measured a lower resistance than Fert, who studied heterostructures with up to 60 layers.

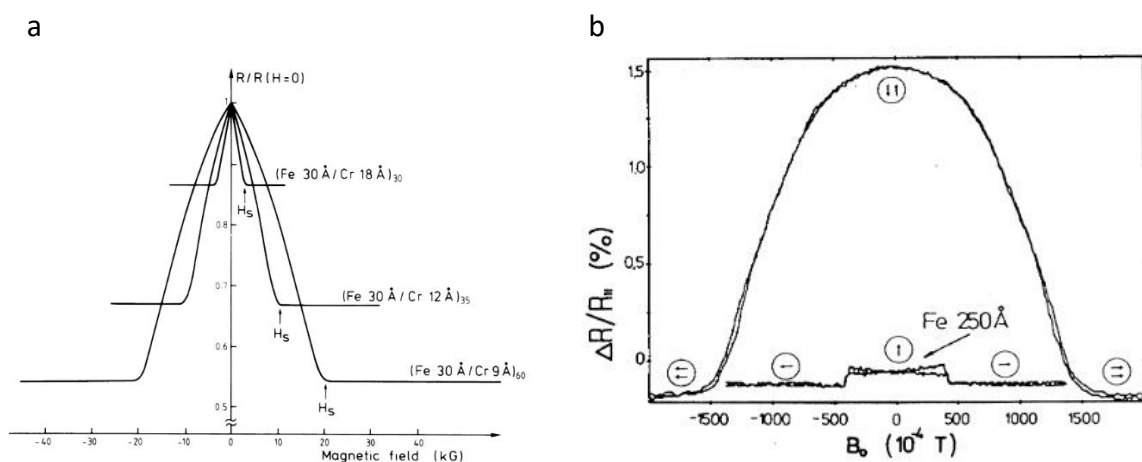


Figure 1.1: Measured GMR effect (a) in Orsay, with up to 60 multilayers of Fe and Co at low temperature 4.2K [1] and (b) at room temperature with trilayers of Co and Fe in Juelich [2]. Depending on the external magnetic field the resistance inside of the stack change.

GMR was the key idea for reading heads on hard disks. With the GMR, detecting the magnetisation is possible by simply using electric currents. This technology made it possible to improve the interface between finite current pulses and permanently storable states in an elegant way. This enabled computers to be used for commercial purposes on a large scale, enabling cloud computing and big data and is, therefore, a fundamental building block for information technology. Along with the possibility of measuring tiny changes in magnetic fields by means of electric currents, the physical effect of GMR also offers an application as a sensor for these fields. Another application that is already available as a commercial product is magnetic random-access memory (MRAM). The heart on which the entire concept of MRAM is built is the magnetic tunnel junction (MTJ).

1.2 MAGNETIC TUNNEL JUNCTIONS

A magnetic tunnel junction consists of two ferromagnetic layers separated by a tunnel barrier. Depending on the magnetisation direction of the two magnetic layers, the total resistance across the junction differs. One distinguishes between the parallel and the antiparallel configurations. In the parallel case, the magnetisation of both layers is pointing in the same direction. For the antiparallel case, the magnetisation of the layers is pointing in opposite directions. When a voltage is applied across the junction, electrons tunnel through the insulating barrier from one ferromagnetic electrode to the other, giving rise to the phenomenon known as tunnelling magnetoresistance (TMR). The TMR signal changes by switching through the two magnetic configurations, leading to two resistance states. The ideal expected resistance versus magnetisation behaviour is shown in Figure 1.2a. When a large magnetic field is applied, the magnetisation of both electrodes is facing in the same direction. As the external magnetic field decreases (blue curve), the magnetisation of the free layer with lower magnetic anisotropy (in this case, the top layer in Figure 1.2a) will flip first, causing a step-like increase in resistance. When the field reaches zero, the magnetisation of the free layer is antiparallel to the fixed layer, resulting in a high resistance state. As the field becomes negative (red curve), the magnetisation of the free layer flips back to parallel with the fixed layer, causing a step-like decrease in resistance. The whole process is reversible.

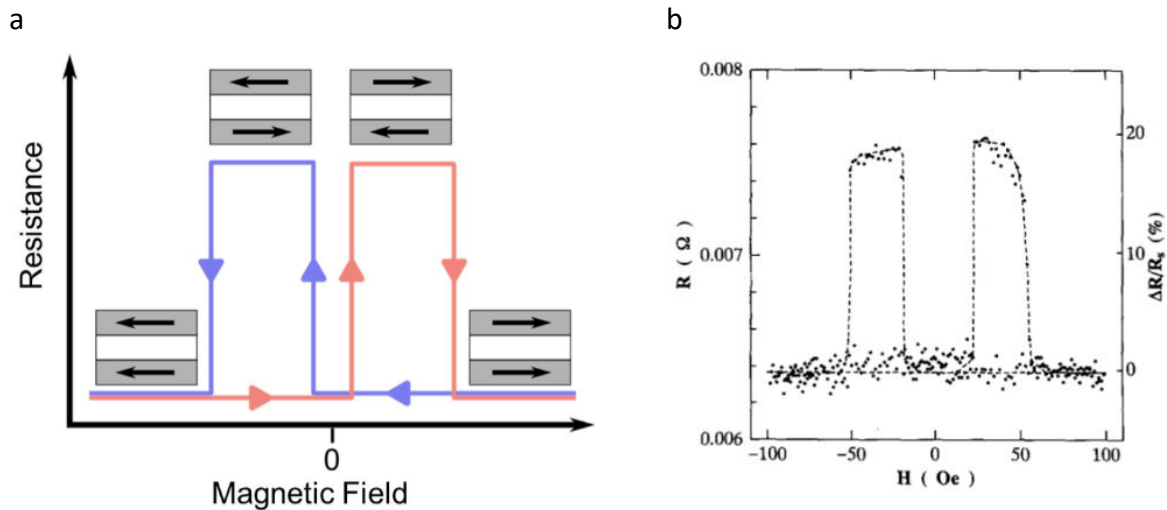


Figure 1.2: a) Shown is the ideal curve for magneto resistance measurements. In the initial position both magnetic layers have the same orientation of their magnetic moments. When the external magnetic field is changed, the free (top) layer changes its magnetic orientation accordingly before the fixed layer does. The electrical resistance is increased compared to the initial state. At a certain applied field, the bottom layer switches as well, resulting in a low resistance state again. The whole process is reversible (blue and red curve). (b) Measured tunnelling magnetoresistance by Miyazaki and Tezuka as a function of the applied magnetic field. The magnetic tunnel junction was composed of Fe/Al₂O₃/Fe, leading to a TMR effect of 18 % at 300K. From [3].

Once the external field surpasses the coercive field of the pinned layer, leading again to a parallel configuration of both ferromagnets, the resistance drops back to its initial value. The analogue behaviour can be tracked when the external magnetic field rises from negative to positive values (red curve). Illustrative, experimental results measured by Miyazaki and Tezuka with a Fe/Al₂O₃/Fe MTJ [3] are shown in Figure 1.2b. Two

different resistive states are recorded, symmetrically spaced around 0T. Here, a TMR signal of around 18% is reached by swiping through the external magnetic field.

To explain this behaviour, Jullière proposed a model in 1975 that neglects spin flips during the tunnelling process and instead considers spin-conserved tunnelling between the same spin sub-bands. In this framework, spin is conserved during tunnelling, allowing the model to describe the TMR effect in terms of the spin-dependent density of states [4]. Consequently, the resistance of the MTJ depends on the polarisation of the spins.

$$TMR = (2P_1P_2)/(1 - P_1P_2) \quad (1.1)$$

where P_1 and P_2 are the spin polarisations of the free and pinned ferromagnetic layer. The spin polarisation describes the imbalance between spin up and spin down electrons defined as

$$P = (N_{\uparrow} - N_{\downarrow})/(N_{\uparrow} + N_{\downarrow}) \quad (1.2)$$

with $N_{\uparrow}$ and $N_{\downarrow}$ the density of states (DOS) at the Fermi level for majority and minority spin electrons, respectively. The most common spin-polarised metals of spintronics are the ferromagnetic 3d-transition metals iron, nickel, and cobalt. The non-vanishing magnetisation can be attributed to the positioning of the Fermi energy (E_F). In the case of iron, nickel and cobalt, E_F lies within the 3d and 4s orbitals. While the 4s orbital is delocalised and attributed to the electrical conductivity of the metals, the electrons in the 3d orbital mainly cause magnetic behaviour. Depending on the position of the Fermi energy and the asymmetry of the DOS for the different orientations of the spins (Figure 1.3), the total spin does not cancel out and leads to a non-disappearing spin component.

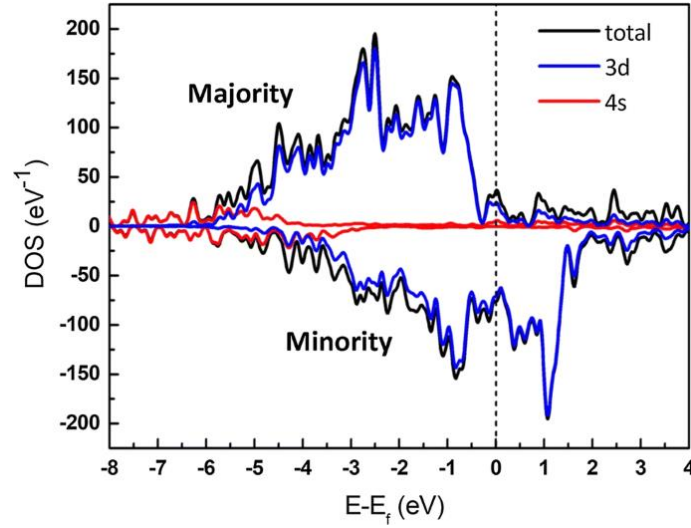


Figure 1.3: Density of states of Co plotted against the energy. It can be seen that more minority spin states are available at the Fermi energy from the 3d orbital. The sum of majority and minority spins does not cancel out at the Fermi energy, such that the Co is magnetised. From [5].

Introducing the dielectric tunnel barrier separates the GMR from the TMR effect. While the GMR effect is mainly determined by the scattering effect of spins from opposite orientations and interfacial scattering, the similar TMR effect can be explained by the use of quantum mechanics. When the tunnel barrier is sufficiently thin, electrons can tunnel from one conductive layer to the other. If both layers are ferromagnetic and their magnetisations are aligned, the density of spin states with matching orientation at the Fermi level is significantly higher (Figure 1.4), as indicated by the thicker red arrow. Thus, the probability for those majority spins is enlarged to tunnel to the other layer. The band asymmetry when the magnetisation of the two layers is antiparallel leads to a reduced tunnel probability due to a lack of accessible states. If a voltage is applied and the current runs through the junction, the total resistance can be measured and increased for the antiparallel configuration, leading to the TMR effect. The following formula expresses the normalised value of the TMR

$$TMR = (R_{AP} - R_P)/R_P, \quad (1.3)$$

with the resistance R_{AP} and R_P for the antiparallel and parallel configuration, respectively.

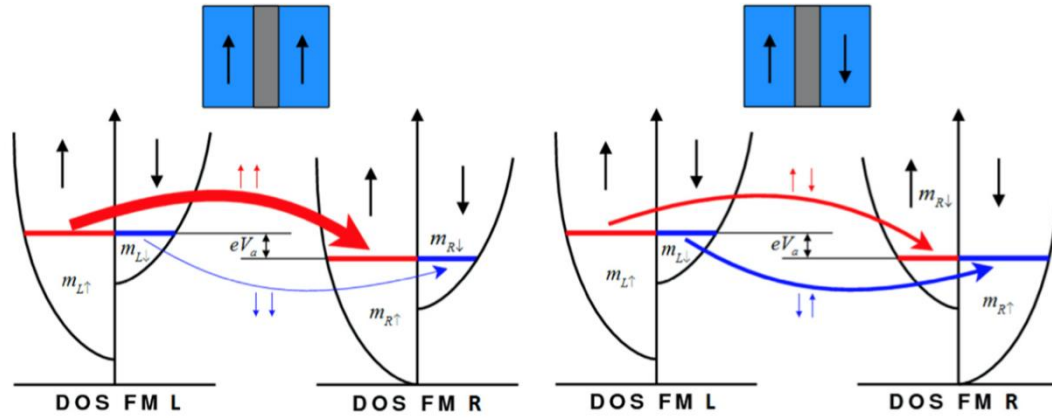


Figure 1.4.: The density of states for the majority and minority spins of two ferromagnetic in a TMJ configuration. The difference in tunnelling probability for the parallel and antiparallel configuration of the magnetic layers is indicated by the thickness of the transition arrows. The effect of the applied voltage and the relative masses is also shown. From [6].

A significantly large TMR effect was first measured in 1995 by Miyazaki *et al.* [3] and Moodera *et al.*[7]. Miyazaki and Tezuka tracked the TMR effect on a Fe/Al₂O₃/Fe stack. They achieved a TMR of 30% at 4.2K and 18% at room temperature (Figure 1.2 and 1.5b). Moodera *et al.* measured TMR effects in the same range using a CoFe/Al₂O₃/Co device. his observation led to increased interest in using Al₂O₃ as a tunnel barrier, as it enabled significantly higher TMR values compared to earlier measurements, reaching around 10%[8],[9]. Miyazaki and Tezuka explained their high TMR value by the fact that they were able to produce an insulating tunnel barrier with appropriate cleanness and uniformity. They mentioned that the increasing barrier quality could further increase the value. Hence, they emphasise the influence of the insulating layer and the importance of the interface between the electrodes and the tunnel barrier. By carefully optimising the systems, a TMR value of 80% was achieved (Figure 1.5).

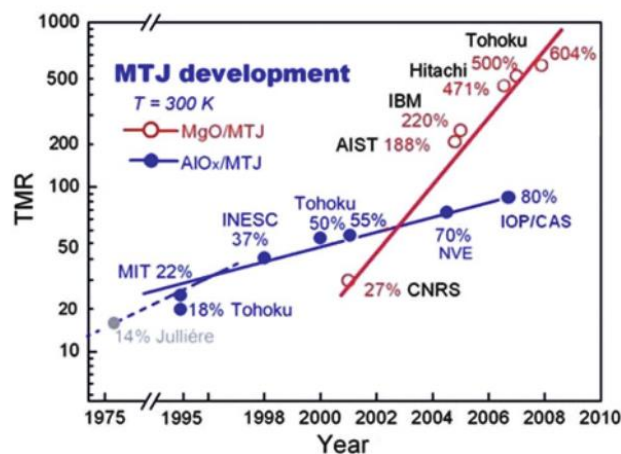


Figure 1.5: Selected TMR values were measured by different groups on a logarithmic scale over the years. The blue dots indicate tunnel junction with Al₂O₃ as tunnel barriers, while the red data represents MgO as an insulator in MTJ. The tendency of high effects is in favour of MgO. From [27]

Building on this progress, Wei et al. [10] embedded a $\text{Co}_{40}\text{Fe}_{40}\text{B}_{20}/\text{Al}_2\text{O}_3/\text{Co}_{40}\text{Fe}_{40}\text{B}_{20}$ stack into a more complex environment of multilayers. The insulating aluminium oxide was 0.6nm thick, and a TMR effect of 80% was measured at room temperature. With their sample, they were able to spin polarise the current through the tunnel junction at 4.2K up to 58%. Even though Al_2O_3 as a tunnel barrier is giving reasonable results and the purity of the layer during the growing process was improved, it still suffers from the fact that it has an amorphous structure and is infused with pinholes. Therefore, it is hard to characterise and model the interface between the electrodes and the aluminium oxide.

Beyond structural considerations such as cleanliness and uniformity, the choice of tunnel barrier material itself plays a crucial role in determining the sign and magnitude of the TMR effect. Teresa et al. [11] demonstrated this by comparing two junctions with identical magnetic electrodes but different barriers $\text{Co}/\text{STO}/\text{LSMO}$ and $\text{Co}/\text{ALO}/\text{LSMO}$. Despite using the same magnetic layers, the TMR signal was observed to be positive for Al_2O_3 (Figure 1.6a) and negative for SrTiO_3 (Figure 1.6b). Given that the spin polarisation of LSMO is known to be positive, this inversion in TMR sign can only be explained by a barrier-dependent change in the effective spin polarisation of cobalt at the Fermi level. In other words, the tunnel barrier influences whether Co appears spin-polarised positively or negatively, depending on its interaction with the electronic structure of the barrier material. Interestingly, when both Al_2O_3 and SrTiO_3 are combined in a heterostructure barrier (Figure 1.6c), and the same electrodes are used, the TMR signal is again positive. This further underscores the complex role of barrier-induced interface effects in spin-dependent tunnelling.

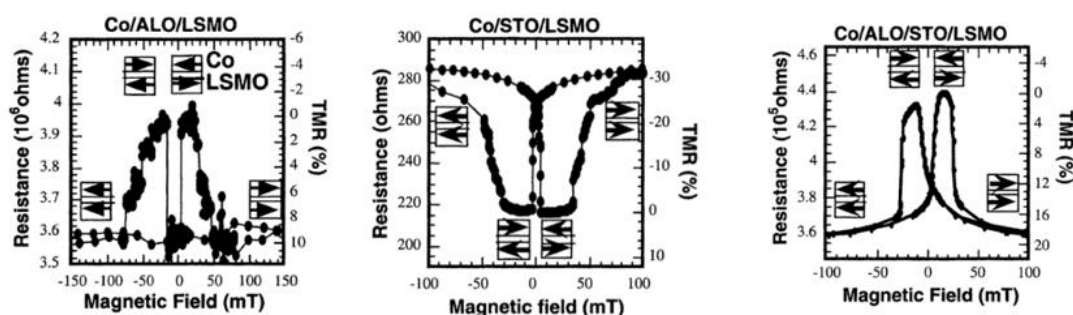


Figure 1.6: Measured TMR signals for different junctions at 40 K . (a) consists of a $\text{Co}/\text{ALO}/\text{LSMO}$ stack, (b) of $\text{Co}/\text{STO}/\text{LSMO}$ and (c) of $\text{Co}/\text{ALO}/\text{STO}/\text{LSMO}$. LSMO as an electrode is always positively spin-polarised. The sign of the TMR effect depends on the interface between the Co and the insulator. From [3]

Teresa et al. argue that this implies that the spin polarisation of Co is mainly determined by the ferromagnet/insulator interface and not by the propagation through the whole barrier. The negative spin polarisation of cobalt appears from the d band, which is at the fermi level determined by minority spin-down electrons (see equation 1.2 and Figure 1.3). When the ALO is in contact with the cobalt, the total TMR

signal is positive, which implies that ALO enables mainly the d electrons to tunnel through the barrier. However, the TMR sign is negative when STO shares an interface with cobalt. This means that this time, the s electrons, which are mainly negatively spin-polarised in the case of cobalt, can penetrate the junction. It was shown that the materials in different layers directly influence each other and, therefore, the total TMR signal.

Butler et al. [12] proposed with first-principles calculation that MgO could outperform Al_2O_3 . The crystalline structure allowed to model the tunnelling conductance, depending on the symmetry of the Bloch states in the electrodes and the evanescent states into the tunnelling barrier as well. They were able to predict that by using MgO as a layered material, the tunnelling electrons are in the majority Bloch ones, while the minority electrons are coming from interface resonance states. This means that it is theoretically possible to select the type of spin polarisation which is desired by using an appropriate tunnel barrier since the hybridisation of the states near the interface is dependent on both materials. Those predictions and the fact that there is a priori information about the origin of the tunnelling electrons lead to intense research with MgO barriers (Figure 1.5). Parkin et al. [13] measured a TMR effect of 220% with a CoFe/MgO/CoFe heterostructure, resulting in a spin polarisation of 85%. The highest reported TMR signal at room temperature so far was measured by Ikeda et al. [14] in 2008, with 600% at 300K. The tunnel junction was consisting of $\text{Co}_{20}\text{Fe}_{60}\text{B}_{20}/\text{MgO}/\text{Co}_{20}\text{Fe}_{60}\text{B}_{20}$. This knowledge was used for building magnetic random access memory (MRAM), which is so far the most prominent example of integrating MTJs in applications.

1.3 MRAM AND BEYOND

The limitation of volatility and energy consumption bottlenecks the dominating system of dynamic random-access memory (DRAM). In DRAM, information is stored in capacitors that operate under voltage control and require constant refreshing to prevent data loss, leading to high energy demands. This energy-intense process can be overcome by utilising non-volatile systems like MRAM, where the information is stored in MTJs, which retain data even without external energy. Currently, there are two generations of MRAMs which are commercially available. The first generation is based on an external magnetic field (Savtchenko switching) and the second is based on a spin-transfer torque (STT-MRAM) [29]. Both are characterised by using the tunnelling magnetoresistance effect (TMR), and differ only in the way how spins in one (Free layer) of the two ferromagnetic layers are redirected. The change in a generation goes along with higher writing speeds, packing density and lower power consumption since the second generation uses the spin-transfer torque mechanism, enabling the direct switching of the free layer through electron spin currents instead of relying on external magnetic fields, leading to more efficient switching. Figure 1.7 shows a

conceptual SST-MRAM cell. The two magnetic layers, free and pinned, are separated by a dielectric layer, the tunnel barrier, which is usually below 2 nm in width. This structure builds the heart of the MRAM.

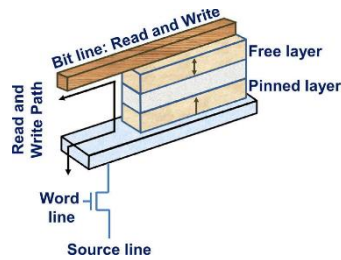


Figure 1.7: The basic design for an STT-MRAM is shown, including the read-/write line and the word line to address the MTJ, consisting of a free and a pinned layer separated by a thin dielectric tunnelling layer. From [30].

The thin layer heterostructure is addressed via the word and read-/write line. Depending on the relative orientation of both layers, the resistance of the whole structure is either high (antiparallel configuration) or low (parallel configuration). Thanks to the high magnetic anisotropy, the pinned layer has a fixed magnetisation, whereas the free layer can switch the direction of magnetisation. This allows the change between the parallel and antiparallel configuration of magnetisation concerning both layers; thus, two states of different resistances can be realised.

Various companies like Everspin, TSMC and Samsung offer MRAM solutions for customers. By now, the products are at an early stage and in terms of data storage size behind the classical DRAM, but with increased interest in the industry, scalability is achievable. Figure 1.8a displays a optical image of an embedded MRAM from TSMC. Embedded points out the integration of the MRAM directly on the System-on-Chip (SoC). Thus, they are distinguished from standalone MRAMs only by the way of integration and thus by the operating efficiency of data communication. The figure also shows a TEM image of the MTJ in the cross-section. Figure 1.8b shows the solution of Everspin's SST-MRAM based on CoFeB as a ferromagnet and MgO as a tunnel barrier. Everspin offers by now the highest capacities storage of up to 1GB. The standalone solution is especially interesting for application in data centres and industrial applications, while the before-mentioned eMRAM from TSMC or the 28nm technology from Samsung aim to be implemented in IoT or wearable applications.

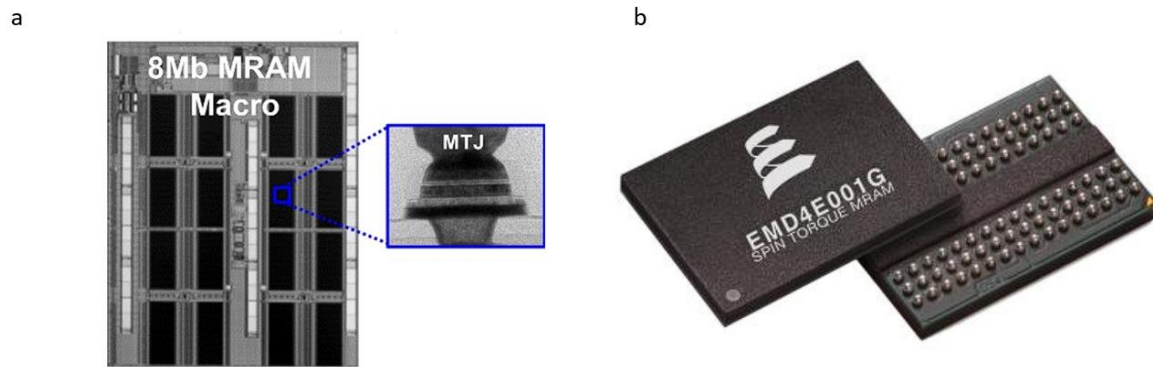


Figure 1.8: Commercially available MRAM from TSMC (a) and Everspin (b). a) Shows a top view on an MRAM chip with a TEM cross section on the embedded MTJ. b) MRAM solution offered by Everspin.

Up to now, MRAM technology has primarily relied on traditional ferromagnets like Co, NiFe or CoFeB with Al_2O_3 or MgO as tunnel barriers, based on the good spin filtering effects in these material combinations. Among those CoFeB/MgO is the dominating material choice for STT-MRAM, due to its crystalline structure. With the ongoing research on the 3rd Generation MRAM based on spin-orbit switching of the free layer (SOT-MRAM), heavy metals like Pt, Ta and W are introduced in the MTJ design to utilise strong spin-orbit coupling. While not commercialised yet, the SOT-MRAM offers promising decreases in power efficiency and writing speed. Overall, MRAM technology is evolving rapidly, capturing growing interest from the industry as a promising solution to overcome the limitations of volatile memory. Furthermore, emerging architectures such as in-memory computing, stochastic neuromorphic, and quantum computing are being explored. These cutting-edge technologies call for the exploration of new material systems with novel functionalities and tailored properties. In this vision, 2D materials open a new promising perspective for next-generation computing.

2 2D MATERIALS

The discovery of magnetoresistance marks an influential moment in the field of spintronics, unlocking the ability to manipulate electron spins for enhanced data storage and processing. Following this breakthrough, magnetic tunnel junctions have been introduced, pushing the limit of the devices and their performance further to powerful, non-volatile memory technology. However, as traditional materials approach their physical and technological limits, 2D materials can present new opportunities for advancing spintronic devices. The research domain of 2D materials emerged in 2004 with the successful exfoliation of graphene, an atomically thin graphite film, by Novoselov and Geim [15]. Since then, it has aroused great interest among researchers and industry. On the one hand, their unique characteristics make them attractive for basic research. On the other hand, they offer new opportunities for companies and consumers for thin, powerful, fast and flexible electronics. In this chapter, the potential of graphene and its integration into MTJs will be explored focusing on its impact on spintronic devices. Furthermore, the rapidly growing field of 2D ferromagnets will be introduced, discussing the state-of-the-art in 2D ferromagnetic materials and the challenges they present for future applications.

2.1 INTRODUCTION OF GRAPHENE

2D materials are defined by their electronic confinement in one spatial dimension, distinguishing them from 3D, 1D, and 0D systems, where charge carriers are free or confined in three, two, or all three dimensions, respectively. This dimensional restriction results in structures with atomic-scale thicknesses (typically in the angstrom range) in one direction, while the lateral dimensions remain significantly larger. Those unique size scales result in an exceptional surface-to-volume ratio, which promotes surface interaction with other materials. Moreover, their ultra-thin nature allows for a quantum mechanical perspective, offering insights into their fundamental properties. Recent discoveries made with 2D materials are the high measured electron conductivity [16], the quantum hall effect at room temperature [17], the study of quantum electrodynamics in the form of the Klein paradox [18],[19], the first time measured electron supercollimation [20], the experimentally probing of dark excitons [21] or the twisted layer graphene [22],[23] causing superconductivity [24]. Those achievements promote fundamental research as well as industrial innovation. The unique van der Waals (vdW) gap in 2D materials, which separates the layers within the material from each other by weak interaction, allows the exfoliation of the material, furthermore stacking different materials on top of each other despite their lattice mismatch. The physical properties of one of the materials can then be impinged on the other through proximity effects, leading to artificially tailored materials suited to

advance the recent state of the art towards downscaling computational units, reducing energy consumption and going towards multifunctional devices.

Graphene, the pioneer of 2D materials, consists of carbon atoms arranged in such a pattern that they construct a hexagonal, sheet-like lattice (Figure 2.1a). Carbon has eight electrons in total, of which four belong to the valence band. Since a carbon atom is bonded to three neighbouring atoms, there is a sp^2 hybridisation (Figure 2.1c). In this case, the 2s orbital merges with the two of the 2p (p_x , p_y) orbitals in such a way that the leftover electron can form a π bond through the p_z orbital. Between the three sp^2 orbitals is an angle of 120° . The stronger σ bonds hold the carbon atoms together, while the weaker delocalised π bonds ($2p_z$ - $2p_z$ overlap, perpendicular to the carbon plane) are responsible for the high conductivity.

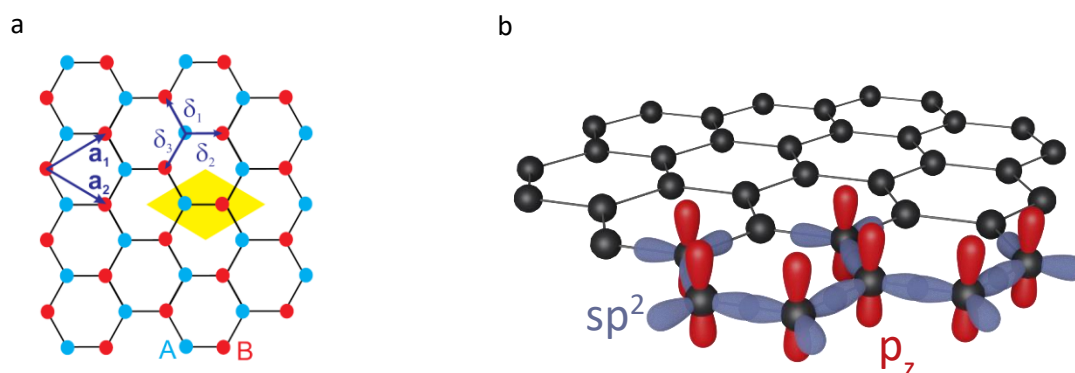


Figure 2.1: a) Sketch of the atom lattice of graphene in real space with the sublattices A and B. Shown is a unit cell (yellow) and lattice vectors a_1 and a_2 . b) Reciprocal space of the graphene lattice with the first Brillouin zone. From [25]. c) Graphical illustration of the sp^2 hybridisation in graphene forming σ bonds and the p_z orbitals leading to π bonds.

A unit cell with two carbon atoms can describe the crystal lattice. The lattice vectors of graphene can be written as $a_1 = a_0(1/2, \sqrt{3}/2)$, $a_2 = a_0(-1/2, \sqrt{3}/2)$ with $a_0 = \sqrt{3}a$, where a is the distance between two carbon atoms ($a = 0.14$ nm). Notably, the two carbon atoms are not equivalent due to their relative position regarding their neighbours, thus forming sublattices A and B (Figure 2.1a). Translating lattice A into lattice B requires a lateral translation of 142 pm and a rotation of 60 degrees. The π bond forms delocalised states for the electron, leading to a band dominating around the E_F and is responsible for graphene's high conductivity. This band structure is shown in Figure 2.2, consisting of a valence band ($E < 0$) and a conduction band ($E > 0$). The especially interesting features are the touching points between both bands, called Dirac points. They are at the corners of the Brillouin zone and six in total. At those points, the bands have a cone-like form. No band gap exists, so sometimes graphene is called a zero-gap semiconductor.

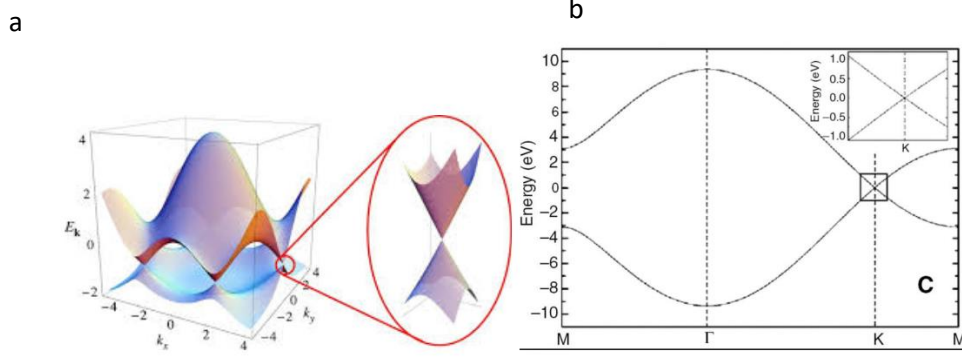


Figure 2.2: a) 3D plot of the energy dispersion relation of graphene with the six Dirac points (enlarged). b) The band structure of graphene is along a specific path in reciprocal space. The inset shows the linear behaviour of the valence and conduction band in the vicinity of the Dirac points. From [26],[27].

In the ground state, the valence band is completely filled, and therefore, the Fermi energy is precisely at the Dirac point. Expanding the energy dissipation around this point leads to the following dispersion relation

$$\epsilon(k) = \pm \hbar v_F |k| \quad (2.1)$$

with the constant Fermi velocity v_F which is a constant. This Fermi velocity is independent of the energy or momentum (usually $v = k/m$). This mass-less dependency reminds to photons or neutrinos, which the mass-less Dirac equation can describe. The non-existent gap between the two cones makes graphene interesting in the field of electronics. The expression for the effective mass

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 \epsilon}{\partial k^2}. \quad (2.2)$$

This way, the effective mass is inversely proportional to the curvature of the band. Graphene is unique because the dispersion is linear, meaning that $m^{*-1} = 0$, and thus the effective mass is not well defined. The lack of band gap makes it resemble the energy distribution of photons $\epsilon(p) = cp$, where now the Fermi velocity plays the role of speed of light.

All these exceptional properties make graphene a versatile model system for studying not only relativistic-like quantum phenomena, but also novel electronic, mechanical, and optical behaviours in two-dimensional systems. At the same time, certain limitations, such as the absence of a natural band gap restrict its use in conventional semiconductor technologies. These factors have driven the exploration of a broader class of 2D materials, each offering unique combinations of properties.

2.2 BEYOND GRAPHENE

Since the successful mechanical exfoliation of graphene in 2004, the field of two-dimensional materials has expanded rapidly. While graphene remains the most studied example due to its exceptional properties like high tensile strength, its high Young modulus or its flexibility, numerous other 2D materials have since been isolated and characterised. These include systems such as hexagonal boron nitride (h-BN), black phosphorus (BP), and entire families like transition metal dichalcogenides (TMDs), oxides (TMOs), or layered double hydroxides (LDHs), each with distinct physical characteristics (Figure 2.3).

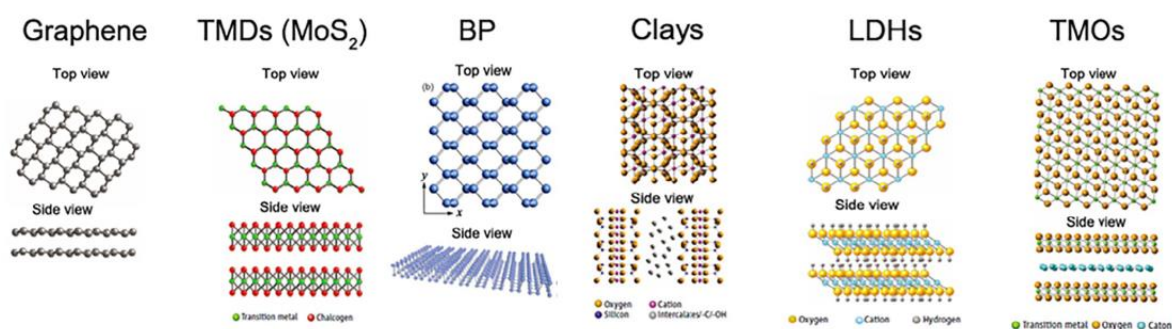


Figure 2.3: Graphical representation of the crystal structure of selected 2D materials or groups. From left to right: graphene, transition metal dichalcogenides (TMDs), black phosphorus (BP), silicate clays, layered double hydroxides (LDHs) and transition metal oxides (TMOs). Adapted from [28].

The intrinsic properties of the materials can differ considerably from each other. While CrTe_2 is an electrical conductor, MoS_2 and WS_2 are semiconductors, and h-BN is an insulator. The variety of these materials allows for the creation of tailored materials suiting the needs of specific devices. Each TMD is characterised by its own bandgap in relation to the Fermi level. Soon after, graphene h-BN gathered attention due to the structural similarities but electronic differences:

2.2.1 Hexagonal Boron Nitride

Hexagonal boron nitride (h-BN) shares a structural similarity with graphene, featuring a honeycomb lattice where boron (B) and nitrogen (N) atoms alternate, bonded through sp^2 hybridisation (Figure 2.4a). The stacking sequence of the AA' pattern does not contain a shift between the layers but an inversion of the N and B atoms with respect to the adjacent layers.

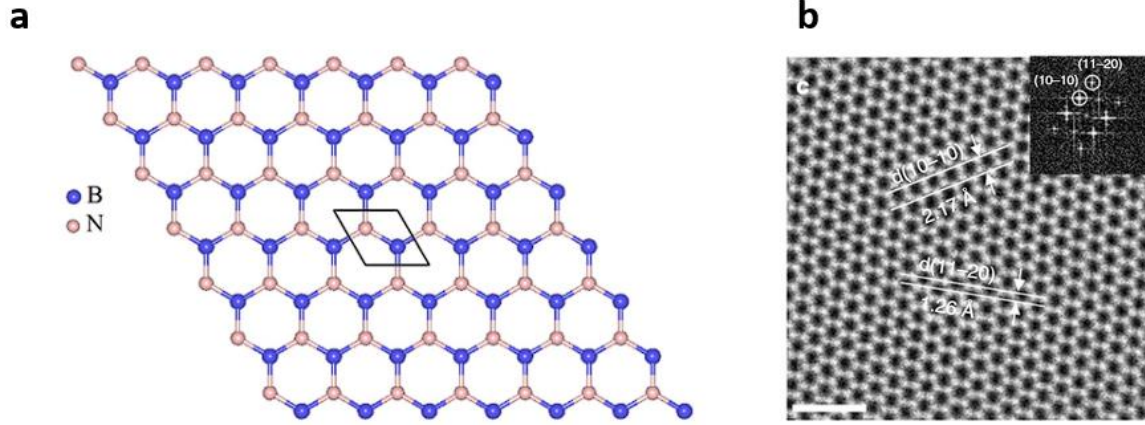


Figure 2.4: a) Structure of monolayer h-BN. The boron and nitrate atoms for a honeycomb lattice are ordered alternating. B) TEM image along the c-axis of multilayer h-BN, indicating the AAA stacking. From [29],[30].

This stacking distinguishes it from the graphene's ABA arrangement. Figure 2.4b shows the honeycomb lattice of h-BN by TEM measurements. The intrinsic properties of h-BN differ significantly from graphene. Most notably, its electronic band structure classifies it as an insulator, with a wide bandgap of approximately 6eV. The bandgap changes when thinning down the material to the monolayer case and goes from an indirect bandgap in bulk (M-K points) to a direct in the monolayer (K point)[31] (Figure 2.5).

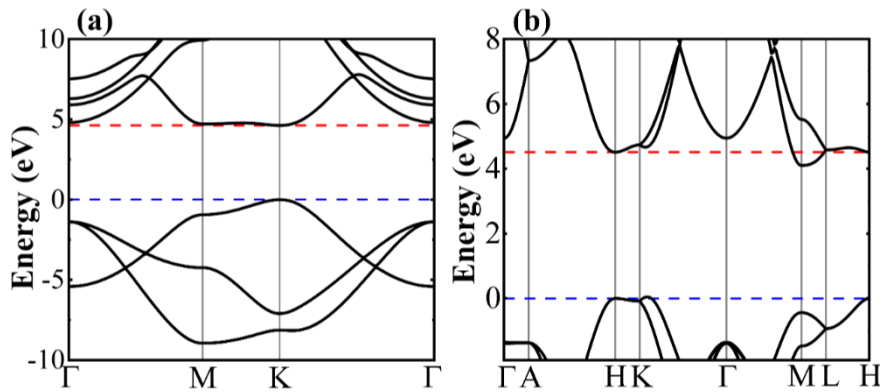


Figure 2.5: Example of h-BN calculated bandstructure for the monolayer (a) and bulk (b) form. The Blue and red dotted line indicates the direct bandgap, which is only the lowest bandgap in in the monolayer case. From [32].

The insulating characteristic and thickness depended band structure makes h-BN an outstanding candidate for integration into spintronic devices. Beyond serving as a tunnelling barrier for spintronics, h-BN's exceptional compatibility with graphene electronics comes from the well-matched lattice parameters, which allows great implementation into heterostructures. Moreover, h-BN functions as an excellent passivation layer, offering protection against external contamination. Its atomically flat surface and minimal dangling bonds preserve the intrinsic properties of adjacent

materials, making it an ideal choice for enhancing the performance and stability of 2D material-based devices.

2.2.2 TMDs

The gap between (semi) metal and insulator in the vdW material class is covered by the transition dichalcogenides (TMDs). They can be represented by the general formula MX_2 , where M represents the transition metal (e.g. molybdenum (Mo) or tungsten (W)) and X stands for the chalcogen (i.e. sulfur (S) or tellurium (Te)). TMDs typically crystallise in two primary phases, 2H and 1T (Figure 2.6). In both configurations, the transition metal atoms are sandwiched between layers of chalcogen atoms. The 2H phase, which is more commonly found, is characterised by a trigonal prismatic arrangement of chalcogen atoms, leading to an ABA stacking sequence of the atomic planes. In contrast, the 1T phase structure solidifies in an octahedral unit cell, where the layers are arranged in an ABC configuration. The electronic properties of these phases are distinct. The 1T phase generally exhibits metallic behaviour, attributed to the overlap of the transition metal's d-orbitals at the Fermi energy level, where the metal is surrounded by six chalcogen atoms in the octahedral coordination. Conversely, the 2H phase is typically semiconducting due to its lower packing density, which increases the localisation of electrons and facilitates the formation of a bandgap.

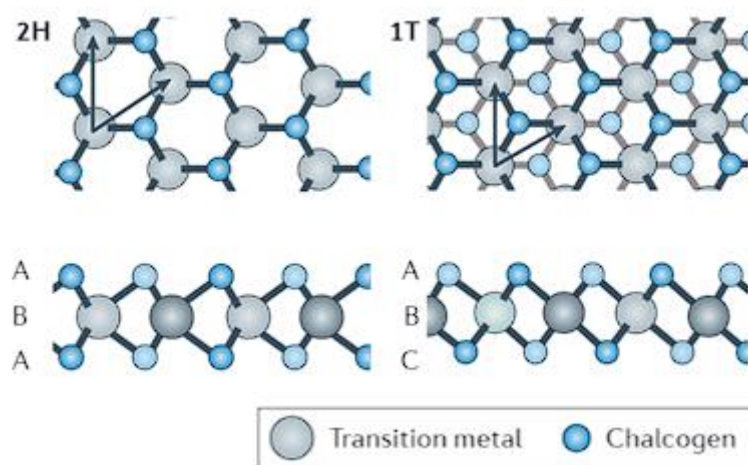


Figure 2.6:8 Trigonal prismatic 2H phase (a) and octahedral 1T (b) of TMDs in top and side view. The 2H phase is characterised by an ABA stacking sequence for the transition metal (grey) and chalcogen atoms (blue), while an ABC stacking can be found in the 1T phase. From [33].

The chemical composition of TMDs determines the bandgap in the 2H phase. Variations in atomic size within the structure directly affect the bandgap. Heavier atoms, both among transition metals and chalcogen atoms, are generally associated with smaller bandgaps. Figure 2.7 illustrates a selection of TMDs and their corresponding bandgaps. As shown, the bandgap varies significantly between different materials, expanding the range of options available for spintronic

applications. By fine-tuning the composition of TMDs, the functionality and performance of devices can be precisely tailored to meet specific requirements.

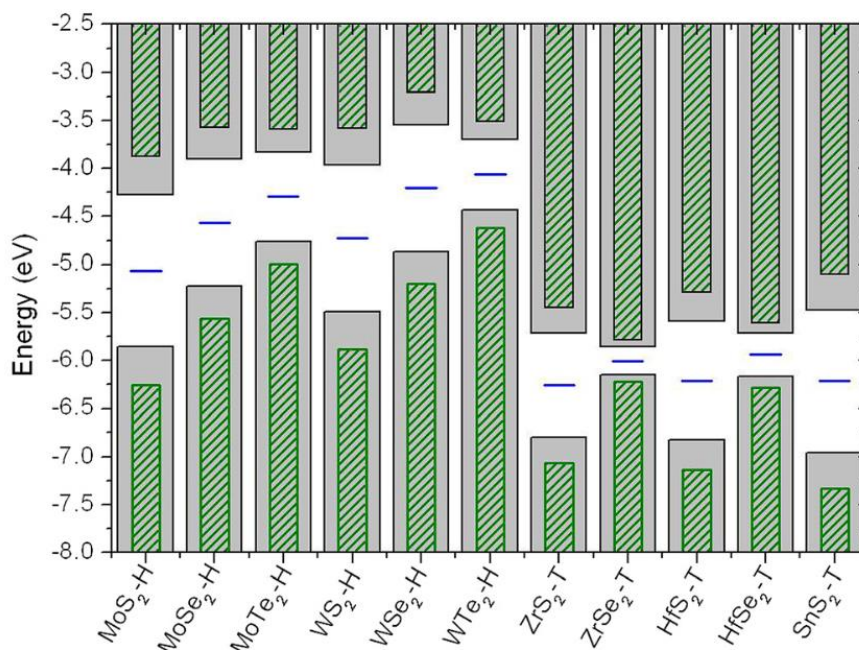


Figure 2.7: Band gaps for several selected TMDs in the 2H or 1T phase. A strong variety in position and size of the bandgap highlights the possibility of tailoring devices with well-chosen TMDs From [34].

The bandgap of TMDs is influenced by various factors like composition, thickness, adjacent materials and external stimuli. Like hexagonal boron nitride (h-BN), the band structure of TMDs is strongly influenced by the number of layers. Monolayer TMDs often exhibit a direct bandgap, whereas bulk or multilayer TMDs transition to an indirect bandgap due to interlayer interactions. Furthermore, the size of the bandgap can change from higher values at the ML limit to lower once in a multilayer. For example, the well-studied material MoS₂ has, in the monolayer case, a direct bandgap around the K point of about 1.9 eV [35] (measured by PL Figure 2.8) [35]. This bandgap reduces gradually with the number of layers towards the bulk value of 1.29 eV. Padilha *et al.* carried out calculations that were able to reproduce the change in the band gap of MoS₂. For bulk MoS₂, they observed an indirect band gap dominated by the maxima in the valence band near the Γ point [36]. The interaction between the out-of-plane orbitals of MoS₂ with the neighbouring layers leads to an increase in the energy of the valence band around the Γ -point. The in-plane orbitals, on the other hand, remain unaffected by the interlayer interactions. If the number of layers is reduced to a monolayer, the interlayer interactions disappear, and the in-plane orbitals dominate the band structure. In this state, MoS₂ shows a direct band gap, as the energy states at the K-point remain stable (governed by the in-plane orbitals).

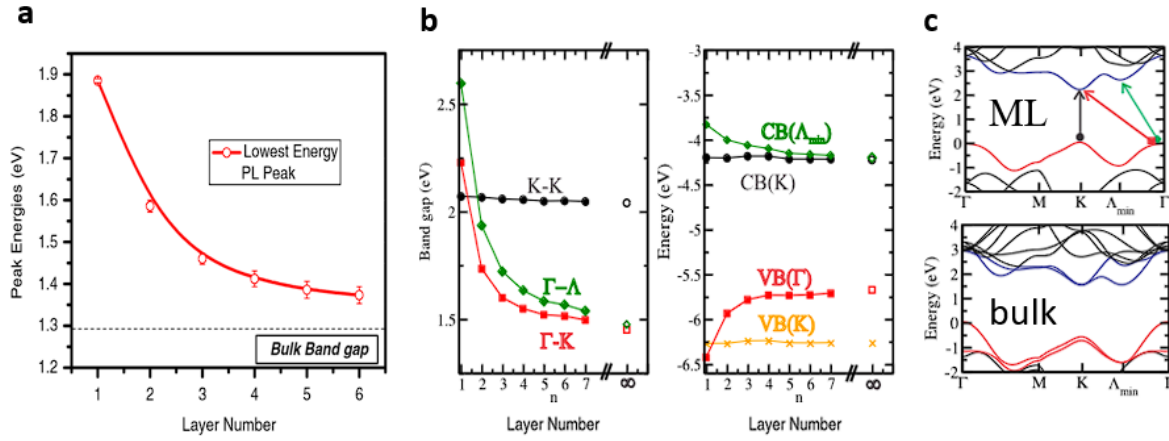


Figure 2.8: Layer-dependent band gap evolution in MoS_2 . a) experimentally determined bandgap by photoluminescence (PL). The band gap reduces with an increasing number of layers. Theoretical calculations confirm the findings; it not only reduces the band gap, but it also changes from direct in the monolayer case (black arrow in c; K-K transition in b) to indirect for two or more layers (green in b and c). From [35],[36]

Figure 2.8c indicates by a black arrow the direct bandgap in the monolayer MoS_2 case. When going the bulk, the red arrow becomes dominant as the valence band shifts upwards in energy. This change in bandgap is illustrated in Figure 2.8b. The left panel shows the size of the bandgap, clearly stating the K-K to Γ -K transition when going from monolayer to bilayer.

The sensitivity of the bandgap to environmental factors is influenced not only by the number of layers but also by external conditions such as substrates or dielectric environments. Calculations have shown that TMDs are strongly influenced by the neighbouring materials, like HfO_2 , Au, TMDs or the same material in a different phase heterostructure (i.e. MoS_2 2H/1T.) [37],[38].

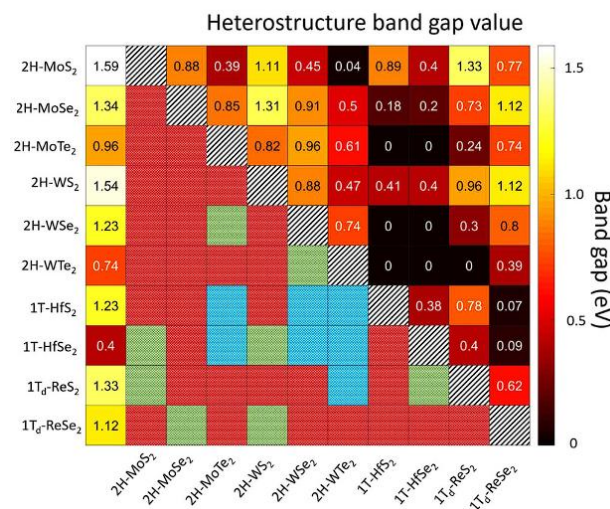


Figure 2.9:9 Band gap values of heterostructures of various TMDs. The calculated bandgap is strongly influenced by the chosen materials. From [39]

The stacking of different van der Waals materials allows the combination of multiple TMDs with each other to create unique properties. Based on the van der Waals nature of the material, lattice mismatch does not impose an integration problem. Creating the van der Waals heterostructures allows to go beyond the intrinsic properties of individual layers, unlocking new tailored devices for application. A broad range of band gaps can be achieved with only a handful of materials. This tunability makes TMDs highly versatile for applications in optoelectronics and nanotechnology.

2.3 MTJs WITH GRAPHENE

In 2007, Karpan *et al.* [40] proposed, based on tight-binding theory, that graphene could lead to a 100 % spin-polarised current when used as an insulating barrier between two ferromagnetic materials, whether Ni or Co. Due to the low lattice mismatch between graphene and Ni and Co, it is possible to extract electrons from minority characteristics. This can be explained by the fact that the K points of graphene and the electrode are at the same position in k space. Because the ferromagnets at the K points are dominated by minority spins (see Figure 2.10), while the Fermi surface for the majority exceeds space, expect the Γ and K points. Since the graphene Dirac K points are related to the conduction of graphene, the overlapping orbitals filter out the majority of electrons, leading to a spin polarisation of up to 100 %.

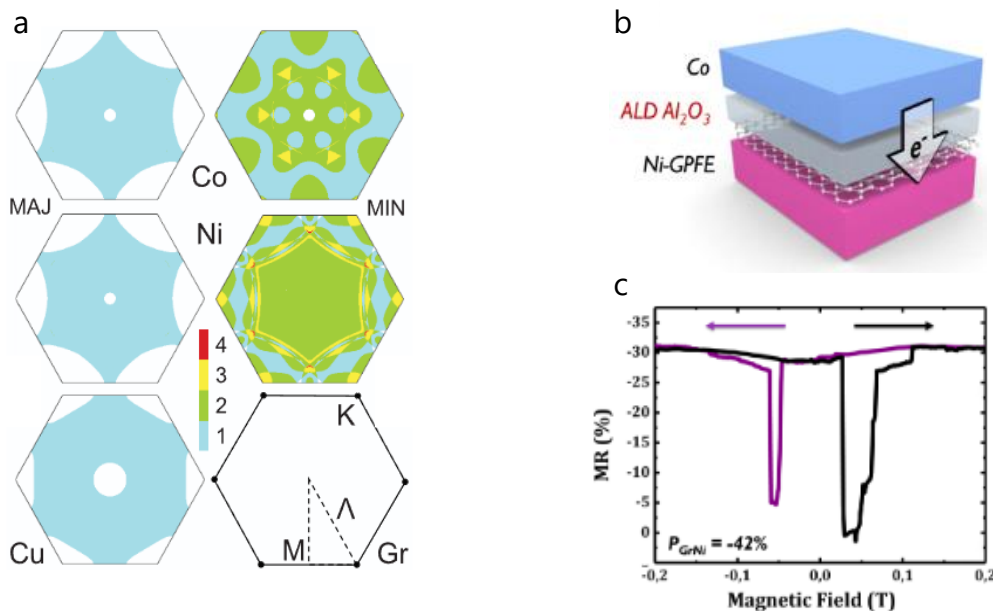


Figure 2.10: a) The calculated Fermi surfaces for majority and minority spins for Co and Ni are shown. As well as the Fermi surface for the majority of spins for Cu. The spin-filtering effect is attributed to the overlap of states at the K points between graphene and Co or Ni. From: b) Sketch of an MTJ consisting of Co/ Al_2O_3 /Graphene/Ni, where the alumina is deposited with ALD. c) Magneto transport measurement of the MTJ shown in b. The spin filtering effect proposed by Karpan can explain the negative TMR effect. From [40],[41]

Also, an increase in spin polarisation with increasing graphene monolayers is predicted. The first magnetic tunnel junction with exfoliated graphene was realised by Mohiuddin *et al.* [42] in 2008. They used a $\text{Ni}_{80}\text{Fe}_{20}/\text{graphene}/\text{Ni}_{80}\text{Fe}_{20}$ design to measure a TMR effect of 0.4 %. The gold layer was deposited to block the oxidation effects of the bottom electrode while the graphene was exfoliated. In the absence of the gold layer, the results indicate that the graphene layer combined with an oxidation of the first few layers of the $\text{Ni}_{80}\text{Fe}_{20}$ is sufficiently large to minimise the direct coupling between the two magnetic electrodes. When the $\text{Ni}_{80}\text{Fe}_{20}$ layer is passivated with gold, an increase of the GMR effect by a factor of 10 was observed. The integration of graphene into magnetic tunnel junctions is a crucial step in the realisation of high magnetoresistance. This is due to the interfaces between graphene and electrodes. Rough, oxidised, defective surfaces should be avoided. As a result, various approaches to integrating graphene have been tried out. Besides the exfoliation method, there were attempts to transfer the graphene by wet transfer (see below). The measured MR signal was 2 %. Due to the wet transfer and the chemical reactions involved, this integration method still suffers from oxidation. Dlubak *et al.* [43] made a breakthrough by growing graphene directly on the nickel electrodes by chemical vapour deposition (CVD). With this technique, the oxidation of the electrodes can be effectively prevented, and the electrodes can be passivated 18 months [44]. Unlocking significantly higher magnetoresistances.

Utilising these CVD Gr/Ni electrodes, Martin *et al.* [41] exploited the protective characteristics of graphene to avoid oxidation of Ni ferromagnet, maintaining a clean interface for the deposition of an ultra-thin Al_2O_3 barrier via atomic layer deposition (ALD). The measured large TMR signal of -31% indicates a clean interface and the absence of a NiO_x layer, highlighting the importance of interface quality in sustaining spin-polarised transport. By effectively passivating the Ni surface, graphene not only prevented degradation but also ensured a highly spin-polarised interface, reinforcing its role as a protective and functional interlayer for achieving high TMR in MTJs.

The work of Piquemal-Banci *et al.* [45] focused on epitaxial monolayer Gr on Ni (111) with $\text{Ni}(111)/\text{graphene}/\text{Al}_2\text{O}_3/\text{Co}$ and $\text{Ni}(111)/\text{graphene}/\text{Co}$ stacks. A key finding was the significant difference in spin polarisation at the Ni/Gr interface depending on the electrode configuration. In the $\text{Ni}(111)/\text{Gr}/\text{Al}_2\text{O}_3/\text{Co}$ junction, the Ni/Gr interface exhibited a spin polarization of $P_{\text{Ni/Gr}}^{\text{Tunnel}} = -20\%$, whereas in the $\text{Ni}(111)/\text{Gr}/\text{Co}$ structure, direct contact between graphene and Co resulted in $P_{\text{Ni/Gr}}^{\text{Direct}} \approx 50\%$, leading to a high TMR $> 80\%$. Since monolayer graphene is expected to have a weak K-point filtering effect, this enhancement cannot be explained solely by conventional spin filtering mechanisms. Instead, first-principles calculations showed that strong hybridisation at the Co/Gr interface modifies the density of states of graphene, increasing the number of majority spins at the Fermi level. This effect boosts the spin polarisation of the tunnel current, leading to the observed increase in TMR. These results demonstrate that interface hybridisation is a key factor in optimising spin

transport in graphene-based MTJs. More recent results with epitaxial multilayer Gr/Ni(111) structures, combining interfacial and band structure spin filtering effects, have led to TMR > 160%.

The presented findings with graphene demonstrate the potential of 2D materials in enhancing MTJ performance, particularly through spin filtering and interface engineering. While graphene is a semi-metal, the rich family of 2D materials offers a variety of semiconductors and insulators to be used in MTJs.

2.4 MTJs BEYOND GRAPHENE

Early work on 2D MTJs beyond graphene has been extended using materials like h-BN [46], MoS₂ [47] and WS₂ [48]. These pivotal findings underline the potential of the 2D materials as tunnel barriers and are presented in the following

As an insulating material, h-BN is well suited as a tunnel barrier for the integration into magnetic tunnel junctions. Early works by Dankert *et al.* integrated the material between two ferromagnetic electrodes [49]. They created Ni₈₀Fe₂₀ (Py)/h-BN/Co and Co/h-BN/Co heterojunctions by preparing the bottom electrode and transferring CVD-grown h-BN on top. During this process, the exposition of the bottom electrode to the ambient conditions could not be avoided, leading to oxidation or contamination on the h-BN/FM interface. The top layer was then sputtered onto the h-BN. Room temperature TMR signals of 0.3% and 0.5% have been observed. While those results show the successful realisation of proof-of-concept devices for implementing 2D materials as tunnel barriers, they also highlight the difficulties related to clean interfaces accompanying the integration process.

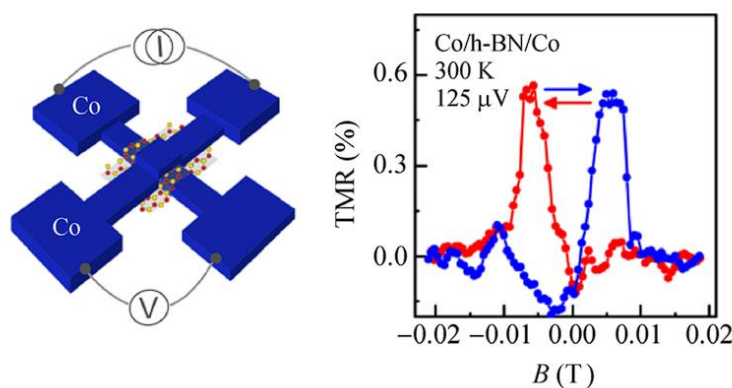


Figure 2.11: Magnetic tunnel junction of Co/h-BN/Co. The left side shows a sketch of the junction with the two cobalt electrodes separated by h-BN. The right side shows a measured TMR signal of about 0.5% at 300K. From [49].

Similarly to the presented case of graphene, Piquemal-Banci *et al.* [50] tried to

overcome the degradation of interface issues by direct growth of h-BN by CVD on Fe. This avoids the transfer process of h-BN onto the ferromagnet, thus avoiding the oxidation process of the FM. The top cobalt electrode was evaporated onto defined patterns to act as a top electrode (Figure 2.12a). The non-linear I(V) (Figure 2.12b) indicate tunnel behaviour with TMR measurement of 6% initially, later increased to 50% with optimized growth recipes. The extracted spin polarisation at the interfaces was determined to be two orders of magnitude higher than the reported values by Dankert *et al.* highlighting the importance of clean integration processes.

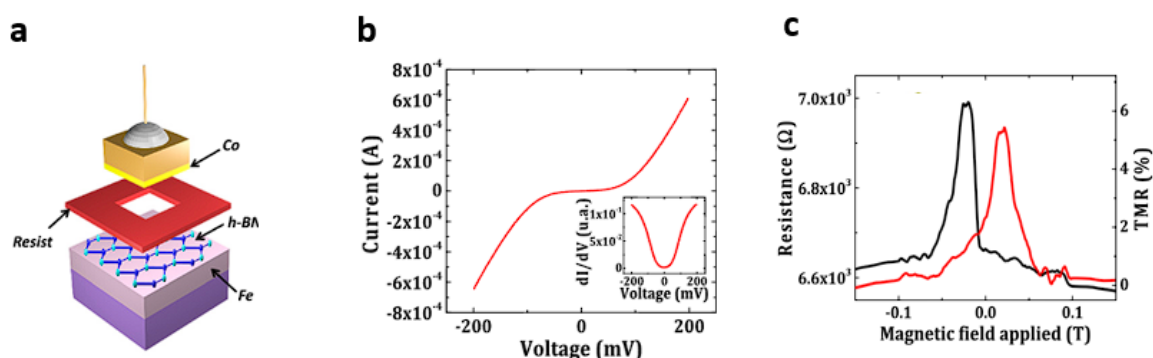


Figure 2.12: a) Fe/h-BN/Co, fabricated through direct growth of the h-BN on iron by CVD. MTJ. The non-linear I(V) curve indicates tunnelling behaviour, solidified by differential conductance in the inset. A Resistance change across the junction as a function of the applied magnetic field of up to 6% has been observed. From [50].

A direct growth of the h-BN/FM interface was also pursued by Asshoff *et al.* for h-BN based MTJs [51]. A pre-patterned aperture in a SiN_x is used to be able to contact the suspended 2D material from both sides. The flake is brought onto the hole by dry transfer and then contacted from each side by either NiFe or Co electrodes. Through this technique, a clean interface between the h-BN and FM is preserved, leading to a TMR of around 1%. Aside from being smaller than the CVD-grown results from Piquema-Banci *et al.*, it is still an order of magnitude higher than implementing h-BN through non-protective procedures.

In further studies, the group around Piquemal-Banci investigated the influence of the interfaces between h-BN and ferromagnets in greater detail [52]. They fabricated Co/h-BN/Co and Co/h-BN/Fe MTJs using bilayer and monolayer h-BN, respectively. In both cases, h-BN was deposited onto the lower electrode using CVD, while the upper electrode was applied via evaporation. TMR measurements revealed a sign change in the Co/h-BN/Co junction (Figure 2.13a). Under negative bias, the TMR shifted from +12% (at 10 mV) to -4% (at -10 mV). In contrast, the magnetoresistance of the Co/h-BN/Fe junction remained consistently positive (Figure 2.13b) across the entire measurement range, reaching values of up to 50%.

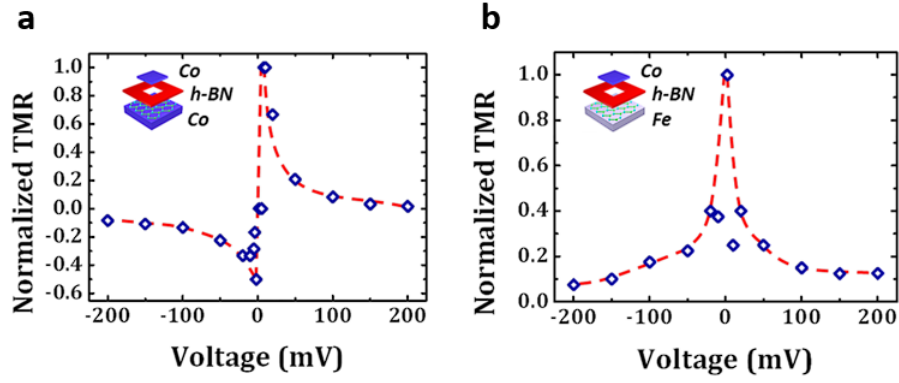


Figure 2.13: TMR measurements across a Co/h-BN/Co (a) and Co/h-BN/Fe MTJ. The TMR signal changes sign in the case of the Co/h-BN/Co, which is not prominent for the Co/h-BN/Fe junction. The red lines are guidelines for the eye, and the inset shows a sketch of the junction [52].

Using the Jullière model, the spin polarisation for the h-BN/Co interface was determined to be approximately 25%, while that for the h-BN/Fe interface was about 80%. However, the change to negative TMR in the Co/h-BN/Co junction can only be explained if one of the Co/h-BN interfaces exhibits negative spin polarisation. This result is initially unexpected, as symmetrical junctions are typically assumed to have identical interfaces. The researchers conducted DFT calculations, showing that the electronic band structure of h-BN is strongly influenced by the nature of its bonding to ferromagnetic materials.

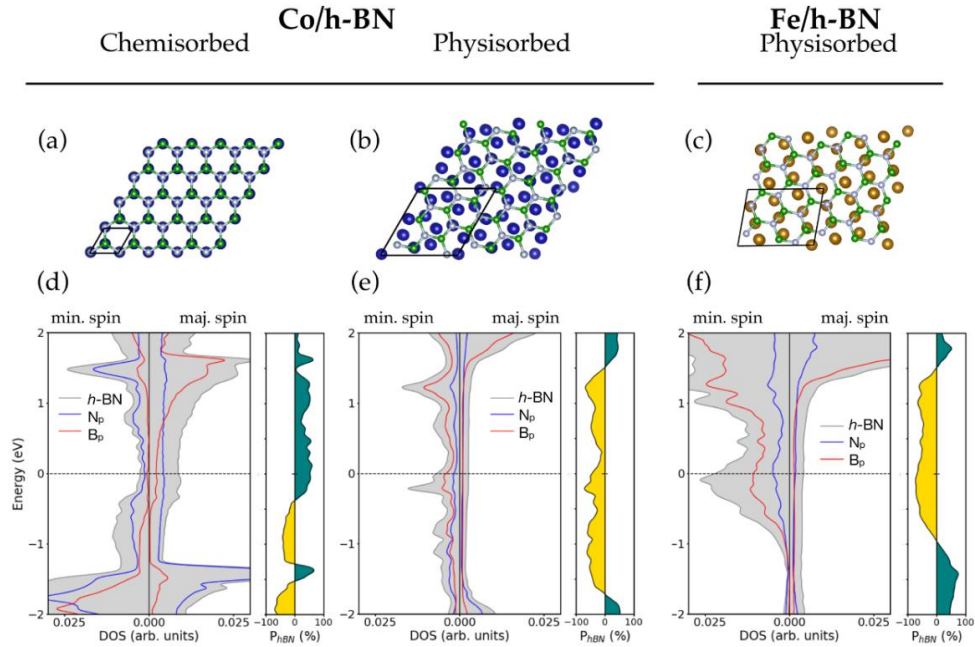


Figure 2.14: Band structure of h-BN on Co and Fe in the chemisorbed and physisorbed configuration. Sketch of the chemisorbed (a) and physisorbed (b,c) structure of h-BN and ferromagnet. The low lattice mismatch allows a chemisorbed and physisorbed Co/h-BN interface, while only the physisorbed Fe/h-BN configuration is stable. Chemisorption is reflected in the band structure of h-BN, which becomes metallic and is dominated by majority spins opposing the physisorbed case, where the Fermi level is governed by minority spins [52].

Due to the small lattice mismatch between h-BN and Co, chemisorption can occur (Figure 2.14). In contrast, the significant lattice mismatch between h-BN and Fe prevents chemisorption, resulting in physisorption. The chemisorption between h-BN and Co leads to a significant alteration in the band structure, causing h-BN to transition from an insulating to a metallic state. Furthermore, the spin polarization of the chemisorbed interface is inverted compared to that of the physisorbed interface. The findings suggest that the lower interface is chemisorbed due to the high-temperature CVD growth process, while the upper interface, formed through the gentler evaporation process, remains physisorbed. Thus, the Co/h-BN/Co junction is, in fact, not symmetric and is characterised by two distinct interfaces with unequal signs of spin polarisation. This explains the transition to negative TMR signals. In contrast, the Co/h-BN/Fe junction contains only physisorbed interfaces, leading to consistent spin polarisations and a positive TMR. These findings highlight how interface chemistry shapes the electronic and spintronic properties of MTJs, prompting further exploration of other 2D materials with diverse bandgap characteristics. One such material is MoS₂, which offers unique opportunities for integration into MTJs while presenting its own set of challenges

The first integration of MoS₂ into a junction was achieved by Wang *et al.* (2015) [53]. CVD-grown MoS₂ was transferred onto previously sputtered Py electrodes using a polymer-assisted transfer process. During this transfer, the bottom electrode underwent oxidation. After the polymer was removed with acetone, the top electrode was deposited via evaporation.

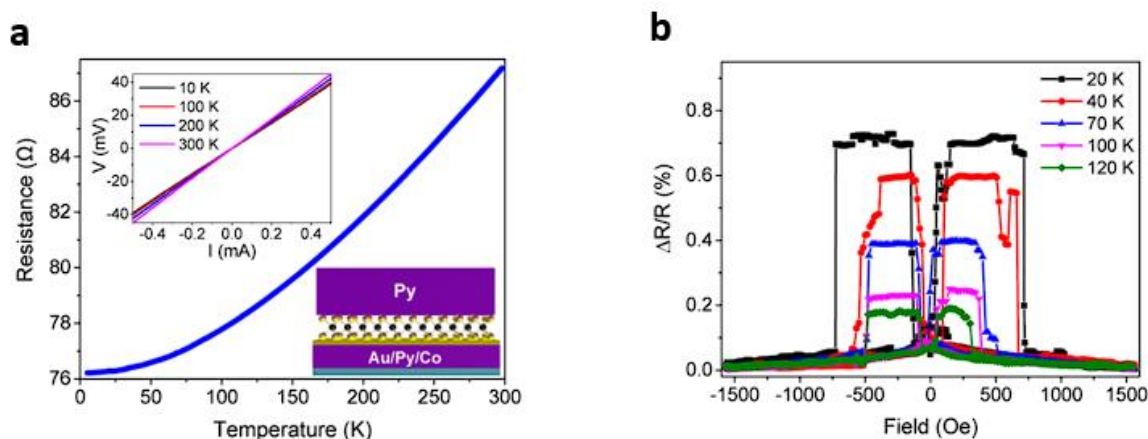


Figure 2.15:10 Integration of MoS₂ in an MTJ with Py electrodes (see inset a). The linear I(V) curve indicates a metallic behaviour for the MoS₂. Measurements of magnetoresistance at various temperatures show a change of resistance of up to 0.7% From [53].

Although MoS₂ is a semiconductor, transport measurements revealed a metallic character of the 2D material, which the authors attributed to hybridisation between MoS₂ and the magnetic electrodes and supported the assumption by theoretical

calculation, demonstrating the influence of orbital hybridisation on the band structure of MoS₂. Magnetotransport measurements showed an MR value of 0.4%. To prevent the oxidation of the bottom electrode, a thin gold layer was applied in a subsequent step. While this protective layer reduced the spin polarisation of the current, it effectively prevented interface degradation, resulting in a higher MR value of 0.7%.

Dankert *et al.* utilised a 0.8 nm thick AlO_x layer to protect the bottom Py electrode from oxidation [54]. The MoS₂ was transferred onto this protective layer, resulting in a Py/AlO_x/MoS₂/Co junction, with Co serving as the top electrode. These improvements enabled them to achieve a TMR of up to 2%. Theoretical calculations indicated that MoS₂ exhibits metallic properties at the interface, as observed in the work of Wang *et al.*, while a bandgap is preserved in the central region of the MoS₂ layer.

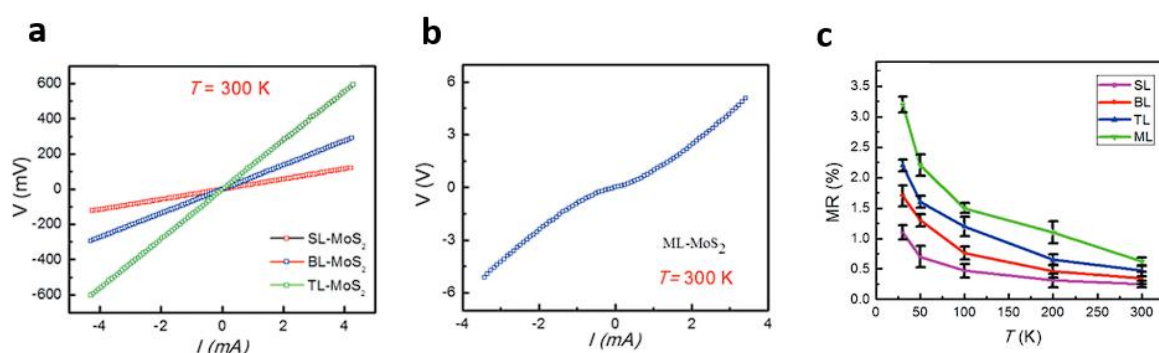


Figure 2.16: Current-voltage characteristics of mono-, bi-, tri- (a), and multilayer (8.1 nm, b) MoS₂, sandwiched between Ni and Co electrodes. While a few layers of MoS₂ are metallic, multilayer MoS₂ becomes semiconducting again. c) Shows the evolution of the MR signal with an increasing number of layers. Higher layer numbers enhance the spin filtering effect in MoS₂. From [55].

A similar behaviour was observed by Khan *et al.*, who studied the development of tunnel junctions as a function of the layer thickness of MoS₂ [55]. Mono-, bi-, tri-, and multilayer (8.1 nm) MoS₂ were positioned over holes in a silicon membrane and contacted on both sides with magnetic electrodes (Co and Ni). Layer-dependent voltage measurements revealed that mono-, bi-, and trilayers exhibited metallic behaviour (linear I(V) curve, see Figure 2.16a), while multilayer MoS₂ showed insulating properties, indicated by the non-linear current-voltage relation in (Figure 2.16b). This supports the findings of Dankert *et al.*, who suggested that MoS₂ functions as an insulator beyond a certain thickness. Furthermore, the magnetoresistance (MR) of the different junctions was measured. The results showed a trend of increasing MR values with higher layer thickness (1.1% for monolayers up to 3.2% for multilayers). The authors also pointed out that spin scattering at the FM/TMD interface, caused by defects such as sulphur vacancies, reduces overall spin polarisation and contributes to lower MR values in thinner layers.

Overall, the experimentally observed MR values of a few percent are lower than the theoretical expected values. For instance, Zhang *et al.* [56] predicted by DFT

calculation to achieve MR values up to 64% in Co/MoS₂/Co junctions and Dolui *et al.* [57] estimated the magnetoresistance of 300% for Fe/MoS₂/Fe junctions by first-principle calculations. A reason for reduced spin polarisation in MoS₂, and thus, reduced MR values, is given by Galbiati *et al.*, who investigated the mechanisms of charge and spin transport in MoS₂ multilayers using conductive tip atomic force microscopy (CT-AFM) [58]. Exfoliated MoS₂ flakes were deposited on a Co/Al₂O₃ substrate, with resistance measurements revealing that large-area flakes displayed low resistance while isolated flakes were electrically insulating. These findings confirm that the injected current spreads laterally within the MoS₂ plane before tunnelling through the Al₂O₃ barrier into the cobalt layer. Favoured lateral transport, instead of direct vertical tunnelling, leads to a significant reduction in resistance when current flows across a larger flake area.

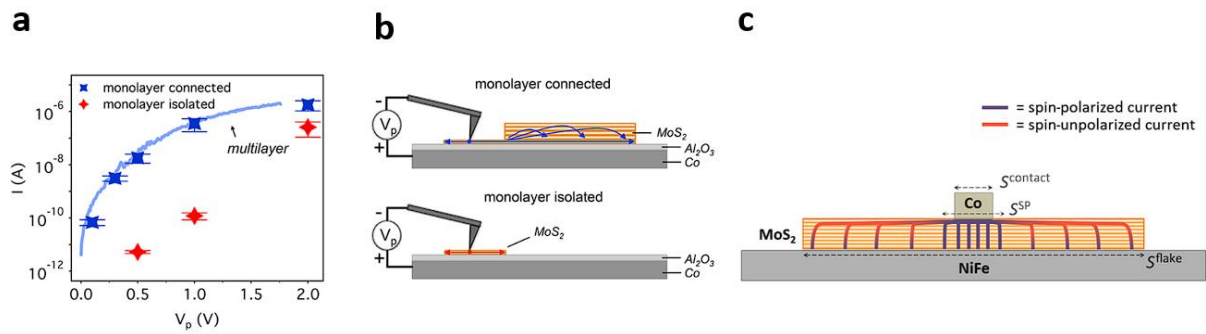


Figure 2.17: (a) Resistance of isolated and connected monolayer MoS₂ on Al₂O₃/Co. (b) Schematic representation of the experimental setup for connected and isolated monolayer MoS₂ configurations. The connected monolayer enables lateral current flow before tunnelling through the Al₂O₃/Co interface, whereas the isolated monolayer restricts current flow. (c) Spin-polarised and spin-unpolarized current transport in a magnetic tunnel junction with a MoS₂ flake, highlighting spin depolarisation due to lateral current spreading across the flake before tunnelling, reducing the overall MR. From [58],[59].

The authors further demonstrated that isolating parts of a flake increased resistance. For that, they cut off a few layers of MoS₂ from large flakes. While the few layers appeared priori conductive, they measured an increase in resistance once the flake was separated from the larger parent structure (Figures 2.17a and b). These findings align with the hypothesis of lateral current spreading. This phenomenon directly implies the spin transport in magnetic tunnel junctions. Due to the spin diffusion length in MoS₂ (~hundreds of nanometers), lateral transport leads to spin depolarisation (Figure 2.17c). The reduced spin polarisation lowers the observed MR values in MTJs, thereby underestimating the actual MR performance. Their study shows that minimising flake size relative to the junction area could preserve spin polarisation and enhance MR signals.

It has been shown that 2D materials like graphene, h-BN and TMDs are of high potential for integrating them into MTJs. Graphene has shown high spintronic

performances and, at the same time, reduced oxidation at interfaces. With h-BN and TMDs, a wide variety of bandgaps are available, enabling the tailoring of bandgap-related devices like MTJs to maximise efficiency. While these materials have been explored as tunnel barriers, the field of magnetic 2D materials enables the integration of 2D ferromagnets as electrodes, creating full 2D MTJs. *It can give the opportunity to enhance spin filtering effects and allow dynamic control of their magnetism due to proximity effects and gating.*

3 MAGNETISM IN 2D MATERIALS

3.1 INTRODUCTION

2D vdW magnetic materials offer rich opportunities for analysing magnetic theories due to their lowered dimensionality and utilising new functionalities for spintronic devices. The atomic thickness control and crystallinity enable the study of universal phenomena like the critical exponents and, thus, can improve and deepen the understanding of statistical physics and magnetic theory. The critical exponents describe specific physical properties like specific heat, magnetic susceptibility, spontaneous magnetisation, and coherence length as universal characteristics and are determined around phase transitions. In terms of applications, 2D ferromagnets could pave the way to high-speed spintronic application. Their thin nature allows low-size devices with tailored properties through gating or proximity effects to unlock new functionalities.

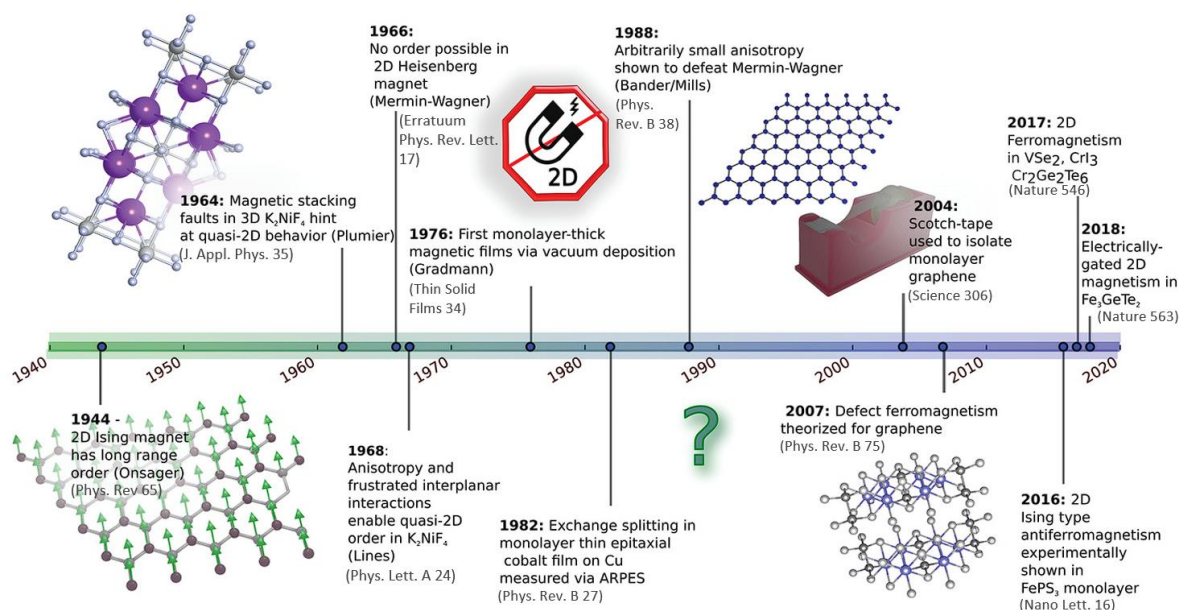


Figure 3.1: This timeline illustrates key developments in the study of 2D magnetism, from theoretical foundations to experimental breakthroughs. Starting in 1944, Onsager demonstrated the long-range order in the 2D Ising model. This is followed by the Mermin-Wagner theorem that 2D Heisenberg magnets cannot exhibit long-range order except when anisotropies are present (1988). 2017 experimentally demonstrated 2D ferromagnetism in monolayers like Fe_3GeTe_2 and CrI_3 . Adapted from [60]

The discovery of van der Waals based magnets allowed to relatively easily access lower crystallographic dimensions ($d < 3$). Reducing the crystal thickness to a few atoms has attracted attention in the magnetic community for many years (Figure 3.1). While the 3D Heisenberg picture was widely applied to bulk magnetic materials, Onsager

proposed the extreme case of magnetic order in 2-dimensional magnetic system in which the magnetic moments can only be pointing along one axis (Ising model). This reduction of the spin degree of freedom from 3 dimensions (Heisenberg model) to 1 dimension would allow the generation of a magnetic order in a monolayer crystal extending in two dimensions. The mathematically rigorous proof that the Heisenberg model cannot allow magnetic long-range order was published in 1966 under the name of the Mermin-Wagner theorem. However, Bander and Mills showed in 1988 that a phase transition from Heisenberg to Ising model happens when the ferromagnet is thinned down to monolayers and uniaxial anisotropy is present. This Ising-like behaviour has been observed in multiple monolayered ferromagnets [61]. Throughout the experimental determination of the critical exponents, comparisons can be made to theoretical values from different models, depending on the dimensionality of the system (d) and spin (n). Apart from the simplistic mean field model in which the independent magnetic moments are exposed to the same exchange field, the three main magnetic models are the Ising, the XY and the Heisenberg model, treating single spins in a nearest neighbour approach.

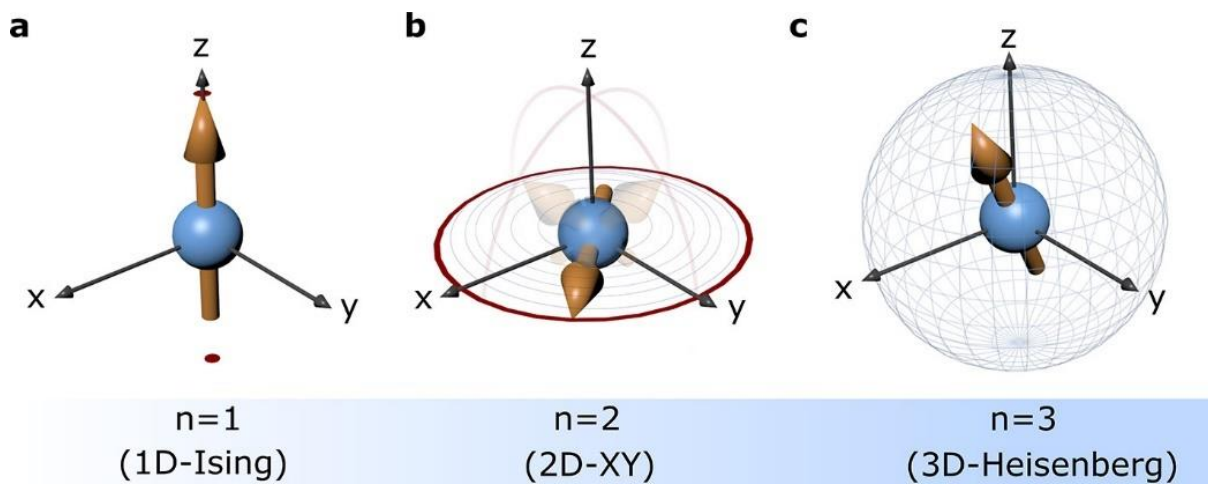


Figure 3.2: Illustration of the different spin models used to describe magnetic systems. a) The 1D Ising model in which spins can only point along the z-axis. b) The 2D XY model is where the spins are free to rotate inside a plane. c) The spin can point in any direction in the 3D Heisenberg model. From [62]

In fact, the Ising and XY models are simplified forms of the Heisenberg counterpart in which the spin dimensionality is restricted to 1 or 2 dimensions, respectively. The Hamiltonian can be expressed as in the following

$$H = - \sum_{ij} J_{ij} (a(S_i^x S_j^x + S_i^y S_j^y) + b S_i^z S_j^z).$$

Where the summation is done over neighbouring atoms i and j. Including J_{ij} the exchange integral and $S^{x,y,z}$ being the spin in either x,y or z direction respectively. While this Hamiltonian demonstrates the Heisenberg model, one can go to the Ising or XY model by restricting the spin dimensionality and thus changing the parameters

a and b ;

Ising model	$a = 0$	$b = 1$	$n = 1$
XY model	$a = 1$	$b = 0$	$n = 2$
Heisenberg model	$a = 1$	$b = 1$	$n = 3$

The Ising model describes, in its basic form, a lattice with allocated spins, which can be of only two different states ($n=1$), commonly referred to as up or down. The spins are interrelated only with nearest neighbours through exchange interaction J . Despite the model's simplicity, it exhibits phase transition and can gather valuable insights into the emergence of spontaneous magnetisations in ferromagnetic materials. Spins described by the XY model can be seen as spins free to direct themselves in a magnetic plane. Thus, it differs from the Ising model through a higher degree of freedom for the spins ($n=2$). In the Heisenberg model, the spins can point in any direction in the 3D space ($n=3$). Visualisation of the three models is shown in Figure 3.2, indicating their degree of freedom regarding the spin orientation. Subsequent to the different models, different physical consequences appear. The models combined with the dimensionality of the lattice have a direct influence on the appearance of phase transitions, the critical exponents, and long-range order. The magnetisation M is proportional to a simple scaling law:

$$M \propto (T_c - T)^\beta$$

With the critical exponent β , the magnetisation behaviour around the transition temperature can be determined, and the critical exponent beta can be used to identify which theoretical model describes the system best. In Table 3.1, the critical exponent for the different models is listed.

Model	Beta	
Mean field	0,5	[63]
3D Heisenberg	0,369	[64]
3D XY	0,345	[65]
3D Ising	0,325	[66]
Tricritical mean field	0,25	[63]
2D Ising	0,125	[67]

Table 3.1: Magnetic models with their corresponding critical exponent

The theoretical models describing the spin alignment in confined planes have offered a framework to understand ferro- and antiferromagnetism in 2D materials. Despite these theoretical foundations, direct experimental confirmation of intrinsic 2D magnetism is difficult. Here, stable monolayer crystals of 2D materials exhibiting magnetic order can be a approach for exploring the reduced parameter space. While supposedly 2D ferromagnets (like NiPS₃, CrSiTe₃ or MnPS₃) have been exfoliated to the monolayer thickness [68]–[71], the first confirmation of antiferromagnetic order was done by Raman spectroscopy on FePS₃ [72]. Optical microscopy and AFM measurements identified the monolayer of about 0.7nm height (Figure 3.3a and b). The number of discovered 2D ML FM is steadily increasing, enlarging the pool of materials and offering great potential for tailored 2D FM for spintronic devices. In the following main key findings of the recent years are discussed.

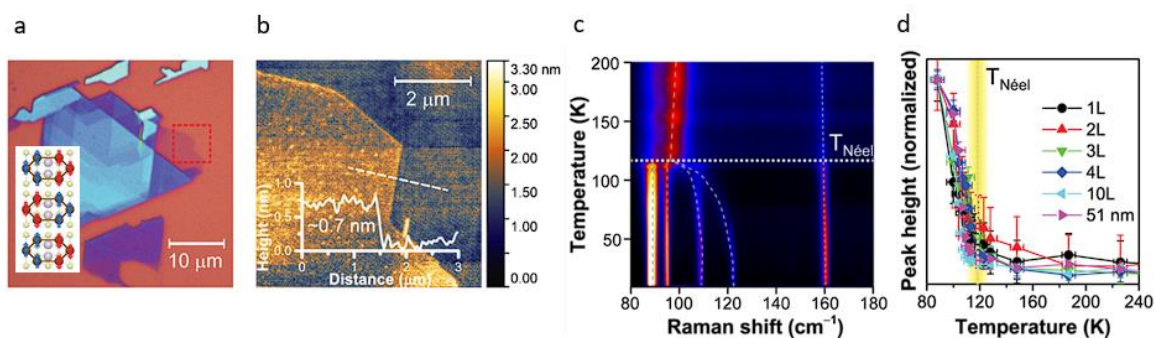


Figure 3.3: Antiferromagnetic order in monolayer FePS₃. a) Optical image of an exfoliated monolayer of FePS₃. The red square indicates where the AFM measurement confirms the ML thickness (b). c) Temperature dependent Raman map of FePS₃. The Raman modes above the Néel split or increase in intensity below 118K due to Brillouin zone folding, indicating antiferromagnetic order. d) The Monolayer Néel temperature of 118K is identical to that of bulk, and no thickness dependent trends are observed. Adapted from [72].

Interestingly, Lee *et al.* measured magnetic order in monolayer van der Waals magnets FePS₃ [72] (Figure 3.3) in 2016. CVT grown FePS₃ has been analysed by XRD to confirm the material's structural integrity. It has been exfoliated on SiO₂, and the help of optical microscopy and AFM measurements has identified the monolayer. Measuring magnetic order in monolayers is inherently challenging due to the low net magnetic signal. This challenge is even more pronounced for antiferromagnetic order, as the opposing spins effectively cancel each other out, making detection and characterisation particularly demanding. Lee *et al.* proposed utilising Raman measurements since the antiferromagnetic order can be seen by splitting the peak located around 100cm⁻¹ in the paramagnetic case when crossing the Neel temperature of 118K. Specific phonon modes located at the M point in the Brillouin zone are poorly Raman active and thus, hard to detect above the Néel temperature. Once the antiferromagnetic zic-zac order (referring to an antiparallel intra- and interlayer alignment of the spins, Figure 3.3a inset) is established (below 118K), the unit cell doubles its size to consider the magnetic order. This zone folding of the Brillouin zone translates the M point onto the Γ point and enables the measurement of the phonon

modes priori located at the M point. Their findings show antiferromagnetic ordering in monolayer FePS₃, and they could not find a shift in the Néel temperature when the number of layers was increased. These pioneering results demonstrated that magnetic order in van der Waals monolayer materials was quickly expanded to include additional materials. In particular, the group of chromium trihalides has garnered significant attention.

3.2 MAIN FAMILIES

3.2.1.1 Chromium Trihalides

The family of chromium trihalides CrX₃ (X = I, Br, Cl) belongs to 2D materials that have gathered early interest as magnetic insulators. CrX₃ are van der Waals materials where each layer forms a honeycomb lattice of chromium atoms sandwiched between halide atoms. The fundamental crystallographic structure is either the monoclinic $2C/m$ or rhombohedral $R\bar{3}$ phase and can change during heat cycling processes. The transition from rhombohedral to monoclinic is 200K, 240K and 420K for CrI₃, CrCl₃ and CrBr₃, respectively [73],[74]. In Figure 3.4, the top view of the two phases is presented. The colours indicate the Cr atoms at different lattices organised in a hexagonal structure. The bottom panel shows the corresponding view perpendicular to the c axis with halide atoms coloured in purple, in which the stacking of the two configurations becomes clearer, indicated by the double-sided black arrow.

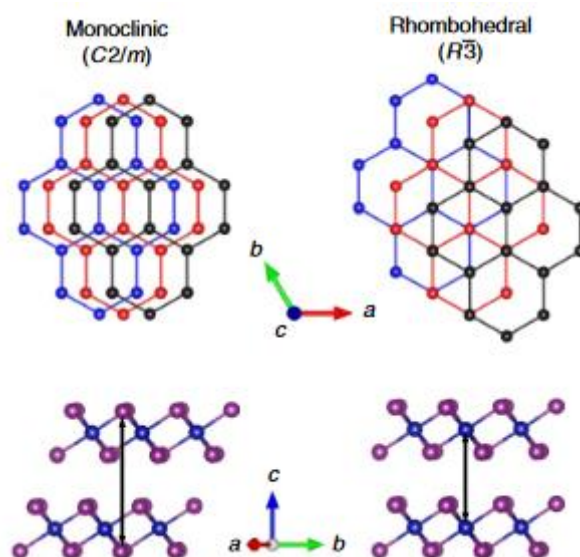


Figure 3.4: Top panel shows the monoclinic and rhombohedral phases of Chromium Trihalides, where the Cr atoms of different layers have the same colours. The bottom panel shows the side view of the layered structure, where the halides are coloured in purple. The different stacking of the phases becomes evident by the indicated black arrow. From [75].

Intralayer magnetism in the chromium trihalides is governed by the Cr atoms, which are organised in one plane. The nearest neighbour Cr atoms couple ferromagnetically, with each leading to bulk ferromagnetism, while the anisotropy determines the out-of-plane (CrI_3 , CrBr_3) or in-plane (CrCl_3) magnetisation axis. The stacking order and thus the wavefunction overlap from adjacent layers directly influences magnetism and can lead to interlayer antiferromagnetism as will be discussed below for the three components.

CrI_3

CrI_3 emerged in 2017 with the first measured hysteresis loop on the monolayer 2D magnet, displaying out-of-plane anisotropy [76]. Due to absolute low magnetic moments in exfoliated material, MOKE measurements were performed to record the switching behaviour of CrI_3 . Figure 3.5 shows the hysteresis cycles for mono-, bi- and trilayers. Interestingly, while a bilayer of CrI_3 showed no hysteresis opening, mono- and trilayer do, indicating antiferromagnetic coupling between layers. The first principal calculation suggests that the change of crystalline order from monoclinic to rhombohedral at 200K [77] induces a change in the p orbital hybridisation between the Iodine atoms of different layers, which mediate the super-superexchange (SSE) between the Cr atoms of adjacent layers. Together with the change of nearest and second nearest neighbours' distances when the crystal structure changes, CrI_3 undergoes a ferromagnetic to antiferromagnetic layer coupling transition [78].

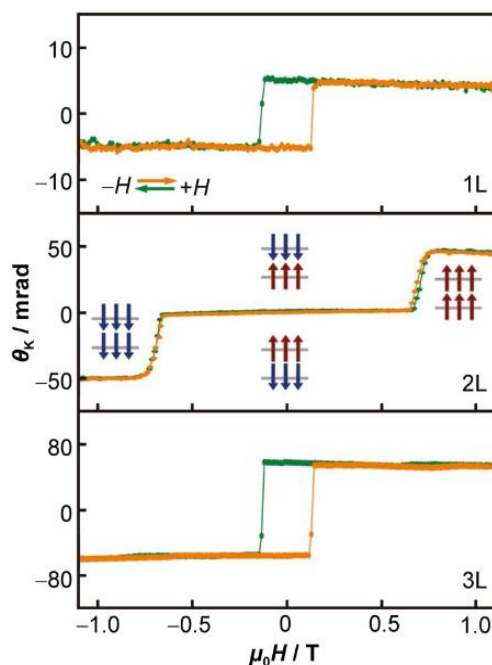


Figure 3.5: Magnetic hysteresis loops of CrI_3 measured by Kerr rotation as a function of applied magnetic field for different layer thicknesses. The mono and trilayer show hysteresis openings, indicating ferromagnetism. The bilayer shows two magnetic transitions, indicating an antiferromagnetic coupling between the layers. Adapted from [76]

CrCl₃

Early CrCl₃ experiments revealed the crystallographic rhombohedral structure in 1930 [79]. In the 40s, magnetic measurements revealed that the curie temperature of bulk CrCl₃ was 16.8K [80]. While a ferromagnetic behaviour of the material was assumed, neutron diffraction measurements later showed an antiferromagnetic transition at 17K [81]. Following their ideas of FeCl₂ and CoCl₂ [81] they find that each layer of CrCl₃ is ferromagnetic in the plane. At the same time, a weak interlayer antiferromagnetic exchange is present, which can be overcome with small external magnetic fields. Their findings were solidified shortly after by nuclear resonance measurements [82]. However, it was not until 2017 that CrCl₃ received relived attention due to McGuire *et al.* exfoliation of the first monolayer [73] (Figure 3.6).

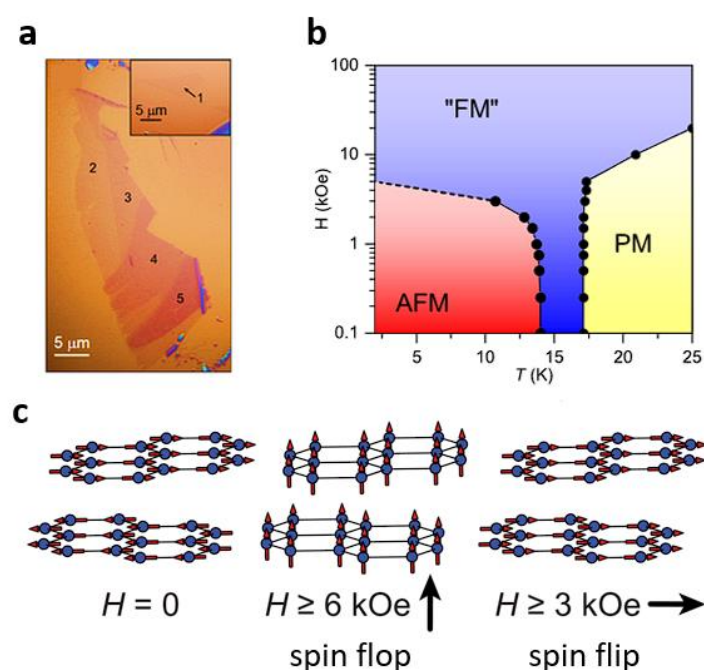


Figure 3.6: Magnetic properties of a few layers of CrCl₃. a) Optical image of exfoliated CrCl₃ flakes with different regions ranging from 2 to 5-layer thickness. The inset shows a monolayer. b) Magnetic phase diagram showing the transition between para-, ferro and antiferromagnetism. Depending on the applied external magnetic field, the in-plane easy axis shifts to out-of-plane (spin flop), (c). If the in-plane field is strong enough, the antiferromagnetic order between the layers can be broken, and the ferromagnetic order is established. Adapted from [73].

Apart from their observation of lattice rearrangement when cooling down the crystal from monoclinic to rhombohedral, their magnetic phase diagram analysis of bulk CrCl₃ found a curie temperature of 17K for low magnetic fields and a Néel temperature of 14K in which the spin lattices of each layer oppose each other. The field needed for spin flipping is higher than for spin flopping (Figure 3.6b). In 2019 Wang *et al.* showed that this antiferromagnetic behaviour sustains up to the bilayer limit [83]. These

findings distinguish CrCl_3 strongly from CrI_3 , in which antiferromagnetic order was observed with out-of-plane alignment; a high magnetic field is needed to force this alignment in CrCl_3 .

CrBr₃

Bulk CrBr_3 was characterised in the 60s, where a T_c of 37K was reported [84]. In 2019, the Curie temperature of 34K for monolayer CrBr_3 was measured using polarisation-resolved magneto photoluminescence and MOKE (Figure 3.7)[85]. They found ferromagnetic order down to monolayers and thickness dependent magnetic characteristics. The total magnetic response is higher when the number of layers increases. Contrasting the antiferromagnetic coupled layers in CrI_3 and CrCl_3 , CrBr_3 couples ferromagnetic, highlighting the unique characteristics of each of those materials. The inset in Figure 3.7a) shows the crystal structure and spin alignment for CrBr_3 . The temperature-dependent magnetic hysteresis loops show a decrease in coercive field when going to higher temperatures and the flattening of the curve indicates the vanishing magnetic moment.

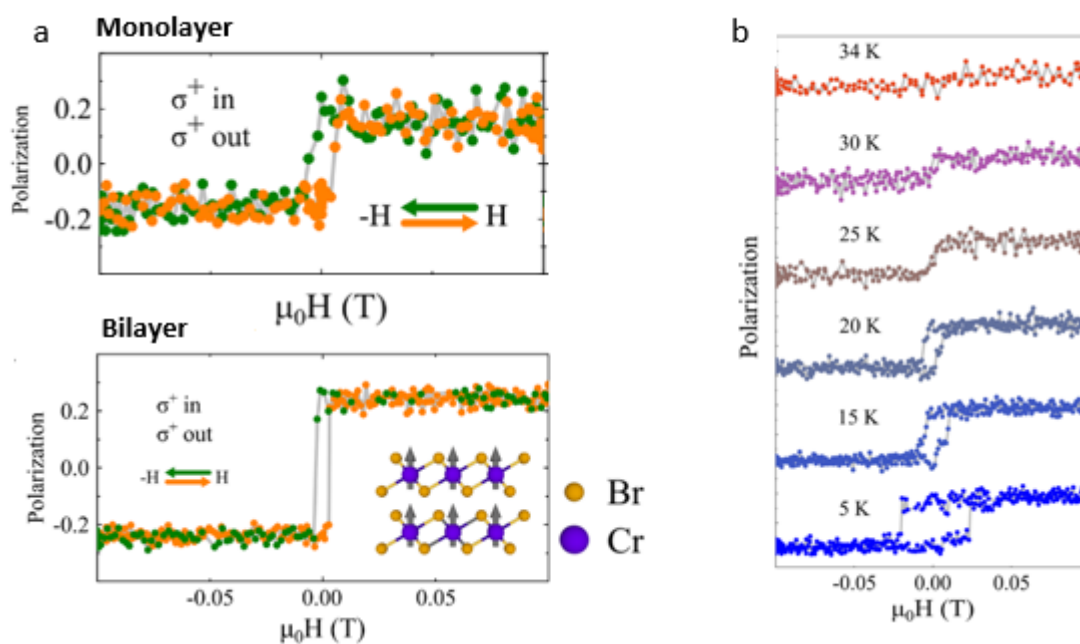


Figure 3.7: Ferromagnetism in CrBr_3 . a) Monolayer CrBr_3 shows a magnetic hysteresis at 2.7K measured by photoluminescence. The bilayer shows similar behaviour, indicating the ferromagnetic interlayer coupling. The inset shows the spin alignment in CrBr_3 . b) Shows the magnetic behaviour in temperature of monolayer CrBr_3 indicating a transition temperature around 34K. Adapted from [85].

A lower T_c of 27K was reported by Kim *et al.* [86] for the monolayer CrBr_3 , measured using magnetic circular dichroism (MCD). As the number of layers increases, the T_c rises, reaching the bulk value of 37 K at a thickness of three layers. They confirmed the out-of-plane anisotropy for mono and multilayers of CrBr_3 , along with relatively weak interlayer interaction. Additionally, they confirmed the ferromagnetic interlayer

coupling by measuring a finite magnetisation with MCD at zero field, whereas antiferromagnetically coupled bilayers would exhibit none.

3.2.1.2 $\text{Cr}_2\text{Ge}_2\text{Te}_6$

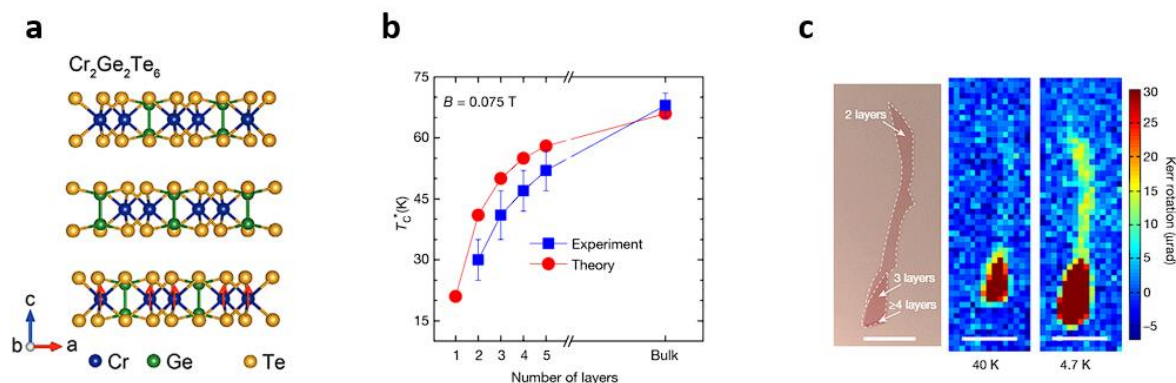


Figure 3.8: Crystal structure of CGT with alternating Te, Ge and Cr atoms in an ABC stacking (a). b) show magnetic response obtained by integrating over neutron scattering peaks at various temperatures and crystal directions. c) Magnetic response of a 40nm CGT flake by Kerr measurements, the inset shows the flake with the measured area marked by the red dot. Adapted from [87],[88].

Another chromium-based van der Waals material is the ternary chalcogenide $\text{Cr}_2\text{Ge}_2\text{Te}_6$ (CGT), first synthesized by Carteaux *et al.* in 1995[89]. The bulk crystal crystallizes in a rhombohedral lattice (space group R3), characterized by alternating layers of chromium, germanium, and tellurium atoms (Figure 3.8a). Each CGT layer consists of edge-sharing CrTe_6 octahedra forming a honeycomb lattice, with Ge atoms occupying interstitial sites between the CrTe_6 slabs. Using neutron diffraction, Carteaux *et al.* determined a Curie temperature of approximately 61 K with perpendicular anisotropy. When CGT is thinned down to a bilayer, magnetic ordering persists at low temperatures, and the Curie temperature becomes thickness-dependent, decreasing with reduced layer number (Figure 3.8b). Figure 3.8c shows an optical image of bi-/tri and multilayer CGT which is illustratively measured by MOKE at 40K and 4.7K, highlighting the layer and temperature dependent net magnetisation of the flake. Evaluation of monolayer CGT was not possible due to the material's rapid degradation under ambient conditions.

3.2.1.3 VSe_2

The measured ferromagnetic order of monolayer VSe_2 by Bonilla *et al.* in 2018 [90] has been a subject of controversy, highlighting the youth of the 2D FM field. Bonilla *et al.* reported strong room-temperature ferromagnetism with an in-plane easy axis in VSe_2 grown on HOPG by MBE. As bulk VSe_2 is paramagnetic, they observed a decrease in magnetic order with an increasing number of VSe_2 layers (Figure 3.9).

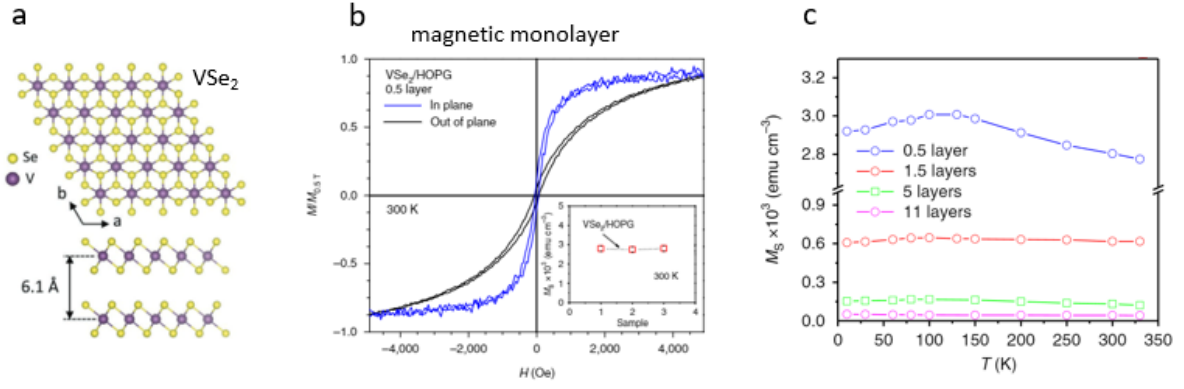


Figure 3.9: Sign of magnetic order in monolayer VSe₂. a) Crystal structure of van der Waals material VSe₂ in the 1T phase with the selenide atoms in yellow and vanadium in purple. b) magnetic measurement of monolayer VSe₂ at 300 K with an in and out of plane configuration. c) layer dependent magnetic saturation in dependence on the temperature. The magnetic order decreases throughout all temperature ranges for thicker VSe₂. Bulk VSe₂ is paramagnetic. Adapted from [90],[91].

In the same year, Feng *et al.* [92] published contradicting results for monolayer VSe₂ grown on bilayer graphene. Their analysis of the electronic structure and XMCD measurements on monolayer VSe₂ showed no magnetism at low temperatures (Figure 3.10). They proposed that charge density waves (CDWs) dominate the instabilities at low temperatures. They supported their findings with DFT calculations comparing spin-polarised and non-magnetic band structures. The non-magnetic calculation is coherent with their findings from ARPES measurements on VSe₂ crystal. This view is supported by the findings of Fumega *et al.* and Coelho *et al.* in 2019 [93],[94]. Fumega's team grew VSe₂ and VSe_{1.8} on HOPG by MBE and measured the magnetic properties using SQUID and XMCD. While the SQUID did not show any trace of magnetic order, the XMCD measurements revealed a small ferromagnetic signal, which they attributed to V impurities located in the van der Waals gap.

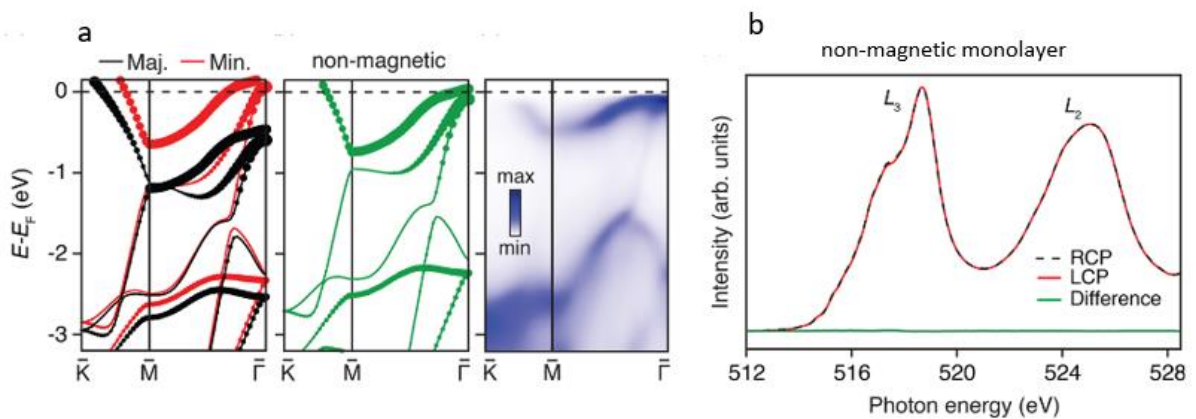


Figure 3.10: Non-magnetic monolayer of VSe₂. a) shows the calculated electronic structure of monolayer VSe₂ in the spin-polarised and nonmagnetic configuration (left and middle panel, respectively) calculated by DFT. The experimentally acquired data is on the right panel in a). It corresponds with the calculated non-magnetic band structure of VSe₂. b) XMCD measurements show no trace of absolute magnetic moment in the monolayer case of VSe₂. Adapted from [92]

Their DFT calculations suggested that the CDWs present in monolayer VSe₂ (also reported by Bonilla *et al.*) open a gap around the Fermi level, preventing magnetic order. Coelho *et al.* supported the nonmagnetic monolayer findings through ARPES studies, which did not reveal any spin splitting of the bands leading to a ferromagnetic state. The importance of atomic vacancies was highlighted by Yu *et al.* [91], who studied chemically exfoliated 1T-VSe₂ flakes. They found ferromagnetism in the monolayer case and observed that increasing defects in VSe₂ stabilised the ferromagnetic order. VSe₂ is highly unstable in air and degrades quickly in the monolayer form. This instability has led to the use of different passivation layers, such as Se (used by Bonilla, Feng, and Fumega) or perfluorodecanethiol (FDT) (used by Yu) to protect the material. The discrepancies in these findings highlight the need for further investigation to fully understand the intrinsic properties of monolayer VSe₂ and the impact of structural phases and defects on its behaviour. By this, VSe₂ remains a controversial element in the 2D ferromagnetic group, pointing out the difficulties in characterising the crystal's integrity and the intrinsic properties which come along with it.

3.2.1.4 The family of Fe_xGeTe₂ (FxGT)

Contrasting the discussion of VSe₂, the robust ferromagnetism in the Fe_xGeTe₂ is now widely accepted. The family of FGT consists of 3 derivatives: Fe₃GeTe₂ (F3GT), Fe₄GeTe₂ (F4GT), and Fe₅GeTe₂ (F5GT). All three ternary components are 2D materials with van der Waal gaps. Their crystal structure and magnetic properties differ from one component to the other, which will be discussed below.

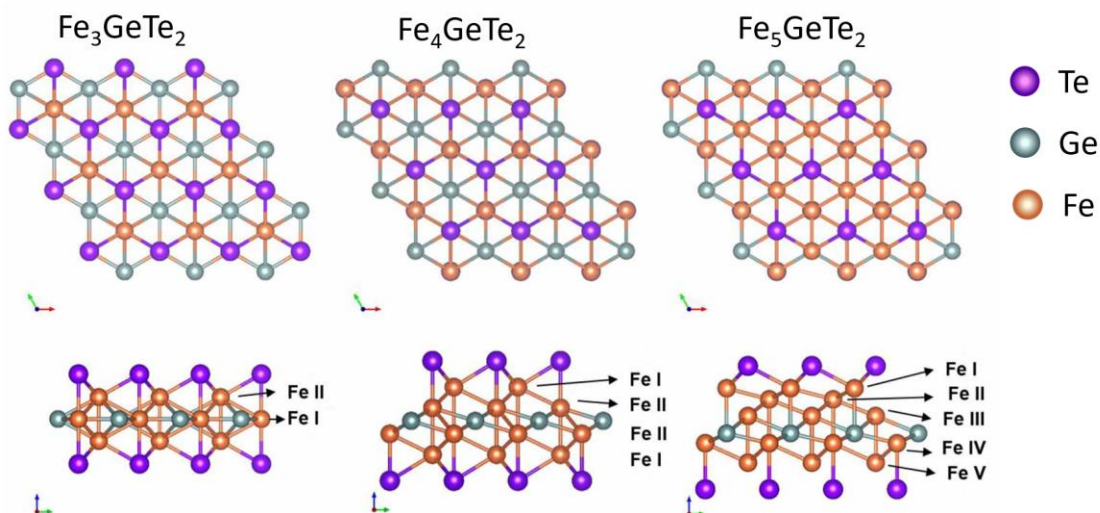


Figure 3.11: Crystal structures of Fe₃GeTe₂, Fe₄GeTe₂ and Fe₅GeTe₂ on the left middle and right, respectively. The top row represents the view along the c axis and the bottom view along the plane, with Tellurium (purple), Germanium (grey) and Iron (orange) atoms. The Iron atoms are labelled according to their sublattices, showing the complex stacking of Fe atoms. Adapted from [95].

F3GT is a hexagonal crystal which can be divided into five planes. The outer two planes consisting of tellurium enclose the other planes of Fe and Ge. The iron atoms in the inner layers can be distinguished from each other because they form different chemical bonds with their surroundings: a distinction is made between ferrous divalent Fe^{2+} and ferric trivalent Fe^{3+} . The ferric atoms are found in the layer directly adjacent to the tellurium (labelled as Fe II in Figure 3.11), while the ferrous atoms are in the middle layer with germanium (Fe I). These five layers together form a monolayer, which is stacked onto others by van der Waals forces. F3GT was first synthesised in 2006 by Deiseroth *et al.* and has been structurally characterised [96]. Using the solid-state reaction, they were able to synthesise the 2D material and determined the crystal structure to be hexagonal $P6_3/mmc$, with $a=b= 3.991(1)\text{\AA}$ and $c=16.33(3)\text{\AA}$.

F4GT consists of 7 planes, where the outer two are Te. As with F3GT, a distinction must be made between the iron atoms in the different planes. The planes adjacent to Te contain ferrous atoms, while the plane in the centre (3,4) contains ferric atoms. Seo *et al.* [97] firstly reported experimental results of this material with nearly room temperature ferromagnetism, synthesised by solid state reaction. They found lattice parameters of $a=b= 4.04(4)\text{\AA}$ and $c= 28.9(3)\text{\AA}$ in a rhombohedral $R\bar{3}m$ configuration. While the a and b parameters are of comparable size to F3GT, the overall slab thickness is larger.

F5GT is the only compound in the FGT family that contains exclusively ferrous iron atoms within the slab. Its crystal structure consists of eight atomic planes: two outer tellurium layers, one germanium layer, and five iron layers, all with the same oxidation state. Stahl *et al.* [98] synthesized F5GT in 2018 by solid-state reaction and determined its crystal structure to belong to the rhombohedral space group $R3m$, with lattice parameters $a = b = 4.0376(4)\text{\AA}$ and $c = 29.164(6)\text{\AA}$ [36]. Among the FGT compounds, F5GT contains the highest number of iron layers, which is reflected in its increased slab thickness.

The derivatives of FGT exhibit magnetic properties at remarkably high temperatures, distinguishing it notably from previously studied magnets such as CrI_3 and CGT and positioning it as a prominent candidate for applications in spintronic devices. However, despite extensive study, the overall magnetic behaviour of FGT remains rich and is still under active investigation. Specifically, higher Fe content within FGT correlates with increased Curie temperatures, as observed in experimental studies. It is noteworthy to mention that the determination of T_c may vary depending on the condition and methods employed, such as Zero Field Cooling (ZFC), Field Cooling (FC), Anomalous Hall Effect (AHE), or Arrott plots. The classification of the FGT family into the derivatives F3GT, F4GT, and F5GT has been fundamental in understanding their distinct properties. Early publications on F3GT, with its relatively high Curie temperature (230K) in bulk [96],[99], brought significant interest to this material. Subsequent reports revealed even higher Curie temperatures for bulk F4GT (270K) [97] and F5GT (270K-310K) [100],

solidifying the importance of this family of materials. However, it is important to note that the sharp distinction between different crystal structures and stoichiometries may not always accurately represent the material due to imperfect growth and the presence of minor phases. Determining the stoichiometry of FGT presents challenges, as various methods offer differing levels of precision and spatial resolution. Some methods provide precise structural analysis on a local level but are limited to grasping the structure of the whole sample. Other techniques may be able to average over the whole sample but are lacking in their ability to detect minor phases or side occupancy of iron atoms within the unit cells. This highlights the need for careful consideration and possibly the integration of multiple techniques to obtain accurate stoichiometric information.

Fe₃GeTe₂

It has been shown that the lattice parameter can be an indicator of the iron concentration inside FGT. Particularly, F3GT exhibits a distinctiveness from other forms owing to a significant difference in the *c* lattice parameter, while F4GT and F5GT demonstrate closer similarities. May *et al.* [80]. It was shown that the Curie temperature drops strongly for bulk material with lower iron concentration (Figure 3.12c).

They analysed CVT grown bulk polycrystalline F_{3-x}GT while *x* varied in the range of -0.1 to 0.25. The Curie temperature went from 140K for F_{2.75}GT to 232K for F_{3.1}GT. Liu *et al.* confirmed the influence of iron stoichiometry on the *T_c* in MBE grown F3GT films on sapphire and GaAs [102]. This drastic increase illustrates the importance of the iron composition of the specimen. They observed smaller in-plane lattice parameters related to lower iron concentrations, while the inverse is found for the *c* direction. For the single crystal F3GT, a perpendicular magneto crystalline anisotropy (PMA) was found (Figure 3.12c).

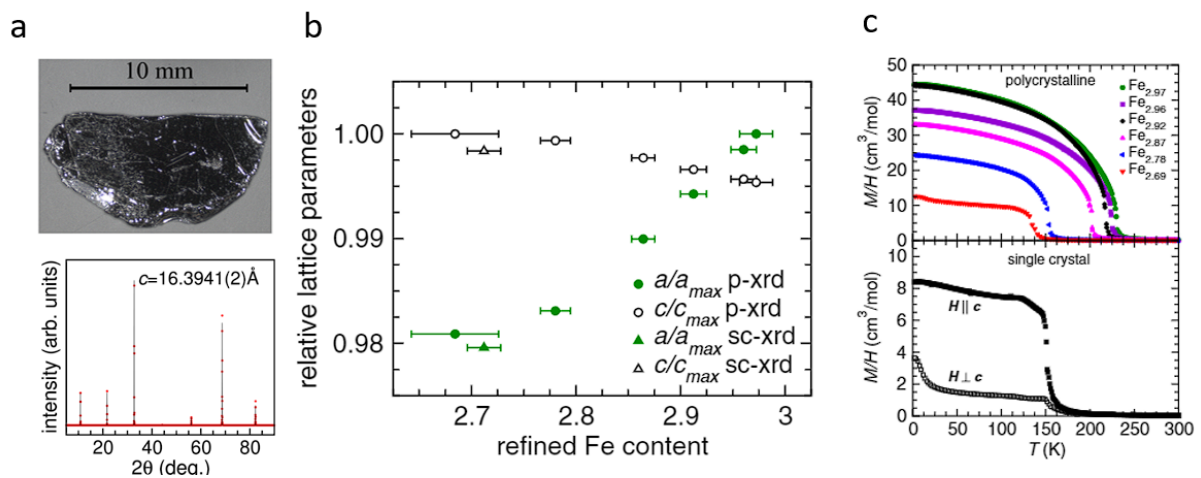


Figure 3.12: F3GT van der Waals magnetic. A) Shows an optical image of a bulk CVT-grown F3GT crystal with the corresponding out-of-plane X-ray diffraction pattern. b) Influence of the iron stoichiometry on the normalised lattice

parameters a and c obtained by powder (pxrd) and single crystal (sc-xrd) XRD. The Iron content in F3GT has a strong influence on the Curie temperature T_C , while the out-of-plane anisotropy is persistent. From [101].

This anisotropy stays perpendicular when F3GT is exfoliated down to monolayers (Figure 3.13a), as Fei *et al.* published in 2018 [103]. By gold-assisted exfoliation, they reached the 0.8nm thick monolayer. Using polar reflective magnetic circular dichroism (RMCD), they were able to acquire a magnetic hysteresis loop on the sample, showcasing the PMA and monolayer ferromagnetism and a Curie temperature of 130K.

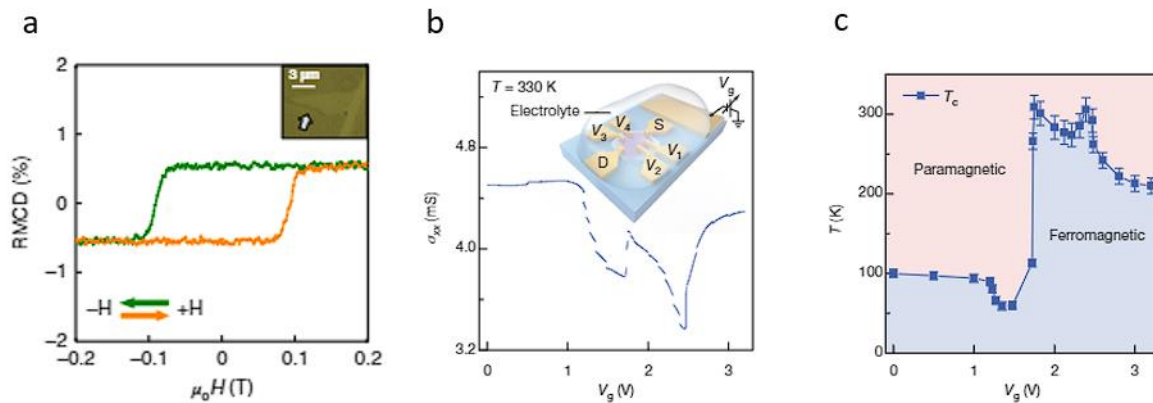


Figure 3.13: Magnetic properties of F3GT. a) First, successfully measured magnetic hysteresis curve of monolayer F3GT by reflective magnetic circular dichroism. b) Conductivity in dependence of the gate voltage of ion liquid gated trilayer F3GT. The inset shows a sketch of the system. The change in conductivity reflects partially the change in magnetic behaviour c). The Curie temperature of F3GT can be pushed towards room temperature by applying an appropriate gate voltage. From [103],[104].

Deng *et al.* confirmed the PMA and monolayer ferromagnetism in F3GT, by relying on alumina assisted exfoliation [104]. Utilising liquid gating with LiClO_4 (Figure 3.13b, inset) on exfoliated CVT grown trilayer F3GT they were able to change the Fermi level of the material. The top gate not only influenced the conductivity of the material (Figure 3.13b) but also increased the Curie temperature of F3GT up to 300K (Figure 3.13c). This increase in T_C can be understood in the framework of the Stoner model, which is applicable for itinerant ferromagnets like F3GT. In this model the magnetic stability is directly related to the density of states at the Fermi level. Modulating the Fermi level via liquid ion gating, the DPS and consequently the stability of the ferromagnetic phase, can be modified enabling the enhancement of T_C towards room temperature. While this highlights the tunability of T_C in trilayer F3GT, the magnetic behaviour of monolayer F3GT appears more fragile. Dang *et al.* reported a lower T_C for monolayer F3GT by Hall measurements (20K) and RMCD (76K) compared to Fei *et al.* (130K). While the sample from Fei *et al.* has been exfoliated on gold, Deng *et al.* used an alumina substrate. The discrepancy in the Curie temperatures could be stain-related

[101],[105] or, as Roemer *et al.* [106] proposed, due to oxidation.

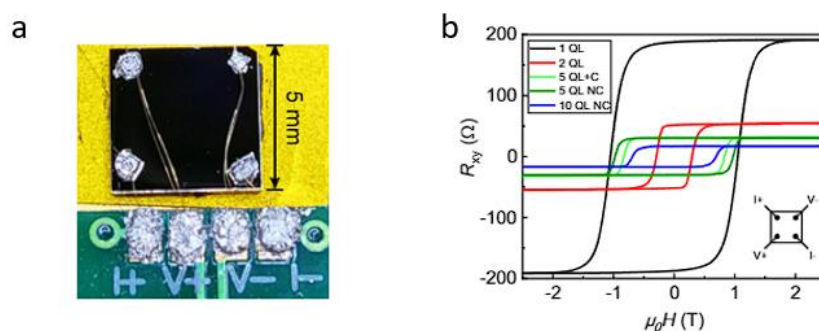


Figure 3.14: Large scale atomically thin F3GT layers grown by MBE. a) Optical image of the grown material on Ge(111) bonded in a van der Pauw configuration. b) Magnetic hysteresis measurements on F3GT samples of various thicknesses. All samples are capped by Te after growth except for the 5 ML NC (non-capped) sample, which shows a higher coercive field than the capped one, indicating an influence of oxidation in the sample. From [106].

They analysed MBE grown F3GT and reported a T_c of 75K (remanent resistance) and 126K (Arrot plot) for monolayers. Notably, they found that resistance measurements on mono- and bilayer samples gave insulating behaviour, while tellurium capped mono- and bilayer samples remained conductive. They attribute the change in conductance to oxidation of the uncapped samples, affecting their electronic properties. Further, the oxidation also influences the magnetic behaviour of F3GT, when comparing five layers thick capped and uncapped samples. The change in coercive field (Figure 3.14b) raises the question of magnetic stability in unprotected F3GT, likely due to surface degradation by oxidation. Their findings further demonstrate the possibility of fabricating F3GT on a large scale, which is a requirement for more systematic applications. Despite the different reported T_c values for monolayer F3GT, all three groups reported an increase in T_c when the number of layers increased. Other groups reported the increased Curie temperature due to extrinsic effects like heterostructures or ion implantation. Liu *et al.* [83] analysed the influence of stacking F3GT and the antiferromagnet CrSb (CS) by MBE. Through proximity effects at the F3GT/CS interface, ferrimagnetism can be established. Due to the interfacial exchange and increased repetition of F3GT/CS slabs, the Curie temperature is increased drastically. Similar effects have been observed by Wang *et al.* [107] who grew F3GT on (0001) sapphire substrates and Bi_2Te_3 (BT) by MBE. Besides confirming the PMA of FGT, they found an increase of T_c of the F3GT/BT heterostructure up to 400K. Interestingly, the T_c was higher for thinner F3GT samples (400K for 4nm and 230K for 50nm thick F3GT). They argue that the inverse tendency of thinner flakes with higher T_c instead of lower, as reported before, is related to interfacial exchange effects between F3GT and BT. When thinning down F3GT, the interfacial exchange enfolds its full potential since it is in competition with bulk effects; at low thickness, those bulk effects are reduced and the interfacial exchange dominates. Yang *et al.* were able to increase the Curie temperature from 230K to 450K by implementing gallium in

exfoliated 170 nm thick F3GT flakes. By irradiating the material with the Ga for different times, they observed an incremental shift to higher T_C with longer exposure time. Noteworthy is the change from out-of-plane to in-plane anisotropy when reaching higher T_C . While chemical doping can increase the temperature at which the phase transition appears, the underlying mechanism is not fully understood. They propose that the gallium implementation could lead to strain effects shifting the T_C [105] while they cannot fully neglect amorphization or structural changes.

Fe₄GeTe₂

Going to higher Iron compositions, namely F4GT, the magnetic behaviour changes compared to F3GT crystals. Seo *et al.* grew F4GT by CVT and analysed exfoliated flakes down to 7nm [97]. An exemplary flake of 11 layers is shown in Figure 3.15a. Scanning transmission microscopy images revealed the F4GT crystal structure, which is confirmed by energy dispersive spectroscopy to be Fe:Ge:Te = 4.11:1.0:1.85 with slight iron excess and tellurium deficiency. Different methods were used to determine the T_C from bulk to 7 layers (Figure 3.15e), like magnetooptical Kerr effect (MOKE), magnetic circular dichroism (MCD), and AHE. The Curie temperature is reported to be around 270 K, with the surprising tendency to be slightly higher when reaching smaller thicknesses. Apart from the ferromagnetic transition around room temperature, they observed a so-called spin reorientation T_{SR} in their samples. While at temperatures $T > T_{SR}$, the anisotropy of F4GT is in-plane, it switches to out-of-plane at $T < T_{SR}$ (Figure 3.15c). They attribute this to overall small anisotropy of 0,23J/cm³ compared to F3GT 1.03J/cm³. The spin reorientation is the competition of the shape anisotropy and magneto crystalline anisotropy, which scales differently with temperature, leading to a reordering of the spin alignments around T_{SR} .

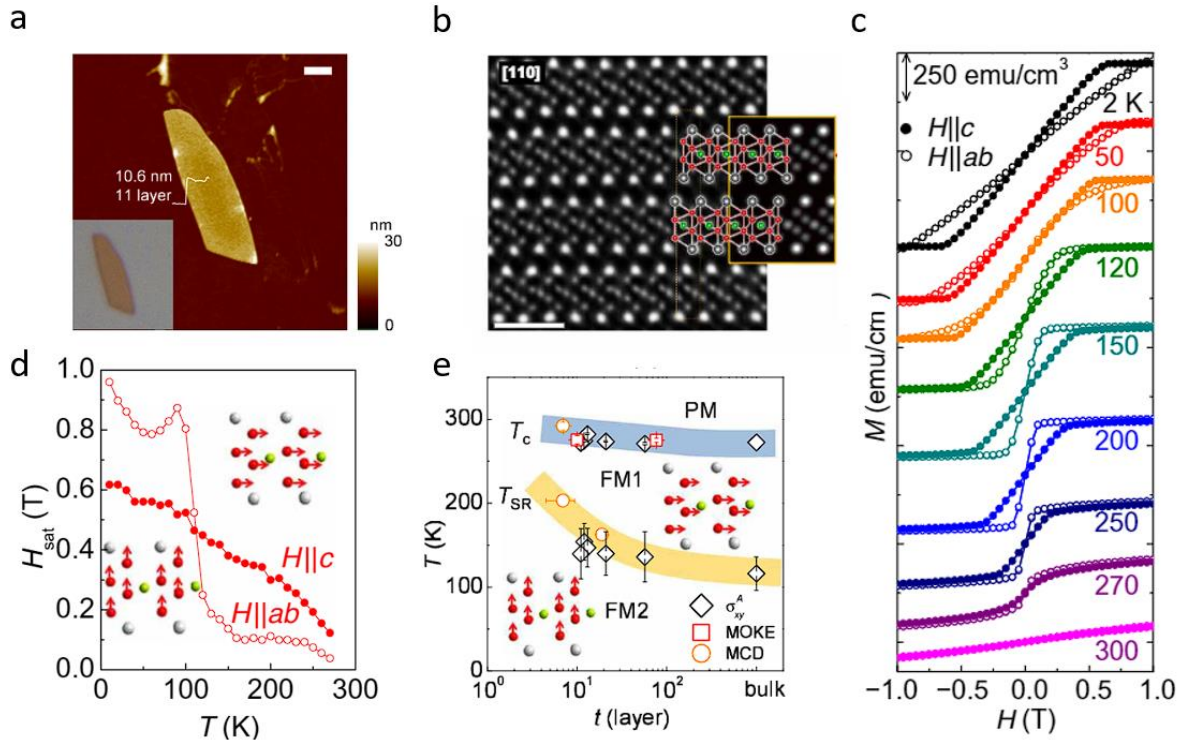


Figure 3.15: Magnetic properties of CVT grown F4GT. a) AFM measurement of an 11-layer thick exfoliated flake with an optical image in the inset. b) TEM images of the material along the [110] direction, confirming the structure of F4GT. c) Magnetic hysteresis measurement at various temperatures along the in-plane and out-of-plane direction (open and closed circles, respectively). The easy axis changes (spin reorientation temperature T_{SR}) between 100 and 120K between out-of-plane and in-plane. d) $M(T)$ curves for the sample illustrating the T_{SR} temperature. e) Curie and spin reorientation temperature for various thicknesses of F4GT. While the curie temperature seems to be relatively stable when thinning down the material, the T_{SR} increases. Adapted [97] .

Fe₅GeTe₂

First synthesised by iodine-supported CVT in 2018 by Stahl *et al.* [108] , it gathers more and more attention due to its intrinsically high Curie temperature of around 280K. While they report that the partial substitution of iron with nickel slightly increases the Curie temperature, May *et al.* [109],[110] published two studies about the bulk and exfoliated material with more magnetic details. An optical image of an F5GT flake is shown in Figure 3.16a, with the black square indicating where the ML height of 0.8 nm was measured by AFM. May *et al.* observe that the magnetic properties can depend on quenching during the growth process (Figure 3.16c). When the sample is cooled down more rapidly, they observe a stronger magnetic response. Ohta *et al.* [111] confirmed that the growth history related to the magnetic properties when they compared a few layers of F5GT. They observed a higher coercive field for quenched layers (Figure 3.16b). May *et al.* also report the anomalies of the $M(T)$ curve (between 100K and 270K) in which the overall magnetisation peaks. May *et al.* proposed that either ferrimagnetic behaviour, iron deficiency, or spin canting were the causes. The low magnetic anisotropy and the $M(T)$ curve illustrate the complex behaviour of F5GT compared to F3GT.

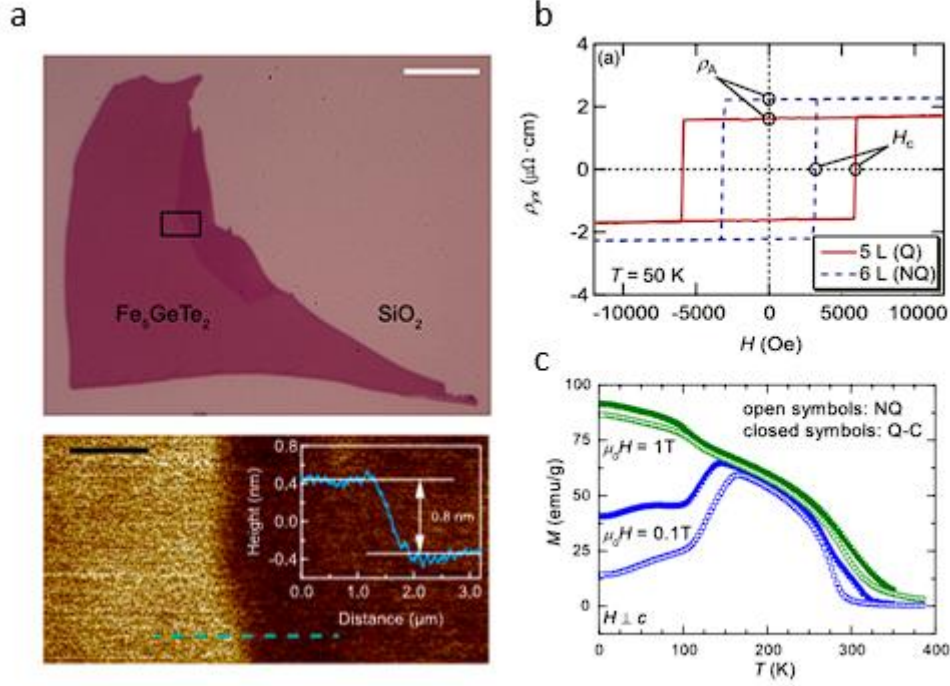


Figure 3.16: Exfoliated F5GT grown by CVT. a) Optical image of exfoliated F5GT on silica. The black box in the image indicates where the AFM measurement took place. There, the single-layer thickness was determined to be 0.8 nm. The growth history has a direct influence on the magnetic properties, as shown in b), where a difference between quenched grown and non-quenched grown samples can be seen. The quenched samples are characterised by higher coercive fields. c) $M(T)$ measurement of F5GT indicating a peak between 100K and 300K. This peak shows the non-trivial magnetic properties of F5GT. From [109]–[111].

Tian *et al.* [112] grew $(\text{Fe}_{1-x}\text{Co}_x)_5\text{GeTe}_2$ by iodine-assisted CVT and analysed the influence of Co doping on the magnetic characteristics of F5GT. They reported an increased T_c to 337K for FGT doped by $x=0.20$ as well as a change in anisotropy from slightly PMA ($x=0$) to in plane. Further, the Co doping suppresses the features observed between 100K and 300K, indicating a suppression of the reordering of the iron atoms in this temperature range. Increasing the doping to values above $x=0.36$, new phases appear. They observed an antiferromagnetic behaviour with spin-flop transitions in the magnetic hysteresis measurements and antiferromagnetic-like phase transitions in the $M(T)$.

Material	Conductivity	Magnetic order	Easy axis	Tc Monolayer	Tc Bulk	Reference
CrI ₃	semi-conductor	AFM	OOP	45 K	61 K	[76],[113]
CrBr ₃	semi-conductor	FM	OOP	34 K	37 K	[84],[85]
CrCl ₃	semi-conductor	AFM	IP	2L 16K	17 K	[73],[81]
Fe ₃ GeTe ₂	metal	FM	OOP	20-130 K	230 K	[103],[104],[106],[114]
Fe ₄ GeTe ₂	metal	FM	OOP $T < T_{SR}$ IP $T > T_{SR}$		270 K	[97]
Fe ₅ GeTe ₂	metal	FM	Weak OOP		273 - 310 K	[115]
Cr ₂ GeTe ₆	semi-conductor	FM	OOP	2L 30 K	61K	[88],[89]
FePS ₃	semi-conductor	AFM	OOP	118 K	123 K	[72],[116]
MnPS ₃	semi-conductor	AFM	OOP		78 K	
NiPS ₃	semi-conductor	AFM	IP	ML not Magnetic 2L 130K	155 K	[116],[117]
CoPS ₃	Semi-conductor	AFM	IP		119	[118]
VSe ₂	metal	FM	IP	330 K under debate	No magnetic order	[90],[93],[94]

Table 3.2: Selection of discovered van der Waals magnets and their properties.

The presented 2D magnetic materials in this section are diverse as summarised in Table 3.2, exhibiting layer-dependent ferromagnetic-antiferromagnetic transitions,

semiconducting or conductive behaviour, and stable out-of-plane or in-plane anisotropy. This variety makes them valuable for analysing magnetic models in 2D and exploring their potential in future spintronic devices. However, challenges remain in achieving consistent magnetic behaviours, as many 2D magnets are highly sensitive to environmental conditions, such as substrate interactions and structural defects. This is especially evident in materials like VSe₂, where conflicting magnetic results underscore the complexity of characterising intrinsic properties. Nonetheless, the relatively young field of 2D ferromagnets holds immense promise, with ongoing discoveries expected to expand the range of 2D magnetic materials. While many 2D magnets have intrinsic low Curie temperatures, experimental advancements, such as ion liquid gating, have successfully raised the Curie temperature of few-layer F3GT to room temperature, pushing the field closer to practical applications.

3.3 MTJs WITH 2D FM ELECTRODES

Spintronic devices in the form of MTJs have started to be explored with 2D ferromagnets like chromium trihalides [119]–[125] and FGT [126]–[129]. FGT, with its intrinsic conductivity, has been primarily utilised as an electrode material, while chromium trihalides, due to their semiconducting nature, are implemented as tunnel barriers. In these configurations, graphene can be used as a non-magnetic electrode. When magnetic tunnel barriers are used, spin-selective filtering occurs within the barrier itself. Applying an external magnetic field drives the magnetic state of the barrier and leads to an overall resistance change. Although high TMR ratios have been achieved with layered antiferromagnetic materials like chromium trihalides, their application in real devices is limited by several factors.

Firstly, achieving substantial TMR effects typically requires high magnetic fields (up to 9 T) to achieve spin flopping. Additionally, the layer-dependent magnetic order (like antiferromagnetic to ferromagnetic transitions as seen for CrI₃) introduces complexities in maintaining consistency during manufacturing. The chromium trihalides cannot be used as an electrode due to their semiconducting nature and further, exhibit low Curie temperatures, limiting their practical usability. In contrast, the ferromagnetic conductor FGT can potentially address these limitations, offering higher Curie temperatures and stable ferromagnetic properties without the need for excessive external fields.

The promising characteristics for FGT as an electrode in MTJs are supported by a growing number of ab-initio calculations that predict high MR values as presented in Table 3.3. They further elaborate on the influence of the different tunnel barriers on the spin transport properties in the MTJs.

Year	Top Elec	Tunnel Barrier	Bottom Elec	Calc. Spin Polarisation	Calc. MR	Ref
2019	Fe ₃ GeTe ₂	Gr	Fe ₃ GeTe ₂		3621%	[130]
		h-BN			6256%	
2020	Fe ₃ GeTe ₂	h-BN	Fe ₃ GeTe ₂	75%	183/252 (1/2 ML)	[131]
2020	Fe ₃ GeTe ₂	InSe	Fe ₃ GeTe ₂		700%	[132]

Table 3.3: Theoretical predictions for magnetic tunnel junction on the base of 2D vdW magnets.

Li *et al.* [130] performed ab initio calculations to investigate the behaviour of MTJs consisting of F3GT electrodes and either graphene, h-BN or vacuum as a spacer between the magnetic electrodes (Figure 3.17a). According to their calculations, the TMR of F3GT/h-BN/F3GT can reach values up to 6300% around the undoped Fermi level (Figure 3.17b) with the spacer layer of h-BN modelled as a monolayer in these calculations. The authors found that the positioning of the Fermi level significantly influences the transmission of minority and majority spins, leading to drastic changes in the size of the TMR effect. Additionally, they calculated the TMR effect for an F3GT/graphene/F3GT stack and an F3GT/vacuum/F3GT stack, resulting in TMR values of 3600% and 13800%, respectively. Notably, is that the high TMR values for the graphene and h-BN barriers are achieved at specific bias values (Figure 3.17b). They observe that a negative bias overall increases the TMR value due to a strong suppression of the tunnel channels in the antiparallel alignment. Whereas in the positive bias regime the spin asymmetry is reduced.

A less pronounced bias effect (Figure 3.17d) is reported by Lin and Chen [131] when describing the TMR in F3GT/h-BN/FGT by spin-dependent scattering channels through F3GT (Figure 3.17c), contrasting with the Jullière model, which assumes spin polarisation at the interfaces. They defined the tunnelling current and, thus, the TMR effect through transmission using the WKB approximation. Due to spin-dependent potential differences around the iron atoms in FGT, the scattering rates for spin-up and spin-down differ, leading to unequal transmission in the parallel and antiparallel states for spin-up and spin-down, respectively. The authors calculated the TMR through scattering for Cu/F3GT/h-BN/F3GT/Cu junctions, where the h-BN was a monolayer and the F3GT layers were either monolayer or bilayer to be 183% and 252% respectively.

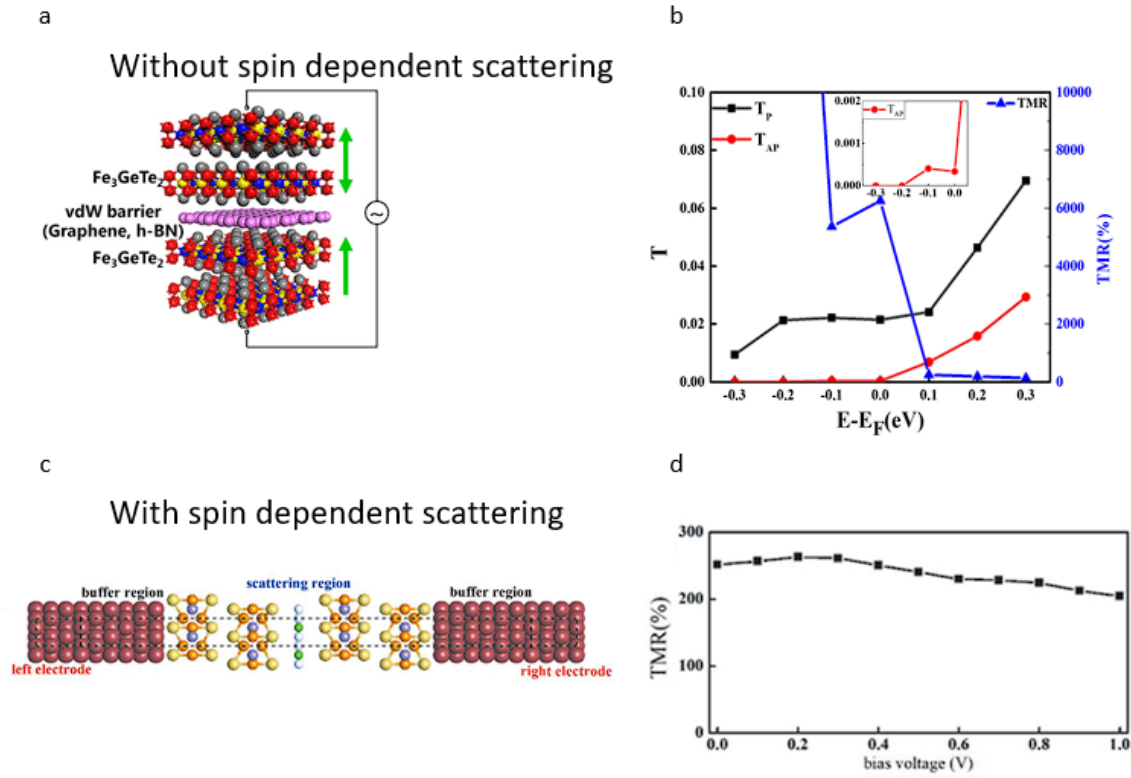


Figure 3.17: Calculated projected performances of a F3GT based MTJ. a) Sketch of the F3GT/h-BN/F3GT MTJ b) TMR depending on the applied bias voltage, showing a strong change in effect with higher applied voltages[130]. c) sketch of the model by Lin and Chen [131] in which the F3GT/h-Bn/F3GT is sandwiched between Cu electrodes. d) Their calculated TMR effect is smaller due to the included spin-dependent scattering in the F3GT layers, leading to values close to the experimentally observed once.

The high potential of F3GT in MTJs is further solidified by DFT calculations from Zhang *et al.* [132]. They investigated the spin valve effect of FGT in combination with the semiconductor InSe. Their calculations regarding an MTJ composed of F3GT/InSe/F3GT showed a strong bias-dependent TMR effect (Figure 3.18), consistent with findings from F3GT/h-BN and graphene junctions. In the parallel state of the two ferromagnetic electrodes, the tunnelling current is purely spin-polarised, and the tunnelling of minority spins is completely suppressed. In the case of the antiparallel configuration, the bias voltage is dependent and can lead to either pure spin-up or spin-down currents. The TMR effect is governed by the bias voltage and can reach values up to 700%.

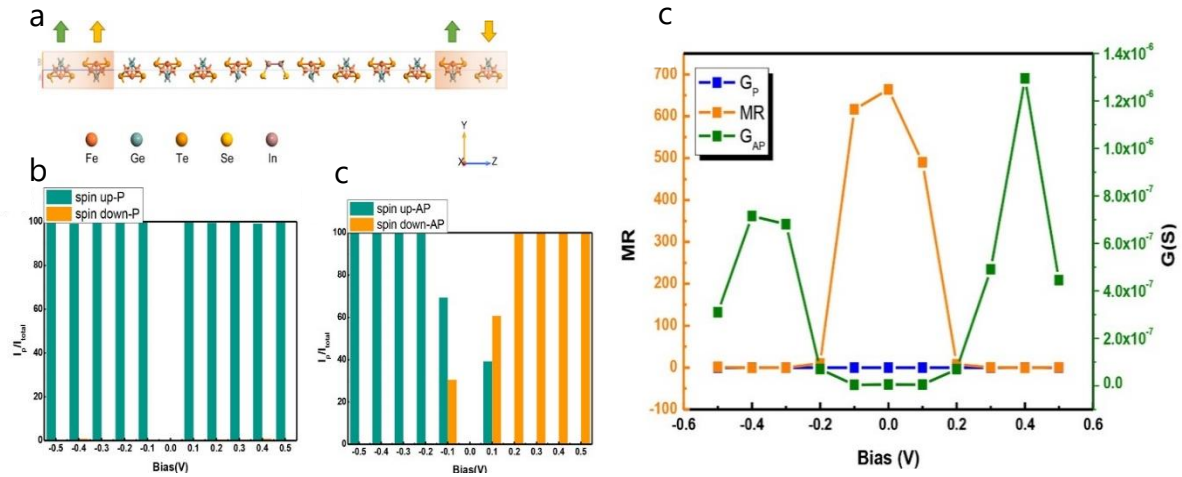


Figure 3.18: Calculated projected performances of a F3GT based MTJ. a) Illustration of the F3GT/InSe/F3GT system. b) Pure spin-up polarisation across the junction in the parallel state, independent of the bias voltage. c) Bias-dependent spin polarisation of spin up and down in the antiparallel state, indicating an “on”/“off” behaviour for different spins. d) Magnetoresistance and conductance across the junction depending on the applied bias. High MR values of up to 700% can be achieved in the calculations. From [132].

The presented theoretical work strongly underscores the potential of utilising FGT in spin valve systems. The high TMR values are of FGT based MTJs up to several thousand percent combined with the bias tuneable TMR value and the intrinsic conductivity of FGT promoted early experimental work of implementing FGT in MTJs. Early studies have focused on understanding the fundamental mechanisms and performance of FGT-based MTJs (see Table 3.4).

Year	Top Elec	Tunnel Barrier	Bottom Elec	Spin Polarisation	MR	Comment	Ref
2018	Fe ₃ GeTe ₂	h-BN	Fe ₃ GeTe ₂	66%	160%	exfoliated; pioneering results, but not reproduced	[126]
2019	Fe ₃ GeTe ₂	Graphite	Fe ₃ GeTe ₂	9.2%*	1.7%	exfoliated	[128]
2020	Fe ₃ GeTe ₂	MoS ₂	Fe ₃ GeTe ₂	12.3%	3,1%	exfoliated	[127]
2020	Fe ₃ GeTe ₂		Fe ₃ GeTe ₂	1.6%*	0.05%	exfoliated	[129]

Table 3.4: Magnetic tunnel junction on the base of F3GT. Results published before the start of the thesis, with F3GT as magnetic electrodes and corresponding magnetoresistance (MR) and spin polarisation (values labelled with * are extracted from the MR signal).

The first MTJ with FGT was realised in 2018 by Wang *et al.* [126] where exfoliated flakes of F3GT/h-BN/F3GT were stacked on top of each other (Figure 3.19a). Hexagonal boron nitride (h-BN) demonstrated its efficacy in earlier MTJs as a reliable tunnel barrier due to its insulating behaviour and controllable thickness at the atomic length scale. Fabricated within a glove box to prevent oxidation, the devices were capped with an additional layer of h-BN. E-beam lithography and CF₄ plasma etching facilitated the patterning of electrodes on both F3GT flakes deposited with Cr/Au. Spin-polarised conductive measurements revealed a TMR effect of up to 160% (Figure 3.19b) in a four-probe measurement at 4.2K, indicating a spin polarisation of F3GT at 66%. Utilising Anomalous Hall Effect (AHE) measurements, the authors demonstrated the independent switching of both F3GT flakes at different coercive fields attributed to variations in flake thickness.

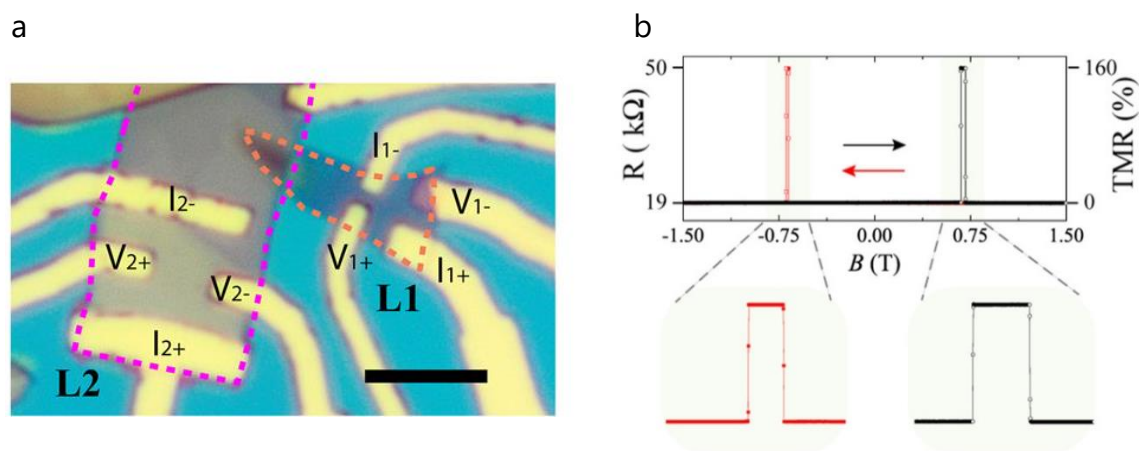


Figure 3.19: a) Optical image of F3GT/h-BN/F3GT MTJ (with L1/L2 as F3GT layers) with Cr/Au contacts on both flakes. b) Magnetotransport measurement across the junction shows a clear transition between the parallel and antiparallel state of the MTJ. From [126].

Kim *et al.* [129] approached the F3GT/vacuum/F3GT junction by creating an F3GT twisted van der Waals gap homojunction (Figure 3.20a). Single flakes of F3GT grown by iodine-supported CVT were exfoliated, with one flake split into two parts using the dry transfer technique and one part positioned on the remaining part at a specific angle of 87°. To minimise oxidation, the entire exfoliation and stacking process was conducted under an inert atmosphere and only exposed to air during the transfer process to the measurement system. This structure led to an F3GT homojunction, with the two flakes separated only by a van der Waals gap. The low interlayer interaction between the two flakes allowed the independent switching of the flakes when sweeping the external magnetic field (Figure 3.20b). The observed magnetoresistance increased with decreasing temperature, reaching values up to 0.05% with decreasing intensity when reaching higher temperatures (Figure 3.20c). The relatively low magnetoresistance compared to the calculated value for F3GT/vacuum/F3GT could be related to the twisting of the two flakes relative to each other and to the nature of the van der Waals bond, which cannot be equated with a vacuum.

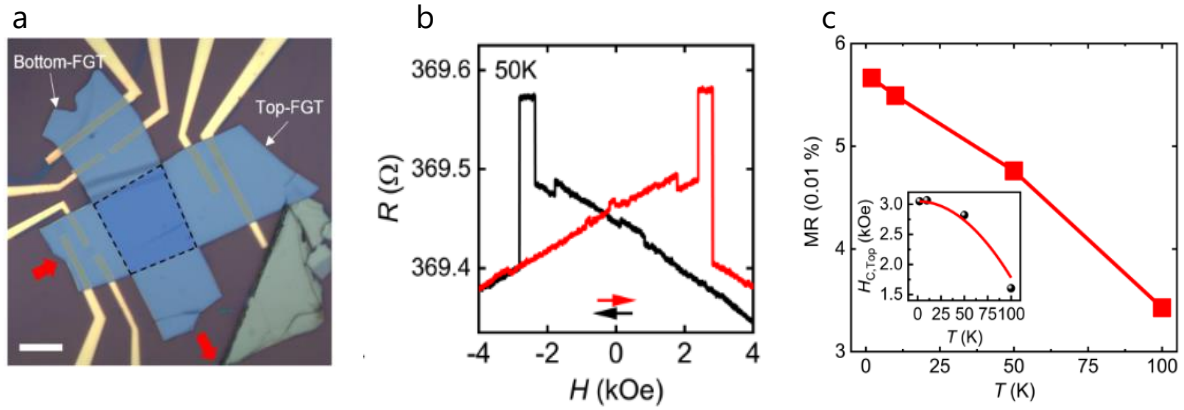


Figure 3.20: a) Optical image of the two F3GT layers stacked on top of each other. The red arrow marks the edge at which the former single flake broke. b) Magnetotransport measurement across the two flakes at 50K. A plateau-like behaviour is visible, indicating the antiparallel state of the two flakes. c) The junction's magnetoresistance decreases with increasing temperature. The inset shows the behaviour of the coercive field of the top flake with increasing temperature. From [129].

Such a structure was realised by Albarakati *et al.* [128] in a lateral configuration, in which the entire stack was measured at once. They fabricated the junctions from exfoliated crystals, with FGT grown by CVD with iodine as a transport agent, stacked on top of each other using a polymer-based transfer technique. Interestingly, they found a three-step plateau behaviour in multiple devices when measuring the magnetoresistance. The field in which the plateaus appear aligns with the measured switches of the two FGT flakes determined by anomalous Hall measurement.

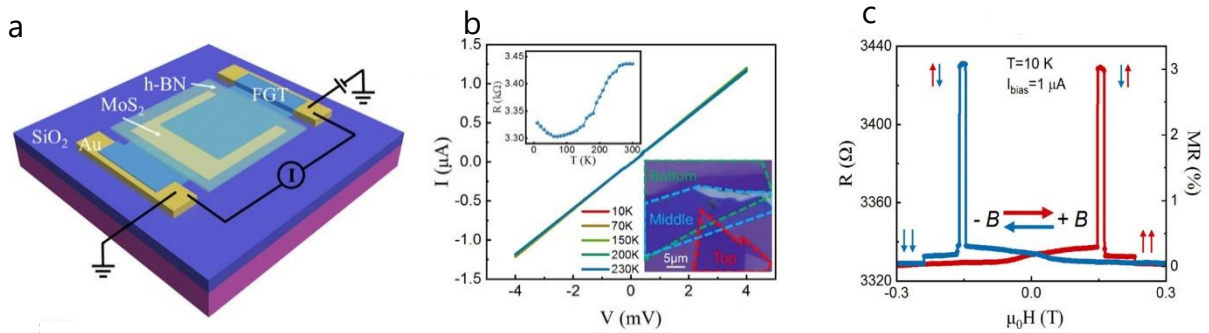


Figure 3.21: a) Sketch of the final junction contact consisting of F3GT/MoS₂/F3GT covered by h-BN as a protective layer positioned on pre-patterned gold. b) The I - V characteristic of the junction shows an ohmic behaviour. The upper inset shows the resistance depending on the temperature, and the lower inset shows an optical image of the junction. c) Resistance vs external field measurements. Two antiparallel aligned states can be distinguished from the parallel configuration by an increased resistance. From [127].

Lin *et al.* [127] fabricated an F3GT/MoS₂/F3GT MTJ by sequentially stacking exfoliated crystals (from HQ graphene) onto pre-patterned gold contacts using dry transfer (Figure 3.21a). The entire stack was covered by h-BN to prevent oxidation of the FGT and annealed to 120°C to remove bubbles and stacking faults between the interfaces. The measured IV characteristic revealed an ohmic contact between FGT and

semiconductor MoS₂, as shown in Figure 3.21b. Subsequently, an MR across the stack was measured (Figure 3.21c). The two FGT flakes of different thicknesses exhibited independent switching fields, which is evident in the MR curve. An MR of 3.1% was achieved, allowing for the determination of spin polarisation to be 12.3%. They explained the relatively low spin polarisation compared to the F3GT/h-BN/F3GT junctions could be attributed to the MoS₂ spacer layer. Spin alignment losses during conduction in MoS₂ and interfacial impurities could limit the spin polarisation in their system. Furthermore, the ohmic contact behaviour of the full junction indicates divergence from perfect crystals and interfaces.

Theoretical studies have demonstrated the high potential of F3GT as a ferromagnetic electrode in MTJs, predicting large TMR effects and tuneable spin transport. However, with the exception of the pioneering but unreproduced work by Wang *et al.*, subsequent experimental efforts have not yet matched these predictions. This discrepancy highlights the material challenges involved in realising efficient FGT-based MTJs, which strongly limits exploitation of FGT 2D FM for spintronics. In particular, the complexity of the spin-dependent transport mechanisms and the sensitivity to interface quality make it difficult to reliably access the intrinsic spin polarisation of FGT. Employing a well-characterised reference electrode, such as Co/Al₂O₃, could thus provide a promising strategy to disentangle these effects and gain clearer insight into the spin transport properties of FGT. Moreover, the broader Fe_nGeTe₂ material family remains an underexplored resource for further optimisation of 2D spintronic devices.

Part B: Results

4 MTJ WITH F3GT

Recent developments in the field of magnetic 2D materials have brought up Fe_3GeTe_2 (F3GT) as a highly promising candidate for integration into magnetic tunnel junctions (MTJs). Its distinct combination of ferromagnetic properties, high Curie temperature, and intrinsic conductivity sets it apart from other 2D magnets, such as chromium trihalides. While chromium trihalides perform well at low temperatures, their limited transition temperatures and semiconducting nature present significant challenges for practical MTJ applications. In contrast, F3GT addresses these limitations, offering a more versatile and scalable alternative.

The combination of F3GT ability to maintain ferromagnetic order down to the monolayer limit, along with out-of-plane magnetic anisotropy is particularly important for spin-polarized tunnelling, a core requirement for MTJs. F3GT's metallic behaviour removes the need for additional conductive layers when it is used as an electrode material. This simplifies device fabrication and reduces potential interfacial complications that can arise in layered heterostructures. Another key feature of F3GT is its responsiveness to external stimuli, such as electric gating and strain, which can modulate its magnetic properties. Gating has been shown to influence its Curie temperature, shifting the magnetic to paramagnetic transition up to room temperature, which is a critical threshold for practical applications (see chapter 3). This tunability makes F3GT an exciting material for exploring both classical MTJs and more advanced, multifunctional spintronic devices. Additionally, F3GT's van der Waals structure supports efficient exfoliation and integration into nanoscale devices. These exceptional properties establish F3GT as a promising material for integration into MTJs, offering both enhanced performance in spintronic devices and valuable insights into its unique magnetic and electronic behaviour at the nanoscale.

To analyse the spintronic potential of F3GT, an asymmetrical MTJ consisting of $\text{F3GT}/\text{Al}_2\text{O}_3/(\text{Co}/\text{Pt})_n$ is fabricated. F3GT serves as the top ferromagnetic electrode to be analysed and is paired with the high-quality alumina tunnelling barrier and a bottom Co/Pt multilayer reference electrode (Figure 4.1).

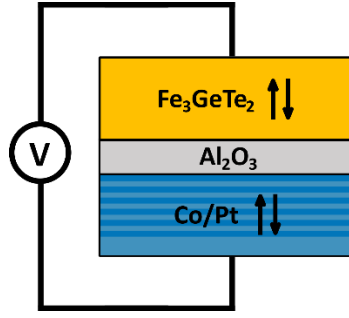


Figure 4.1: Schematic representation of the junction consisting of the 2D ferromagnetic Fe_3GeTe_2 top electrode to be analysed, Al_2O_3 as a tunnel barrier, separating F3GT from the Co/Pt bottom electrode serving as a reference spin analyser.

The choice of this specific configuration was driven by maintaining the intrinsic properties of the F3GT 2D layer and integrating it in a manner that allows us to use well-studied materials to analyse its spin properties. The alumina tunnel barrier, grown by controlled oxidation, ensures reliable tunnelling behaviour with minimal defects. This makes it an ideal choice for separating the two electrodes in the system. Cobalt as a ferromagnetic electrode, has been extensively studied in the field of spintronics and is well-understood in terms of its spin polarization, especially when the transport happens through Al_2O_3 barriers. These properties make $\text{Al}_2\text{O}_3/\text{Co}$ particularly suitable as a spin analyser in this setup. A further motivation for this asymmetrical MTJ structure comes from its ability to provide clearer insights into the properties of F3GT. Previous studies have focused on symmetrical systems, with F3GT serving as both electrodes. While such systems have advanced the understanding of F3GT's overall behaviour, they make it difficult to isolate the contributions of each layer due to their identical nature. In contrast, by introducing a well-characterized material like Co as one electrode, the asymmetrical design enables a more precise investigation of F3GT's unique spintronic properties. This approach provides a stable reference point, facilitating conclusions about the role of F3GT in spin-polarized tunnelling.

To implement this design effectively, the fabrication process was carefully developed to preserve the intrinsic properties of the F3GT layer while minimizing its exposure to ambient conditions. Given the sensitivity of 2D materials to external stimuli and environmental degradation, the process was designed to be as non-invasive as possible, ensuring a clean and controlled environment throughout. By employing established techniques such as magnetron sputtering, exfoliation in a glovebox, and atomic layer deposition (ALD) passivation, the fabrication sequence remains straightforward while maintaining the integrity of the materials. The overall workflow, illustrated in Figure 4.2, highlights how the components of the MTJ were assembled step by step in a clean and precise manner.

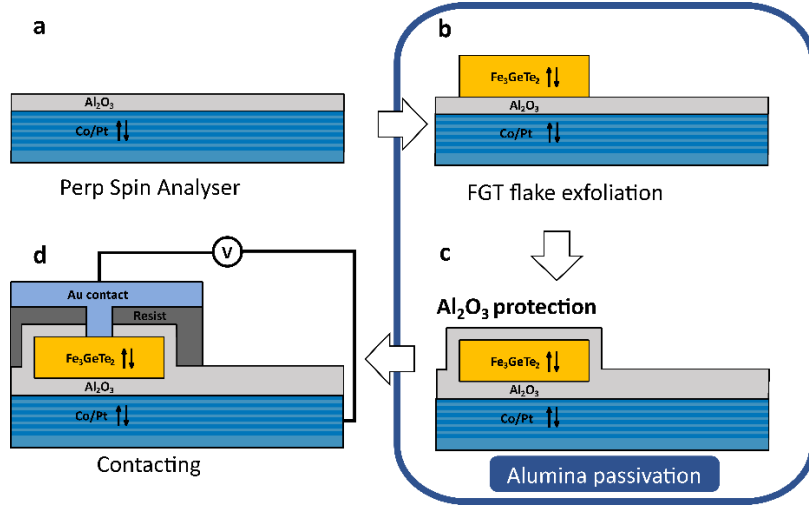


Figure 4.2: The fabrication process of the final MTJ is schematically illustrated. Initially, the reference electrode is produced through sputtering (a). This electrode, comprising a multi-layered Co/Pt structure, is grown by magnetron sputtering, onto which aluminium is deposited in the same process. The reference electrode is then transferred to the glovebox, where FGT is directly exfoliated onto the tunnel barrier (b). In a subsequent step, the entire stack is moved to an atomic layer deposition (ALD) system using a transfer box, which protects the FGT from oxidation. In the ALD system, a 1 nm thick homogeneous alumina layer is applied to the FGT to serve as a passivation (c). The next step involves using laser lithography to create openings for the top contacts on the flakes. Finally, these contacts are fabricated with gold using a sputtering machine (d). The contacts are then connected to a gold chip, enabling measurement in a low-temperature measurement device.

The fabrication of the MTJ starts by the creation of the reference electrode, consisting of a Co/Pt multilayer stack, produced through magnetron sputtering with an alumina (Al_2O_3) tunnel barrier deposited in the same run (Figure 4.2a). The electrode is then transferred to a glovebox, where F3GT flakes are exfoliated directly onto the tunnel barrier to form the magnetic top electrode

(Figure 4.2b). To prevent oxidation of the F3GT layer, the entire stack is passivated with a 1 nm alumina layer using atomic layer deposition (ALD) in a controlled environment (Figure 4.2c). Laser lithography is subsequently used to define openings for the top contacts, which are fabricated by sputtering gold onto the designated areas (Figure 4.2d). Finally, the device is connected to a gold chip for electrical measurements in a low-temperature setup, completing the MTJ fabrication process.

4.1 BOTTOM SPIN ANALYSER

The selection of the reference electrode is crucial and is governed by three main criteria: known spin polarisation, magnetic anisotropy, and scalability. For practical analysis of the unknown spin polarisation of F3GT, it is advantageous to utilise a reference electrode material with well-documented spin polarisation characteristics. The reported out-of-plane (OOP) magnetic anisotropy of F3GT [133],[134] further suggests using a reference electrode exhibiting OOP anisotropy. Scalability and homogeneity of the reference electrode are essential to simplify the fabrication

process and minimise the exposure of F3GT to potentially damaging processes, such as etching.

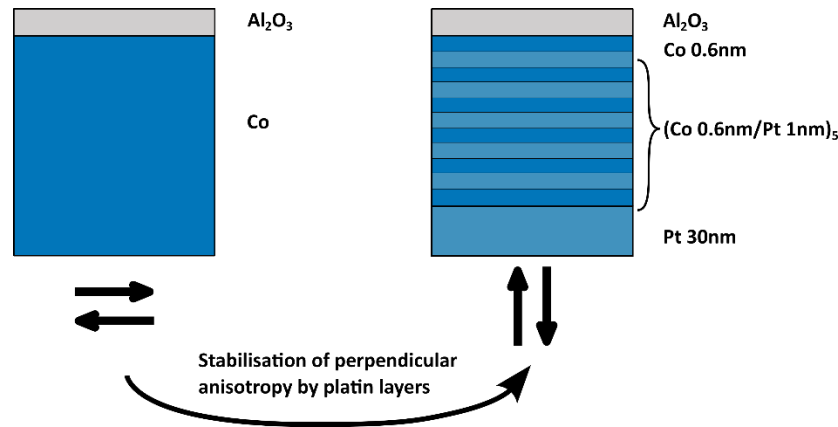


Figure 4.3: Stabilisation of PMA by introducing Pt layers. While thick Co exhibits a in plane magnetic anisotropy, the introduction of thin Pt layers can help stabilising a PMA by interfacial anisotropy. The periodical Co/Pt stack further reinforces the out of plane anisotropy, while a last layer of Co ensures the high spin polarised tunnelling current.

Motivated by these considerations, we chose the well-studied Co/Pt multilayer electrode [135],[136]. This electrode meets all the criteria above and offers additional benefits, such as growing an alumina tunnel barrier *in situ* on top of the Co/Pt. This alumina layer serves a dual purpose: it acts as a tunnel barrier and prevents oxidation of the top Co layer, thereby preserving its magnetic properties. A critical factor in the Co/Pt multilayer design is the stabilization of out-of-plane magnetic anisotropy (OOP) through magneto-interfacial anisotropy at the Co/Pt interfaces (Figure 4.3). In bulk or thicker cobalt films, the magnetization naturally tends to align in-plane due to shape anisotropy and the demagnetizing field. However, the introduction of ultrathin Pt layers adjacent to the cobalt modifies this behaviour. At the Co/Pt interface, strong spin-orbit coupling in the Pt layer induces a magneto-interfacial anisotropy that overcomes the in-plane preference of cobalt and stabilizes the magnetic moments in the OOP direction [137]. The periodic stacking of Co and Pt layers further enhances this stabilization, as the repeated interfaces reinforce the out-of-plane anisotropy. This property is critical for achieving compatibility with the out-of-plane anisotropy of F3GT in the MTJ.

The deposition of the reference electrode is done by magnetron sputtering (Figure 4.4a), resulting in a multi-layered Co/Pt structure. Magnetron sputtering generally works by bombarding a target material with high-energy ions, typically generated in a plasma. These ions dislodge atoms from the target, which then deposit onto a substrate, forming a thin film. This process allows for precise control over the thickness and composition of the deposited layers, which is essential for fabricating high-quality heterostructures. A sketch of the system is displayed in Figure 4.4b.

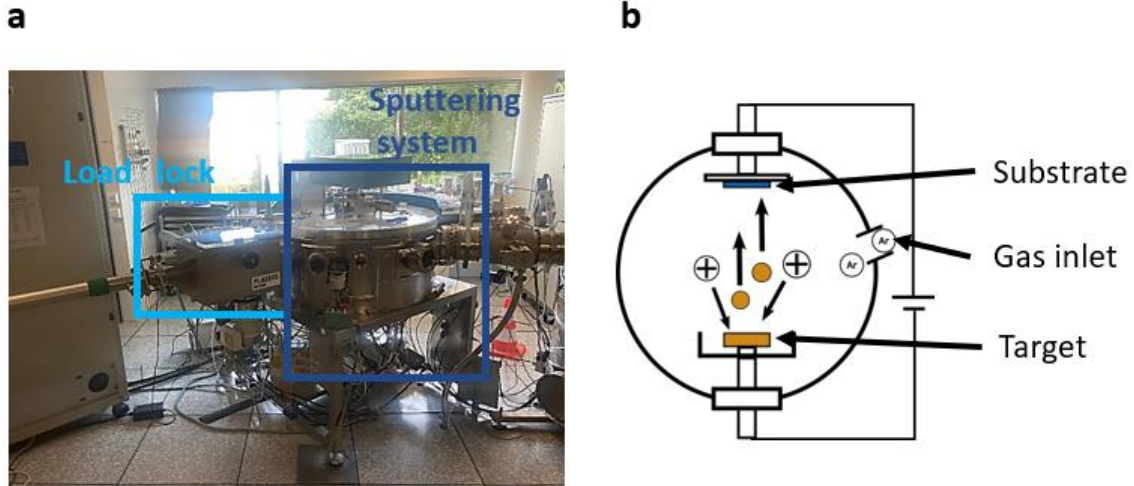


Figure 4.4: a) Image of the sputtering system. A manipulator allows the substrate to transfer from the load lock to the sputtering system. b) Schematic of the sputtering process, where Argon is ionised and accelerated to sputter the target material. The material is deposited on the substrate facing the target, creating homogeneous layers with precise thickness control.

Here, we chose a well-characterized bottom electrode to investigate the spintronic properties of F3GT by using multi-layered Co/Pt structures. To grow the structure, commercially available silicon wafers, topped by 280nm silica, are loaded by a manipulator through a transfer valve into the sputtering chamber (base pressure 10^{-8} mbar). An argon atmosphere of 10^{-3} mbar is introduced to sputter the different materials. The stack involves five repetitions of (Co 0.6 nm/Pt 1 nm) on a 30 nm Pt layer, capped by an additional Co layer (0.6 nm). To complete the structure, 0.6 nm of Al is sputtered on top of the entire stack. Subsequently, aluminium is oxidised up to the Cobalt interface, forming a 1 nm alumina layer. To simplify the device fabrication process, a prior lithographic mask was applied to create large, separated electrodes.

By optical lithography, a mask was defined on the silicon wafer to shape the electrodes in specific forms, facilitating the later fabrication process. For that, an optical resist (SPR 700 1.0 or S1805) was spin-coated onto the silicon and pre-baked. Using UV light, the designed mask could be imprinted into the resist. The resist is developed in a CD26 or MicroDev solution (for SPR700.1 or S1805, respectively), creating the desired electron pattern on the silicon wafer. Once the material is sputtered on top of the resist, the defined bottom electrodes can be achieved by a lift-off step in acetone. The prepared reference electrode can then be transferred into a glovebox, where FGT can be exfoliated on top of it.

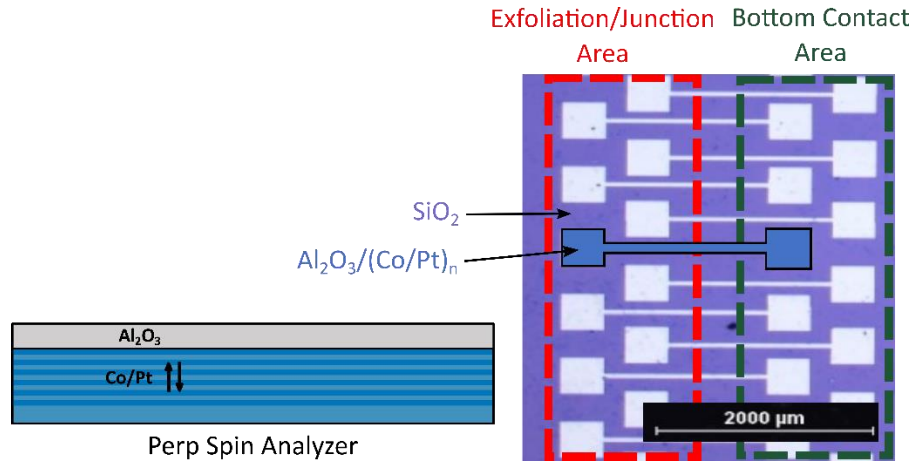


Figure 4.5: Optical microscope image of the patterned silicon wafer with 280 nm silica, featuring handle-like shapes created via optical lithography to facilitate the fabrication process. The handles consist of five repetitions of (Co 0.6 nm/Pt 1 nm) on a 30 nm Pt layer, capped with 0.6 nm of Co. A 0.6 nm Al layer was sputtered on top and subsequently oxidised to form a 1 nm alumina layer.

Figure 4.5 shows the optical image of the created $(\text{Co/Pt})_n$ bottom electrode covered by alumina in the electron shape. The left pad will later be used to bond the MTJ, while the FGT will be exfoliated on the right pad. To verify the out-of-plane magnetic anisotropy needed for the spin analysis of F3GT, the magnetic properties of the stack are measured.

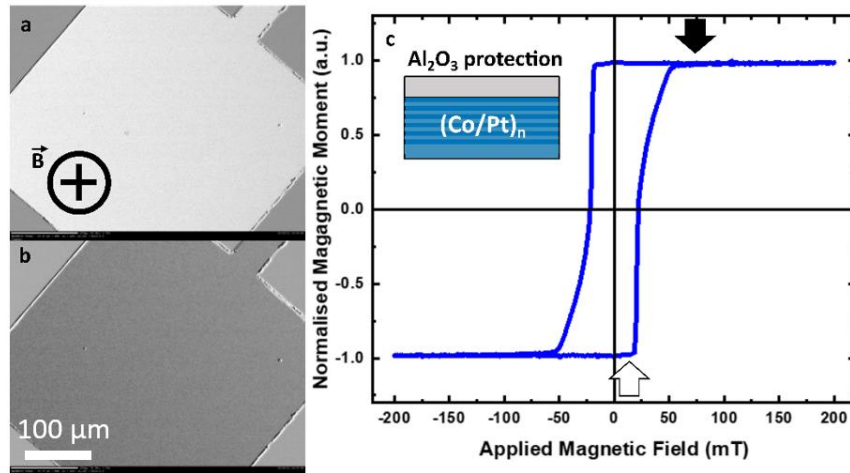


Figure 4.6: MOKE images of the (Co/Pt) multilayer covered by alumina in the down- and upwards saturated state, (a) and (b), respectively. The magnetic hysteresis loop of the system measured by AGFM is shown in (c), indicating the switching properties of the bottom reference electrode with an inset of the structure. The white (black) arrow indicate the B field where pictures (a) and ((b), respectively) were taken. The observed OOP anisotropy of the bottom electrode is well suited to study the OOP anisotropic 2D material FGT.

Figure 4.6 presents the magnetic characterisation of the pre-patterned bottom $\text{Al}_2\text{O}_3/(\text{Co/Pt})_n$ electrode using the magneto-optical Kerr effect (MOKE) and AGFM in an out-of-plane (OOP) configuration at room temperature (RT). In Figures 4.6a and 4.6b, optical Kerr images of the electrode pads deposited by sputtering are visible. The

brightness of the pads in these images depends on their magnetisation. The contrast variations are due to different polarisation of the backscattered light, allowing the technique to record changes in magnetisation. The measured loop at RT by AGFM is illustrated in Figure 4.6c. The relatively sharp transition is associated with the easy OOP axis of the bottom electrode. A high slope overlays the sharp transition after the first switch, and we attribute this to the creation of optically observed domains in the Co/Pt multilayer stacks. The magnetic characterisation of the reference electrode agrees with the need for an out-of-plane easy axis. Thus, it can be used to analyse the spin properties of F3GT, which will be exfoliated on top of it in the following step.

4.2 TOP 2D MAGNETIC ELECTRODE

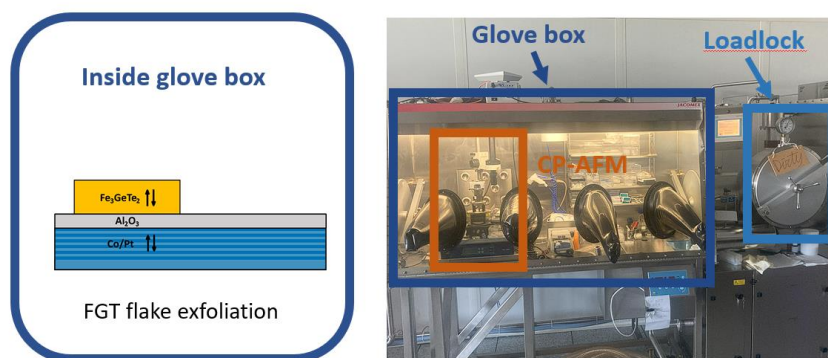


Figure 4.7: Image of the glovebox in which F3GT is exfoliated on top of the bottom electrode. The prepared spin analyser, by sputtering, is transferred through the valve, in which the water and oxygen level is reduced to be below 1ppm.

The FGT bulk crystals are stored inside a glove box with ($\text{H}_2\text{O} < 1 \text{ ppm}$, $\text{O}_2 < 0,5 \text{ ppm}$) (Figure 4.7) in order to avoid oxidation[138]–[140]. The glove box is equipped with an AFM and a transfer load-lock through which airtight boxes can be introduced, allowing the transfer of samples without exposure to ambient conditions (as discussed in the next section). After the bottom electrode is brought into the glovebox, F3GT is exfoliated on top of the sample. It is possible to achieve monolayer thick flakes on various substrates by mechanical exfoliation (“Scotch tape method”) (Figure 4.8) [141]. This process begins by pressing a bulk crystal of F3GT (from “2D Semiconductors”) against a piece of Scotch tape, leveraging the van der Waals forces of the material. Some of the crystal's layers will adhere to the tape. The tape is then repeatedly pressed against itself to further reduce the thickness of the flakes. In the final step, the tape is pressed onto the bottom electrode, leaving randomly sized flakes on top of the $\text{Al}_2\text{O}_3/(\text{Co/Pt})_n$ spin analyser.

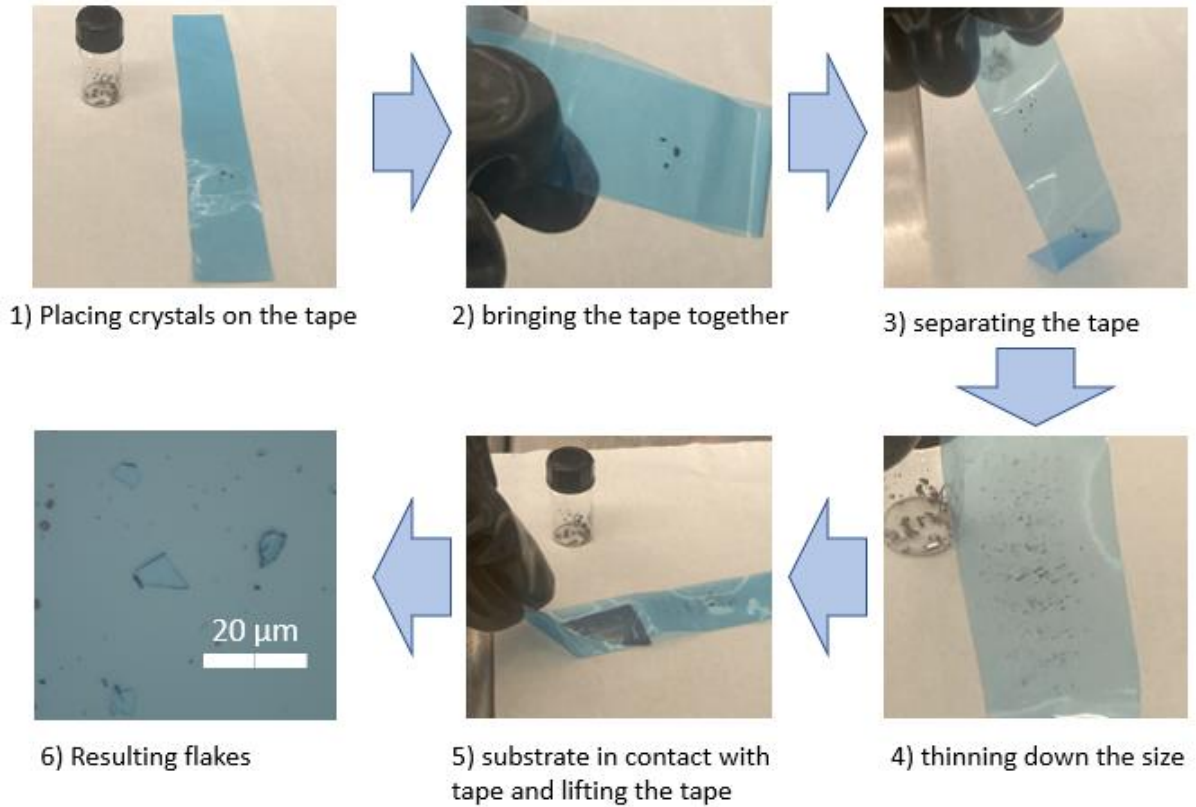


Figure 4.8: Procedure of exfoliating F3GT 1) The process starts with placing the F3GT crystal on tape .2)The tape is folded and pressed together to adhere crystal layers to it, followed by separating the tape to thin down the crystal size (3). This process is repeated (4), progressively reducing the thickness of the flakes. The tape is then on a substrate, leaving behind flakes of varying sizes(5).6) optical image of exfoliated F3GT flakes on SiO_2 .

Figure 4.9 shows an exfoliated flake on top of the bottom electrode $\text{Al}_2\text{O}_3/(\text{Co}/\text{Pt})_n$. The slightly different contrast between the substrate and the exfoliated material allows the flakes to be identified. Figure 4.9b presents the flake is measured with a CP-AFM. The upper part of the image shows the height profile of the flake. The white line indicates where the topography, shown in red in Figure 4.9c, was measured. The optical contrast from the microscope image is shown in black. While the contrast allows the flakes to be located [142], the AFM allows precise measurement of position and thickness. The steep rise in the AFM curve is visible when the AFM tip measures the flake.

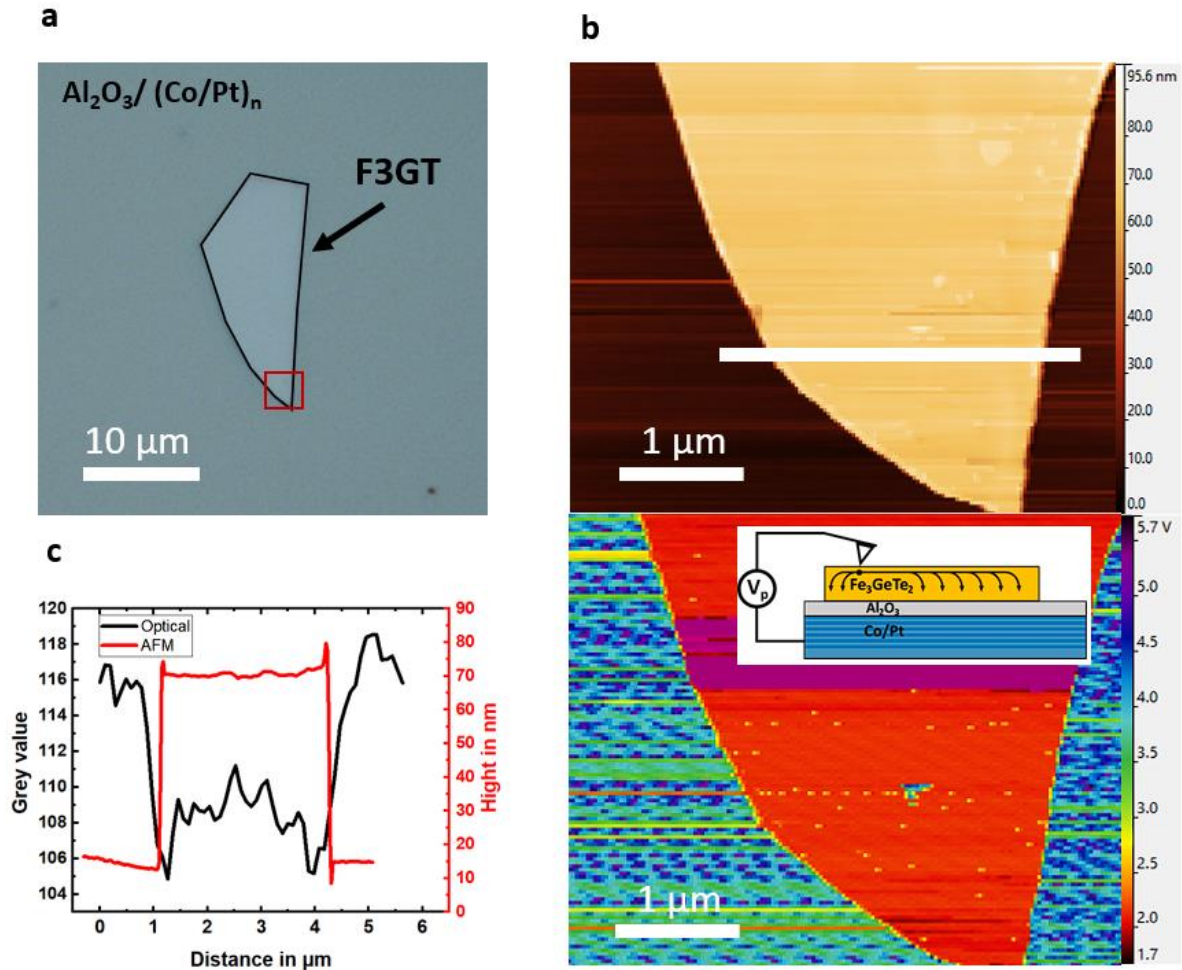


Figure 4.9: a) Optical image of an exfoliated F3GT flake on top of the bottom electrode. The red square marks the region where the AFM images are taken. B) CP-AFM measurement of the flake inside the glovebox, the upper panel shows the topography, and the bottom panel shows the conductivity. The F3GT flake appears conducting despite being exfoliated on the insulating alumina (indicated by green and blue colours). The large contact surface allows a tunnel current to pass into the bottom electrode, making the F3GT appear conducting. The white line indicates where the height profile (c) is measured. C) comparison of the grey value from the optical image and the height measured by AFM. The optical image allows for the identification of flakes, while the AFM has a superior resolution.

The lower part of Figure 4.9b shows the conductive AFM image. Two conclusions can be drawn from this. First, the tunnelling barrier presents high resistance, as indicated by the green and purple colours. This demonstrates the integrity of the tunnelling barrier. Second, the exfoliated flake is electrically conductive. Since the CP-AFM is connected to the Co electrode, this means it is possible for electrons from the CP-AFM tip to spread throughout the entire FGT flake (inset Figure 4.9c). This is enabled by the FGT's electrical conductivity. Due to the large surface area of the FGT, the tunnelling resistance through the alumina barrier is reduced, allowing the detection of the tunnelling current. As a result, the FGT appears electrically conductive even on the thin Al_2O_3 tunnel barrier.

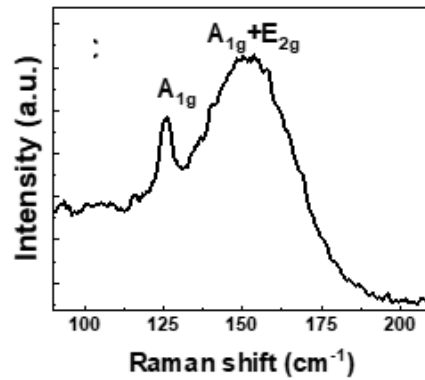


Figure 4.10: Raman measurement of exfoliated and passivated F3GT with A_{1g} and $A_{1g} + E_{2g}$ peaks.

Raman spectrum is displayed in Figure 4.10 for a passivated flake (with alumina by ALD). The A_{1g} and the $A_{1g} + E_{2g}$ peaks are visible [143], [144], indicating the high quality of the exfoliated material. For subsequent lithography steps, minimising exposure to ambient conditions is crucial due to the oxidation of FGT. This can be achieved efficiently by ALD passivating the whole MTJ.

4.3 PASSIVATION AND DEVICE CONTACTING

Using an airtight transfer chamber, the stack is next introduced into an Atomic Layer Deposition (ALD) system (Figure 4.11 a,b) operating in a low-pressure regime. ALD allows a highly controlled deposition of thin films with atomic accuracy. This is due to self-constraining processes which only happen on the surface of the substrate. Sequentially introducing precursor gases, a conformal deposition is possible on complex surfaces. Sequentially introducing precursor gases, a conformal deposition is possible on complex surfaces.

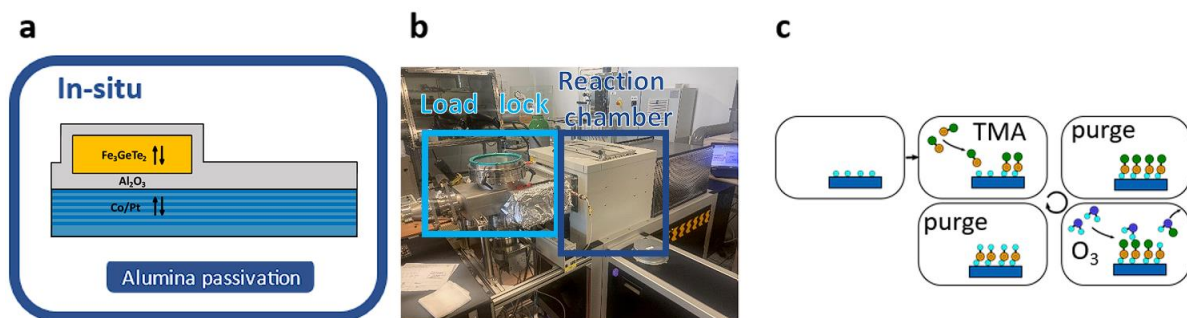


Figure 4.11: a) schematic of the passivation process. b) In the image of the ALD system, on the side of the load lock covered with aluminium foil, a transfer chamber can be placed to allow the transfer of the MTJ stack without being exposed to air. The sample holder can then be transferred into the reaction chamber. c) schematic of the ALD process where the precursors and ozone are flushed into the reaction chamber, creating atomically thin layers, after which the residuals are purged away.

Here, FGT flakes were passivated by a 1 nm alumina layer to protect them for future fabrication processes in ambient air. This passivation process has shown promising results in other 2D materials like Black Phosphorus [145] known to degrade even faster than F3GT. The precursor used is trimethylaluminum (TMA) to source the aluminium, while the reactant ozone is employed as an oxidising agent. After purging the gas lines, the TMA is introduced into the reaction chamber, where it reacts with the surface of the substrate and FGT (Figure 4.11c). Afterwards, the residues are purged out, and ozone is introduced into the reaction chamber, leading to the formation of Al_2O_3 . In the next step, the ozone is purged, and the cycle restarts. The number of cycles is chosen to derive the desired film thickness. With the protective Al_2O_3 layer, the FGT can be exposed to ambient conditions without degradation and can be treated in lithographic processing.

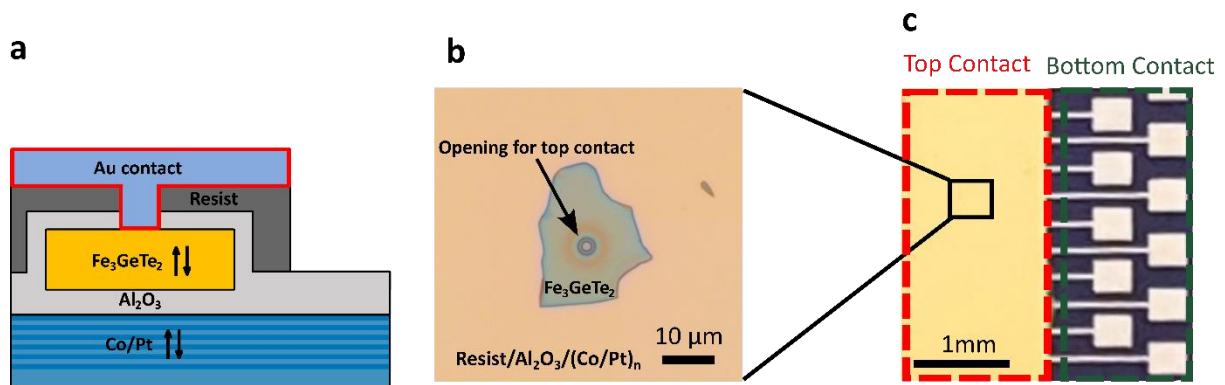


Figure 4.12: a) shows schematically the handle of Co/Pt and the full MTJ stack on the right side. The flake is exfoliated on one side of the handle, and via laser lithography, a hole is opened in the resist (b). Optical image of the opening of the resist (2 μm in diameter) on top of the FGT flake before the deposition of the gold contact (c). The gold contact is sputtered on all openings at the same time. The Pads were mechanically covered to avoid short circuits. The black rectangle shows illustratively where the FGT junctions are placed.

A lithography process was employed to establish contact with the FGT crystal (Figure 4.12a). The flakes were coated with resist S1805, and through UV laser lithography, openings were created on top of the flakes (around 2 micrometres in diameter, Figure 4.12b). The developer dissolved the alumina, enabling direct contact with the flake through sputtering. To minimise air exposure, the lithography process was kept under 30 minutes. It was assumed that only the upper surface of the flake oxidised during this time, while the crucial interface with $\text{Al}_2\text{O}_3/\text{Co}$ remained intact; further thick flakes were used so that the upper oxidation did not affect the magnetism at the interfacial layers. Following this, a 5 nm Ta and 80 nm Au layer were deposited using the same conditions as the previous Co/Pt sputtering process. This two-fold deposition served two purposes. Firstly, it reduced the exposure of the FGT flakes to ambient conditions, preventing further oxidation. Secondly, the gold contact facilitated the connection of the micrometre-sized flake to a ceramic chip, enabling the possibility of vertical transport measurements.

In the last step, the gold pads are connected to a chip, which can be later used to address each MTJ inside of the cryostat. The gold pad is connected to the contacts of the chips by gold wires, which are brought in contact with a 2-component conductive epoxy (Figure 4.13). The same epoxy was used to connect the gold wires and the Co/Pt pads with the gold chip. The purpose of the epoxy is to reduce any force that can be exerted by classical bonding mechanisms, such as ultrasonic vibrations or pressure, not to degrade the MTJs properties, especially the sensitive 2D ferromagnet.

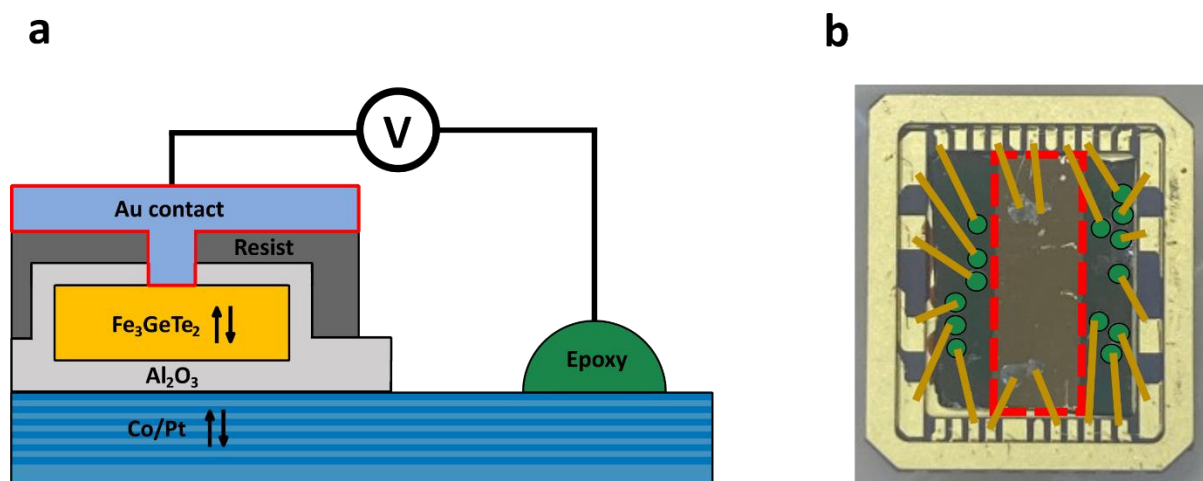


Figure 4.13: a) Schematic of the entire device, where the bottom electrode is connected via wires and conductive 2 component epoxy to the top gold contact of the FGT flake. B) optical image of the wired chip, with the sample in the middle. The gold contact is connected to various contact pads in the chip. Each drop of epoxy is linked to the bottom electrode and to a specific FGT junction.

Once the sample is bonded to the gold chip, it can be loaded into a cryostat for magnetotransport measurements. The priority bonding step allows to directly address the junctions with external measurement electronics. The cryostat enables to cool down the FGT/Al₂O₃/(Co/Pt)_n junction to 4K. This low-temperature environment reduces the thermal noise, stabilizes the spin transport properties and allows a high signal-to-noise ratio. The following section explores the magneto transport properties of the junction to understand the tunnelling behaviour and spin polarisation

4.4 MAGNETOTRANSPORT MEASUREMENTS

In the first step of the analysis, the electrical characteristics of the exfoliated 2D FGT on the reference Al₂O₃/(Co/Pt)_n spin analyser were examined. A voltage sweep was applied across the junction while monitoring the corresponding current response. The resulting I-V curve at 4K (Figure 4.14, black) exhibits a nonlinear behaviour, an indicator of tunnelling transport in magnetic tunnel junctions (MTJs). This characteristic confirms that the Al₂O₃ layer functions as a continuous and uniform tunnel barrier. The measured conductance curve is shown in blue in Figure 14. Around zero bias voltage,

a substantial increase in conductance is observed when applying a bias voltage. The group of Wulfhekel [146] observed a similar dip in spin-polarised scanning tunnelling microscopy (SP-STM) measurements of *in-situ* exfoliated F3GT under UHV. They propose inelastic spin scattering processes related to spin waves to explain this feature.

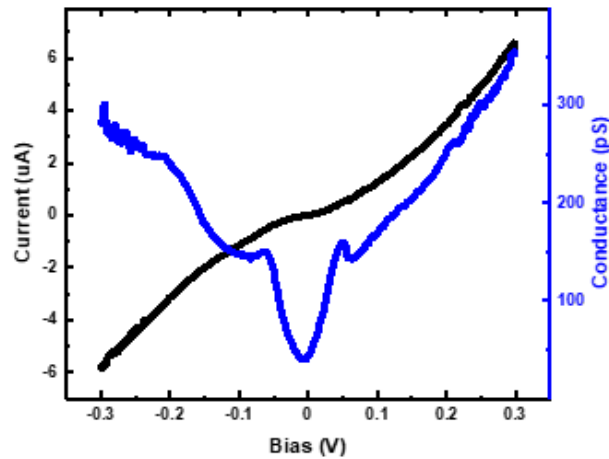


Figure 4.14: measured $I(V)$ and the conductance curve of the full MTJ in black and blue, respectively. The nonlinearity of the current indicates tunnelling behaviour, which can also be seen in the conductance curve. Two peaks appear in the conductance curve, which can be attributed to spin-wave excitations.

Two peaks in the conductance curve can be observed at around 50 meV. Similar peaks have been measured in SP-STM measurements [146],[147] and ARPES [148]. Zhao *et al.* [149] attribute this peak to the ferromagnetic 3d state of FGT. In order to understand FGTs magnetic response in the system, magnetoresistance measurements have been performed, in which the tunnelling current is measured in regard to the applied voltage and external magnetic field.

On the left side of the Figure 4.15, the TMR at 2 mV is shown. The black curve corresponds to the negative sweeping direction of the external magnetic field, while the blue one corresponds to the positive direction. A monotonous decrease in resistance is observed around 0 magnetic field, followed by an abrupt increase. This behaviour is indicative of a magnetic response. The gradual change can be explained by the enlargement of domains in the $(\text{Co/Pt})_n$ bottom electrode, which were observed at room temperature. The growing domains with opposite spin alignment could account for the continuous decrease in resistance, while the abrupt change could be attributed to the magnetic alignment of the FGT flake.

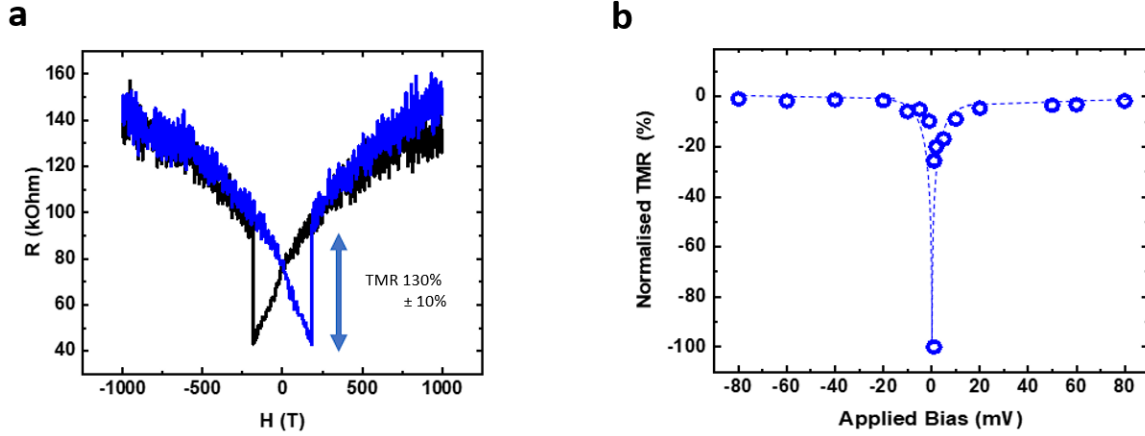


Figure 4.15: a) the Magnetoresistance for sweeping the field from negative to positive (blue) and reverse (black) is displayed. The resistance was measured in an AC+DC configuration, leading to a TMR effect of 130%. b) Magnitude of the bias-dependent TMR effect of another device is shown in c. An apparent increase in the TMR effect towards lower biases can be seen.

Following the Julliere's model for negative tunnelling magnetoresistance defined as $TMR = (R_{AP} - R_P)/R_{AP}$ [150], we measured magnetoresistances up to 130% in AC+DC measurements at low bias. A key observation is the decrease in resistance across the junction when the magnetic electrodes are antiparallely aligned. This behaviour indicates that one of the magnetic layers must exhibit a negative spin polarisation, meaning that minority spins dominate the tunnelling current. Within Julliere's model, we determine the spin polarisation of the magnetic electrodes via $P_{FGT} = TMR/(2 - TMR)$ P_{Co/Al_2O_3} . Here, the choice of Al_2O_3/Co proves essential, as it enables a direct spin analysis of FGT. With its well-characterized positive spin polarisation (pioneer analysis of Moodera *et al.* give a maximum achieved $P_{Co/Al_2O_3} = 45\%$ [151]) we determine the spin polarisation of FGT to be $P_{FGT} = -87.5\%$. The magnitude of the spin polarisation is much higher than most state-of-the-art values reported in chapter 3. Further the sign remained undetermined in previous studies, as symmetric junctions with F3GT on both sides has been utilized [126]–[128],[152], preventing the sign extraction of its intrinsic spin polarisation. We were able to determine for the first time the sign of the spin polarisation of F3GT by relying on the asymmetric MTJ with the known spin polarisation of the spin analyser. Further, it is the highest measured spin polarisation of F3GT so far, indicating a clean fabrication process with intact interfaces and highlighting the potential of the material in implementing it into MTJs.

In Figure 4.15b, the TMR effect of another device is shown in dependence of the applied bias across the junction. The TMR effect stays relatively stable around a few negative percent over a broad range of bias voltage but exhibits a sharp negative peak at low bias voltage.

To understand the negative spin polarised of the FGT, we collaborated with a theory

group at U.C. Louvain (S. Dubois and J.C. Charlier), who performed density functional theory (DFT) calculations within the framework of generalised gradient approximation (GGA). Figure 4.16a illustrates the crystal structure of F3GT with the two inequivalent Fe sites (Fe1 and Fe2). The analysis of the band structure has shown that Fe1 sublattice dominates the minority spin-channel at the Fermi energy. The Fe-d character and partial localisation of these states lead to electron correlation effects. To account for these on-site Coulomb interactions between electrons from the same orbital, a Hubbard U correction is applied to improve the standard GGA approach. Their spin-resolved band structure calculations (GGA+U), shown in Figures 4.16b and 16c, reveal that the Fe1 states still dominate the electronic states at the Fermi level (E_F) minority spin channel after including the coulomb interactions. The colour scale represents the Fe1 d-orbital weight, showing an overrepresentation of minority spins at E_F . This imbalance in spin-resolved density of states (DOS) could be the reason for FGT's negative spin polarization observed in tunnelling experiments. Around the fermi energy mainly the Fe1 subspace is contributing to the spin resolved band structure. Figure 4.16b and c show the spin resolved band structure projected on the Fe1 correlated subspace for majority spins (b) and minority spins (c). The colour scale represents the 3d orbital weight on the bands. A clear overrepresentation of this orbital can be observed for minority spins at the fermi energy. Those minority spins appear to be the reason for F3GTs negative spin polarisation.

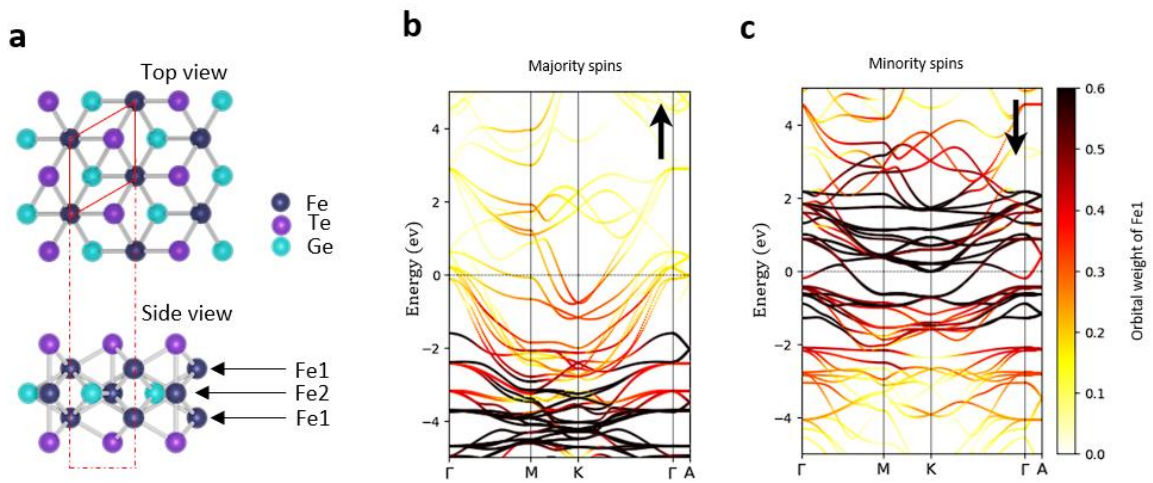


Figure 4.16: a) Crystal structure of F3GT, indicating the two different lattice sites of the Fe1 and Fe2 atoms. Spin-resolved band structure of FGT calculated using generalised gradient approximation (GGA) with Hubbard correction for majority (b) and minority (c) spins.

To further investigate this effect, we computed the spin-resolved Fermi surface of FGT integrated over a 25meV energy window along the z-direction (Figure 4.17). The majority (Figure 4.17a) and minority (Figure 4.17b) spin populations reveal a significant imbalance in k-space occupation. Notably, at the Γ point, which is typically dominating the tunnelling transport, a clear majority-spin depletion and dominance of majority spins can be seen. Figure 4.17c quantifies this spin asymmetry, highlighting a strong

minority-spin contribution (blue regions) at the Γ -point, which directly impacts spin-polarized tunnelling in the FGT/ Al_2O_3 /Co MTJ at low bias. When both ferromagnets are aligned in the parallel configuration, the tunnel probability is drastically reduced for the majority spins due to their absence at the point Γ . The lack of majority spins leads to a dominating transport of minority spins and a negative spin polarisation. When the Co electrode switches its magnetisation, aligning with the minority spin states of FGT, the tunnelling probability for minority spins increases, lowering the junction resistance. At higher bias voltages, additional tunnelling channels beyond the Γ -point become accessible. As seen in Figure 4.17c, the states away from the Γ -point predominantly exhibit majority spin character. While these states appear at similar energy levels, their spatial distribution and electronic structure require a higher energy input to contribute effectively to tunnelling. As a result, they become more relevant at increased bias voltages, where a broader range of states can participate in transport. For FGT those regions are mainly populated by majority spins. Consequently, the expansion of available tunnelling states reduces the imbalance between majority and minority spin transport, decreasing the overall spin polarisation of FGT. This explains the bias-dependent suppression of TMR, as observed in our experimental results.

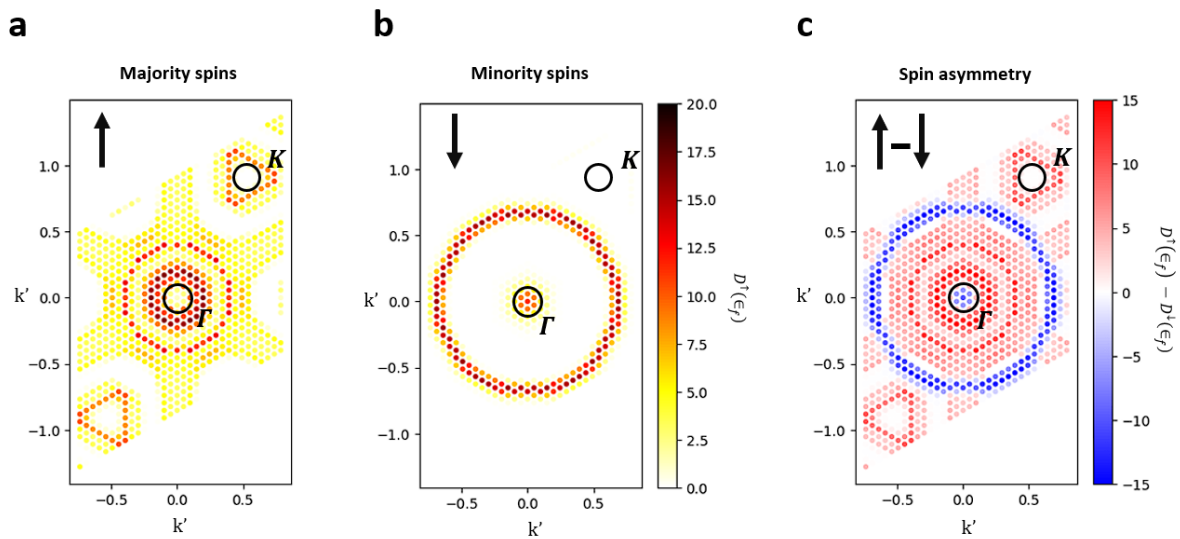


Figure 4.17: Majority (a) and minority (b) spin distribution at the Fermi energy in reciprocal space. The imbalance between spin up and spin down (c) around the Γ point leads to a minority spin-dominated tunnel current in the MTJ.

As a conclusion, we have introduced here technological steps to carefully integrate F3GT into an MTJ (*in-situ*, definition of a tunnel spin analyser) glovebox exfoliation, in situ passivation by ALD, ...). This gave rise to clean interfaces, leading to clean IV signatures of F3GT in our fabricated spin valves. The negative extracted spin signal in our transport experiments are the signature of an interfacial selection of F3GT minority spins. This is strongly correlated by the analysis of ab-initio calculations derived by our collaborators at UC Louvain. This study is a strong demonstration of the FGTs potential for spin valves.

5 GROWTH OF 2D FGT

FGTs unique combination of intrinsic ferromagnetism, metallic behavior, and high Curie temperatures within a van der Waals structure makes it highly promising for spintronic application. This potential was demonstrated in the previous chapter by integrating exfoliated F3GT into a MTJ and measuring a high spin polarisation. Yet, the reliance on exfoliated flakes hinders the scalability, highlighting the need for large-area, uniform film growth. Furthermore, although F3GTs Curie temperature is high compared to other 2D magnets, it is still below RT in many cases, which remains insufficient for practical devices. In fact, achieving large-scale, RT2D ferromagnets thus remains a major challenge in synthesis.

5.1 EARLY STAGE GROWTH OF FGT

The first synthesis of 2D magnets of the FGT family have been obtained through Chemical Vapour Transport (CVT) and solid-state reaction. Indeed, thanks to their ability to produce high-quality bulk materials with excellent purity and structural integrity, those methods have been standing out as the prime methods for synthesising 2D materials, including 2D ferromagnets such as FGT. They have been successfully applied to a wide range of pioneer layered magnetic van der Waals materials, such as CrX_3 ($X = \text{Cl}, \text{Br}, \text{I}$) and $\text{Cr}_2\text{Ge}_2\text{Te}_6$ [73],[76],[88],[153].

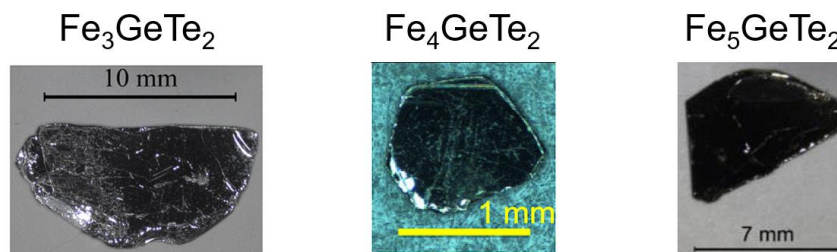


Figure 5.1: Optical image of CVT-grown FGT. Crystals of Fe_xGeTe_2 with varying iron compositions ($x = 3, 4, 5$) were synthesized using the Chemical Vapor Transport (CVT) technique, resulting in flakes ranging from millimeter to centimeter scale. From [97],[101],[110].

Concerning FGT, high-quality crystals of F3GT [103],[104],[154],[155], F4GT [97] and F5GT[109]–[111],[115] (Figure 5.1) have been successfully synthesised.

However to be used in devices, these bulk crystals always require subsequent mechanical exfoliation. Even after a successful exfoliation, their integration remains challenging due to the flake-based nature of the material, making the fabrication of large-area, uniform thin films difficult. Most importantly, their surfaces are almost always exposed making them potentially unfit for spintronics devices. Finally, the synthesis process itself is time-consuming, typically requiring up to 20 days [109],[110]

at temperatures exceeding 625 °C [103],[104],[154],[155], and is therefore not compatible with CMOS technology.

To address these challenges, the community has dedicated a large amount of effort to achieve a direct and scalable pathway to grow large-area 2D materials with precise control over their properties as we will see below.

5.2 TOWARDS LARGE SCALE FGT

Moving beyond the limitations of exfoliation, the first techniques that come to mind when talking about large scale 2D materials is CVD, just after falls the Molecular Beam Epitaxy (MBE). They offer the possibility of directly depositing atomically thin layers onto wafers, enabling scalability, and high material quality.

However, while both MBE and CVD represent promising approaches for the growth of FGT thin films, the initial large-scale growth of F3GT was only achieved by MBE on various substrates: Al₂O₃ [102],[156], GaAs [102], mica [156], Bi₂Te₃ [107] and (111) Ge[106]. The actual growth temperature of F3GT was significantly lower than for CVT being around 300-340°C.

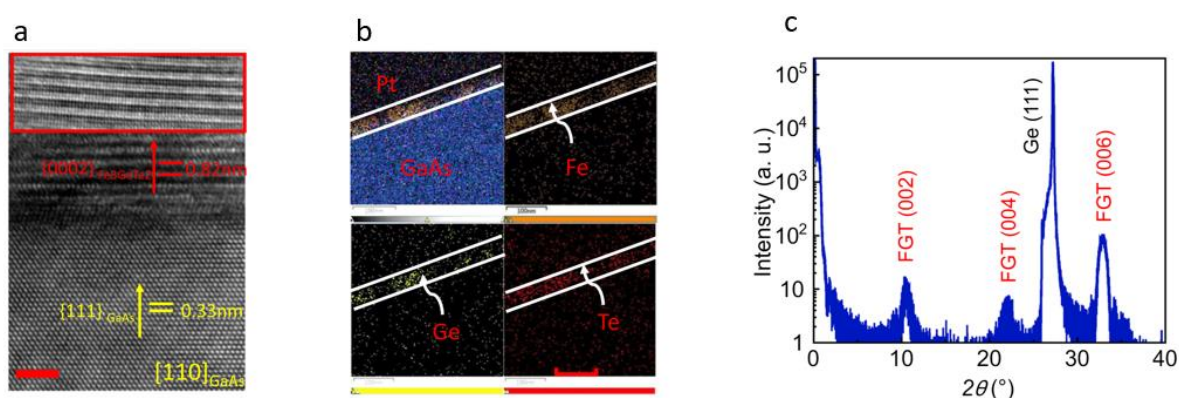


Figure 5.4: Cross-sectional HRTEM image of F3GT grown on (111) GaAs, showing the interface and a layer spacing of 0.82 nm, corresponding to the {0002} planes. The inset (red rectangle) provides a magnified view. Scale bar: 2 nm. (b) EDS mapping of Fe, Ge, and Te within the F3GT layer (between white lines). The GaAs substrate and Pt capping layer (added via FIB) are also visible. Scale bar: 100 nm. (c) X-ray diffraction (XRD) pattern of an 6 layer F3GT film, confirming (001) oriented growth and crystallinity. From [102],[106].

Figure 5.4a presents a cross-sectional high-resolution transmission electron microscopy (HRTEM) image of the Fe₃GeTe₂ thin film grown on GaAs. The interface between the substrate and the film is visible, showing the layered structure of Fe₃GeTe₂. The inset, marked by a red rectangle, provides a closer look at the Fe₃GeTe₂ region, where the measured layer spacing is 0.82 nm, corresponding to the {0002} planes of Fe₃GeTe. Figure 5.4b displays energy-dispersive X-ray spectroscopy (EDS) mapping results, illustrating the spatial distribution of Fe, Ge, and Te atoms within the film, as indicated by the region enclosed between the white lines. A capping layer of

Pt is visible, deposited to facilitate the focused ion beam (FIB) etching. Figure 5.4c shows θ X-ray diffraction (XRD) pattern, which corresponds to an 6 layer F3GT film from Roemer *et al.* [106]. The diffraction peaks indicate that the film is oriented along the (001) direction, as expected for epitaxial growth on Ge(111). Subsequently, Liu *et al.* demonstrated the successful fabrication of F3GT/CrSb heterostructures. CrSb, an antiferromagnet, was chosen due to its minimal lattice mismatch with F3GT ($a = 3.991$ Å for F3GT vs. $a = 4.108$ Å for CrSb), making it an ideal candidate for heterostructure growth. Too long...

While these studies highlighted the capability to produce large-scale 2D ferromagnets [26], the growth of FGT 2D magnets had remained quite challenging. Hence, at the onset of this PhD thesis, only Fe_3GeTe_2 (F3GT) had been successfully synthesised by MBE, and no reports on CVD-grown FGT were available.

5.3 POTENTIAL OF PLD FOR FGT

As such, we decided to push forward a new growth method that we participated in pioneering in the field of 2D materials: Pulsed Laser Deposition (PLD). PLD is a versatile thin-film growth technique that had been widely used for the fabrication of complex oxides[157],[158] and metals [159], but that was only very recently adapted to 2D materials such as h-BN[160], MoS_2 [161]or WS_2 [162] and black phosphorus [163]. The successful deposition of these van der Waals materials suggests that, with optimized deposition conditions, PLD could also enable controlled growth of 2D ferromagnets. In contrast to MBE, where material deposition occurs at a steady, controlled rate, PLD's non-equilibrium nature results in stoichiometric target species arriving at the substrate in short bursts, influencing nucleation dynamics and film morphology in distinct ways. This offers unique advantages, such as fast deposition rates, stoichiometric material transfer, and compatibility with a wide range of substrates, including amorphous surfaces. These characteristics make PLD particularly attractive for exploring the synthesis of Fe_xGeTe_2 thin films.

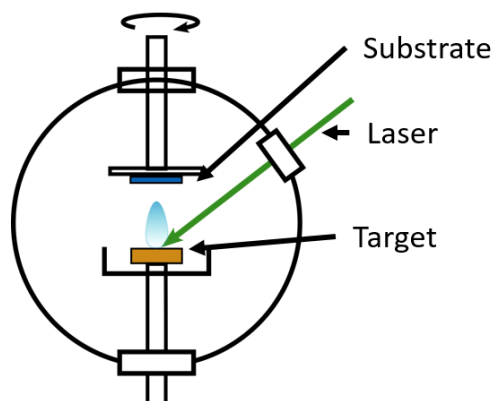


Figure 5.6: schematic sketch of the PLD chamber. The laser hits the target material, creating a plume. The material then deposits on the substrate facing the target, creating 2D layers

PLD relies on the laser ablation of a solid target, where a high-power pulsed laser beam is focused onto a rotating target composed of the desired material. Upon interaction with the laser, the target undergoes rapid heating, vaporization, and ionization, forming a highly energetic plasma plume that expands toward the substrate (Figure 5.6). This plume consists of neutral atoms, ions, clusters, and molecular fragments, all of which contribute to the film formation. The growth process in PLD is influenced by several interdependent factors that determine film quality, composition, and structural properties. Laser parameters, including wavelength, fluence (energy per unit area), and repetition rate, play a crucial role in defining the ablation efficiency and plasma plume dynamics. Higher laser fluence results in greater kinetic energy of the ablated species, which in turn affects surface diffusion and ultimately influences film morphology. Another critical factor is substrate temperature, which governs atomic mobility and crystallization. Higher temperatures generally promote layered growth, facilitating better crystallinity, while lower temperatures may lead to disordered or polycrystalline films, where atomic diffusion is insufficient to achieve an ordered structure. Additionally, background gas pressure modifies the kinetic energy and trajectory of the ablated species as they travel toward the substrate. The introduction of inert gases such as argon (Ar) or reactive gases like oxygen (O_2) or nitrogen (N_2) can impact film density and influence phase formation, either by slowing down particle velocities or by participating in chemical reactions during deposition. Finally, the target-to-substrate distance plays a significant role in controlling the spatial distribution of the ablated species. A shorter distance increases the flux of material reaching the substrate, potentially leading to higher deposition rates but also increasing the risk of defects or non-uniform growth. Conversely, a longer distance allows for better dispersion of species, promoting more uniform film deposition across a larger area.

One of PLD's major strengths is its ability to maintain the stoichiometry of complex materials, as the ablation process transfers elements from the solid target to the

substrate in nearly the same proportions. Additionally, PLD enables *in-situ* target switching, allowing the sequential deposition of multiple materials within a single growth process. This feature makes PLD particularly attractive for fabricating complex heterostructures, where clean and abrupt interfaces are critical. For 2D materials, this opens the possibility of growing fully integrated van der Waals heterostructures, an essential step toward realizing all-2D MTJs. Recent studies by our group have demonstrated the successful growth of heterostructures using PLD, highlighting its potential for precise layer engineering. An example of this is the $\text{WS}_2/\text{WSe}_2/\text{WS}_2$ heterostructure grown by PLD. Figure 5.7a provides a schematic of the PLD growth process, in which individual WS_2 and WSe_2 layers are sequentially deposited to form a well-ordered heterostructure. The successful material synthesis is confirmed by Raman spectroscopy (Figure 5.7b), where the characteristic peaks of WS_2 and WSe_2 are clearly visible, indicating high material purity and distinct layering.

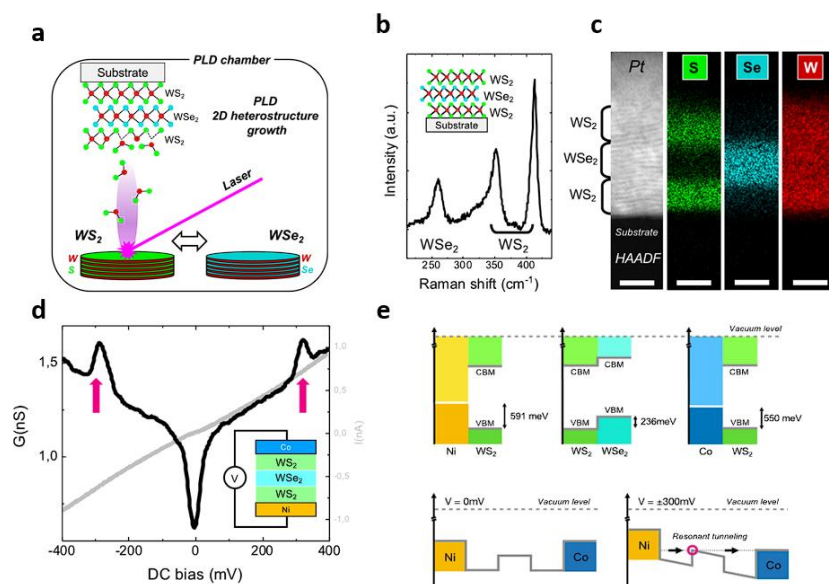


Figure 5.7: (a) Schematic of *in-situ* PLD deposition for 2D heterostructures. (b) Raman spectrum confirming the presence of WS_2 and WSe_2 layers, which is further confirmed by HAADF and EDX elemental mapping of S, Se, and W (c), demonstrating the layered structure. (d) Differential conductance (G) vs. DC bias, showing features consistent with resonant tunnelling when the heterostructure is sandwiched between electrodes. (e) Band alignment and energy level diagrams illustrating the formation of a quantum well in the heterostructure, indicating the sharp interfaces of the 2D semiconductors.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging, along with energy-dispersive X-ray spectroscopy (EDS) element mapping (Figure 5.7c), further verifies the composition and spatial distribution of the S, Se, and W elements across the heterostructure. The electronic properties of these PLD-grown heterostructures reveal their potential for tunnelling devices. In Figure 5.7d, differential conductance measurements as a function of DC bias show distinct conductance peaks, related to resonant tunnelling in the $\text{WS}_2/\text{WSe}_2/\text{WS}_2$

heterostructure. This behaviour originates from the band alignment between the layers, as illustrated in Figure 5.7e, where the conduction and valence band offsets between Ni/WS₂, WS₂/WSe₂, and WS₂/Co interfaces enable controlled charge transport. Notably, at ± 300 mV, resonant tunnelling conditions are achieved, demonstrating the feasibility of using PLD-grown 2D heterostructures in functional electronic devices. Building on the successful integration of 2D TMD heterostructures, a similar approach can be extended to Fe_xGeTe₂ to explore its potential for van der Waals spintronic devices. As will be presented later, most of the FGT samples will be covered by MoS₂ as it can serve as a tunnel barrier and protective layer at the same time. Another key advantage of PLD is its ability to grow films on a wider range of substrates. The fact that highly energetic species arriving at the substrate in clusters might unlock the growth of 2D ferromagnets on non-crystalline substrates. This makes PLD particularly attractive for large-area device fabrication, where single-crystal substrates may not be available or practical. In this work, commercially available Si/SiO₂ substrates were used without additional surface treatments, highlighting the potential of PLD for integrating Fe_xGeTe₂ films into semiconductor-compatible platforms.

While these advantages make PLD an appealing technique, certain challenges must be addressed for Fe_xGeTe₂ growth. In multicomponent materials like Fe_xGeTe₂, stoichiometry is not always perfectly preserved, as different elements may have varying ablation efficiencies due to differences in atomic mass and bonding energy. Thus, a systematic calibration of deposition parameters is required to achieve precise Fe:Ge:Te ratios. Addressing these challenges will be key to ensuring the viability of PLD-grown Fe_xGeTe₂ for spintronic applications. Overall PLD presents a highly promising approach for Fe_xGeTe₂ growth, offering a faster, scalable, and more flexible route to synthesizing 2D ferromagnetic films. The following sections will describe the experimental setup and optimization strategies used to achieve Fe₃GeTe₂ and Fe₄GeTe₂ growth via PLD, focusing on laser parameters, background gas control, and substrate temperature tuning to optimize film quality.

5.4 PLD-GROWN FGT

Exfoliated F3GT shows promising results in terms of performance when implemented into MTJs. Pulsed laser deposition (PLD) could push the limitations further in terms of the scalability of sample sizes and the fabrication of *in situ* deposited full 2D MTJs. In recent years, different TMDs have been grown by PLD, which can be utilised for tunnel barriers or quantum wells. Those experiments have shown the potential of creating clean interfaces between different 2D materials on a large scale [164]. To complete a full 2D MTJ stack, the PLD-grown two-dimensional ferromagnet is missing. The FGT family, with its promising spin properties (like high spin polarisation), seems like a suitable candidate. In the following section, the growth and characterisation of FGT films grown by PLD will be presented.

5.4.1 Fabrication

To investigate the feasibility of PLD-grown Fe_xGeTe_2 , a dedicated PLD system equipped with an Nd:YAG laser was used. The system comprises an optical line, including a frequency multiplier, attenuator, and focusing lens, which directs high-energy laser pulses onto a rotating target composed of the desired FGT stoichiometry. The ablation process generates a plasma plume that propagates toward the heated substrate, where film growth occurs.

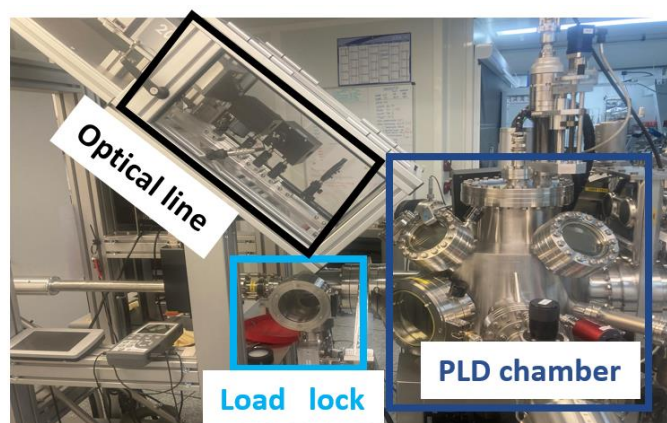


Figure 5.8: Image of the PLD system. The laser pulse passes the optical line consistent with the frequency multiplier attenuator and lens. The sample can be brought into the system's PLD chamber by the load lock.

The deposition chamber is accessed via a load lock (Figure 5.8), allowing controlled sample introduction while maintaining ultra-high vacuum conditions. By adjusting key deposition parameters, such as laser fluence, pulse repetition rate, substrate temperature, and background gas pressure, the growth process was systematically optimised to achieve high-quality thin films with controlled stoichiometry and crystallinity. The growth is done in the following steps.

- 1) Substrate Preparation
 - A silicon substrate with an amorphous 280 nm silica top layer is cut into pieces of 10 mm x 10 mm size.
 - The substrate is fixed on the sample holder, enabling its transfer into the Pulsed Laser Deposition (PLD) chamber.
- 2) Initial Vacuum Setup and Transfer:
 - The substrate is placed in the load lock chamber, and the pressure is reduced to 1×10^{-6} mbar.
 - It is then transferred into the main chamber of the PLD system, which operates under a base pressure of 2×10^{-8} mbar.
- 3) Positioning and Temperature Monitoring:
 - The substrate is positioned facing the targets at a distance of 70 mm.
 - A pyrometer is aligned to record the surface temperature of the substrate.
- 4) Heating and Gas Introduction:
 - The heater is turned on to bring the substrate to the growth temperature.
 - Argon gas is introduced into the chamber, depending on the growth conditions.
- 5) Target Pre-ablation and Growth Initiation:
 - A shutter protects the substrate surface while the targets undergo pre-ablation to clean their surfaces.
 - The sample holder rotation is turned on.
 - The shutter is removed, and sample growth begins.
- 6) Heterostructure Growth:
 - For heterostructures, multiple growths can be performed by changing the target using a carousel and adjusting the desired growth parameters, such as temperature and inert gas pressure.
- 7) Cooling and Sample Removal:
 - The sample is cooled down in an argon atmosphere until it reaches room temperature.
 - The sample is then taken out of the chamber, completing the growth process.

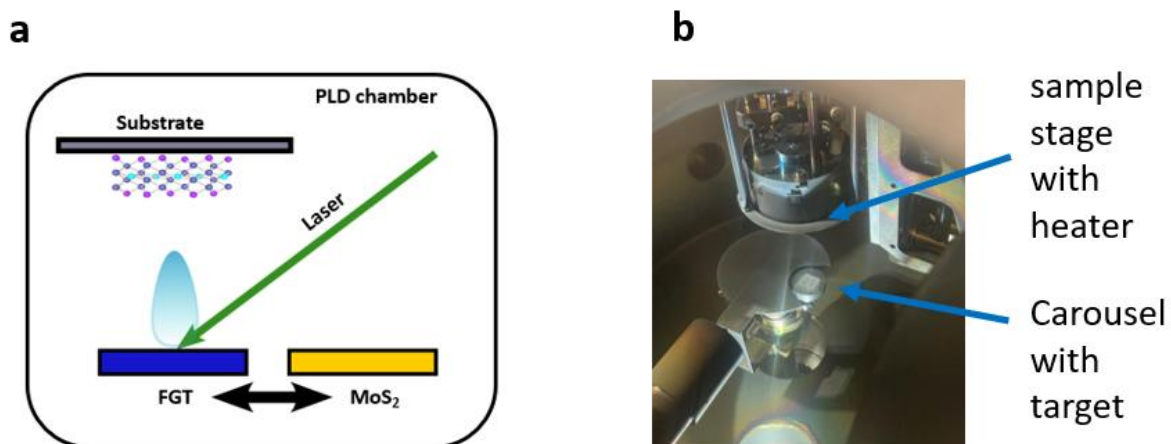


Figure 5.9: a) Sketch of the changeable targets inside the PLD chamber unlocking the growth of 2D heterostructures. b) Optical image of the PLD chamber where a pre-ablated FGT target is visible; the carousel allows the change of target material in a few seconds.

The PLD system is equipped with a carousel (Figure 5.9) that can switch targets quickly *in situ*. Since the targets contain the stoichiometric ratio of the material to growth, we can switch between 6 different targets during the growth. This allows the growth of complex heterostructures *in situ* and functionalises those 2D layers.

5.4.2 Parameter dependence

In the first step, the stoichiometric transfer of the target material as a function of laser energy was studied [165],[166]. Silica substrates were exposed to the ablation of an Fe₄GeTe₂ target using laser fluences ranging from 20 mJ to 150 mJ per pulse. Other deposition parameters were kept constant, including a 2.5 Hz repetition rate of the laser pulses, and the chamber was maintained at room temperature with no background gas. After each deposition, the sample was transferred *in-situ* to the XPS system. By fitting the 2p peak of iron, the 3d peak of tellurium and the 3d peak of germanium, a quantitative trend of the element stoichiometry could be observed. In Figure 5.10, the ratio of Fe/Te and Ge/Te as a function of laser fluence are plotted in black and red, respectively.

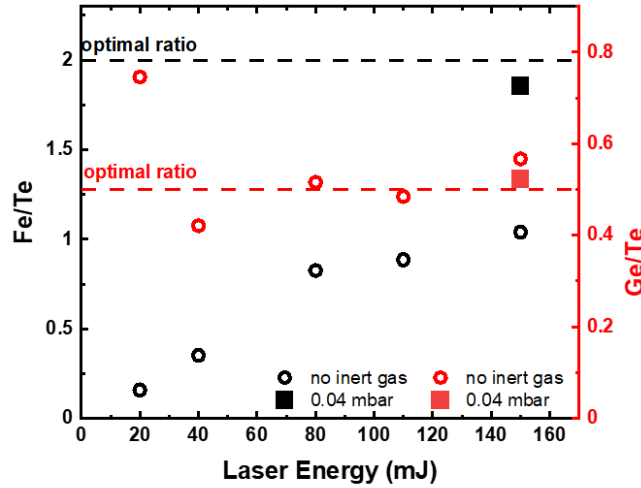


Figure 5.10: Stoichiometric ratio of iron and tellurium in black and germanium tellurium in red. The optimal ratios for a Fe_4GeTe_2 film are marked with a dotted line for each component (black for iron and red for germanium with respect to tellurium). With increasing laser fluence, the ratios are tending towards the suitable composition. However, only by introducing argon gas into the chamber can the correct ratios be achieved.

The dotted lines indicate the optimal ratios for a perfect Fe_4GeTe_2 crystal. The Ge/Te ratio approaches the optimal value for fluences of 80 mJ and above, while at lower fluences, particularly around 20 mJ, a significant deviation is observed. For fluences lower than that, the ratio of Germanium and Tellurium is of, with a striking ratio around 20mJ. However, it remains unclear from this value whether this results from an excessive presence of germanium or a substantial tellurium depletion. A clear trend towards the correct Fe/Te ratio can be observed when reaching higher laser fluences, even though the optimal ratio cannot be reached with the maximum possible fluence of 150 mJ of our PLD setup. These findings demonstrate the strong dependence of stoichiometric transfer on laser fluence, highlighting the need to optimize additional parameters such as substrate temperature and background gas pressure. Introducing argon gas into the chamber will adjust the ratio further, as can be seen by the squares in Figure 5.10. Atomic scattering due to the presence of 0.04 mbar of Ar helps regulate the ratio of evaporated species, promoting better stoichiometric balance in the deposited film[167]. While these optimizations ensure the correct stoichiometric transfer, the formation of a well-ordered crystalline structure requires additional control over substrate temperature. Achieving high-quality Fe_xGeTe_2 films not only depends on composition but also on allowing the atoms to arrange into the correct layered structure. Thus, the next step focuses on tuning the substrate temperature to induce crystallization.

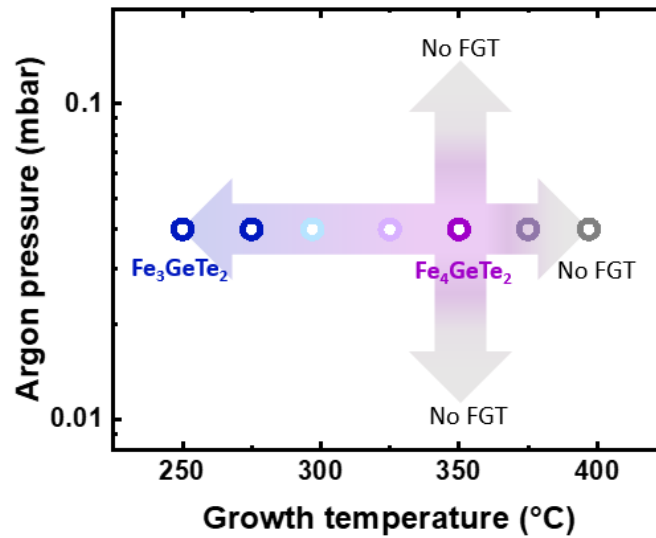


Figure 5.11: Parameter space of the PLD growth of FGT. While Fe_3GeTe_2 and Fe_4GeTe_2 crystallise on the substrate under the same argon pressure, the growth temperature determines in which composite it will condense. Temperatures above 350°C or different Argon pressure conditions do not allow the growth of FGT.

With the stoichiometric transfer optimized, the next crucial step is to achieve proper crystallization of the Fe_xGeTe_2 films. While the previous experiments ensured the correct elemental ratios, the formation of a well-ordered crystal structure requires sufficient atomic mobility, which is primarily dictated by substrate temperature during growth. In the last step, the crystallinity has to be achieved. This was done by changing the substrate temperature. The different temperatures allow the three elements to organise themselves on the surface of the substrate. The parameter space was scanned from RT to 500°C while keeping the laser power at 150 mJ and the repetition rate at 2.5. The main results from this analysis are shown in Figure 5.11, where the crystalline order is indicated in a parameter space map of inert pressure and growth temperature. The crystallisation into an F3GT crystal starts at 250°C , while it has to be said that no points between RT and 250°C could be measured due to the limitations of the pyrometer. The test, relying on the power set at the heating filament at around 200°C , did not show any signs of crystallisation. Combined with no signs of the crystallisation peaks around RT, it suggests that a specific kinetic energy is needed to enable the crystallisation process. As can be seen in Figure 5.11, the type of crystallisation changes from F3GT to F4GT when the temperature is increased to 350°C , while in all the growth processes presented here, the same target composition with a stoichiometric ratio of F4GT was used. A similar requirement for higher thermal energy has been observed in previous studies when comparing the growth temperatures of CVD-grown FGT. Generally, F4GT and F5GT require higher growth temperatures than F3GT. This suggest that F4GT has a higher formation energy than F3GT in order to achieve the crystalline form. Temperatures beyond 350°C are leading to a decrease in crystalline order, which vanishes above 375°C . Control over the inert gas pressure is essential for maintaining

the stoichiometric ratio of the deposited elements. Improper adjustments can change the composite ratio, preventing the correct phase formation and hindering the growth of FGT films.

The structural order of the films was primarily analysed using X-ray diffraction (XRD) (see Figure 5.12), which provided key insights into phase crystallinity.

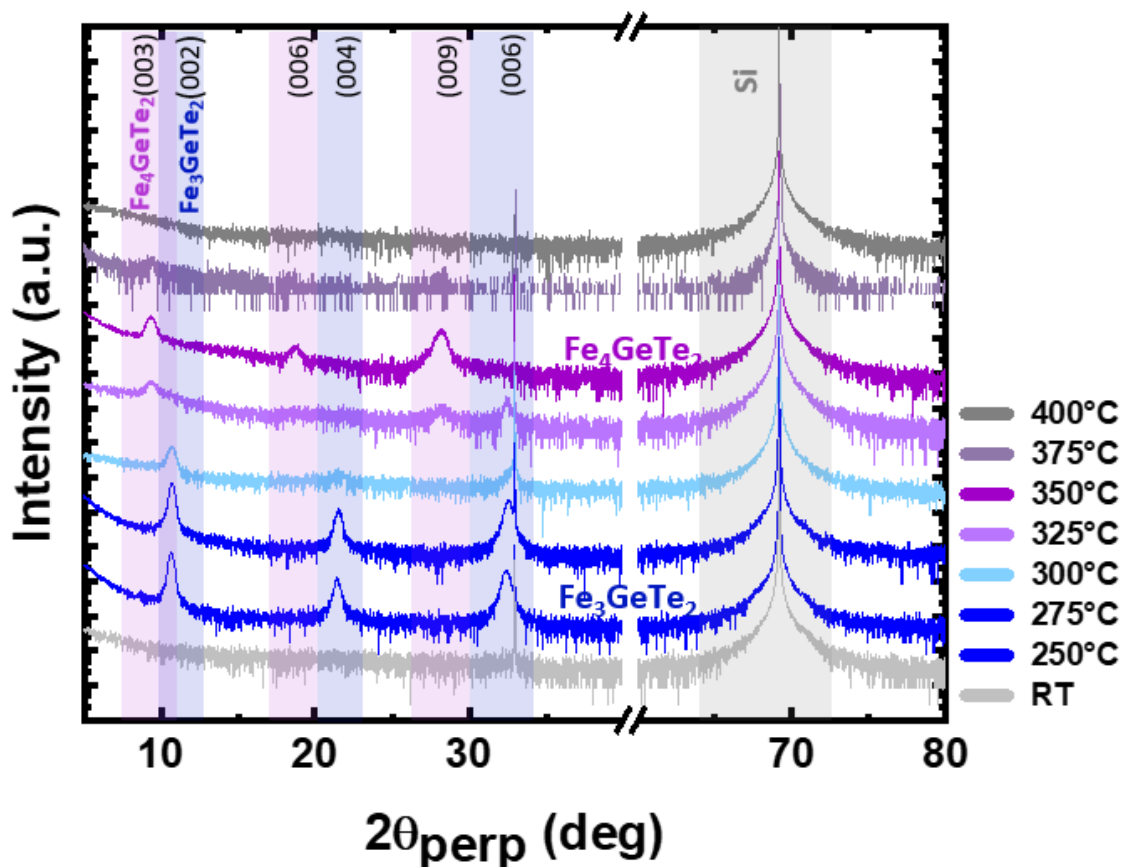


Figure 5.12: Omega 2 theta scans of samples grown under different temperatures but the same Argon pressure (0.04 mbar). The characteristic peaks of Fe_3GeTe_2 shrinks at temperatures above 275°C, and the (003) Bragg peak (and multiples) of Fe_4GeTe_2 appears around 325°C.

Different $2\theta/\omega$ scans of samples grown at various temperatures are shown. No peaks of any crystallisation can be found in the samples grown at RT and 400°C, except for one of the Si-substrate (around 69°C), which is also present for all the other samples. Starting from 250°C to 275°C, three peaks can be found, which can be attributed to F3GT (multiple of the 002 peaks, detailed analysis can be found in the next section). The peaks are getting smaller when the growth temperature increases to 300°C, indicating a degradation of the crystal order. A transition temperature at 325°C was found, and F3GT (006) and F4GT (009) peaks were present. Increasing the growth temperature further leads to a crystallisation of F4GT. No traces of F3GT can be found anymore, and neither can other crystalline structures. Going higher in temperature leads again to a degradation of the crystalline order, vanishing at 400°C. It can be said

that the optimal growth conditions of F3GT are in the temperature window of 250–275°C, and for F4GT is at 350°C. The difference in temperature indicates that the two components have different activation energy necessary to initialise the crystallisation process. The optimized growth condition allows the deposition of F3GT and F4GT which will be analysed regarding their structural integrity, phase composition and magnetic properties in the following.

5.4.3 Fe_3GeTe_2

5.4.3.1 Structural characterisation

The crystal structure of a single layer Fe_3GeTe_2 can be seen from the top view (along the c axis Figure 5.13a) as a hexagonal arrangement of iron (blue) and germanium (cyan) atoms. With tellurium (purple) atoms filling up the center of each hexagon. The side view (Figure 5.13b) illustrates how multiple layers of the van der Waals material are stacked on top of each other, following an ABA stacking sequence. Within each individual F3GT layer, the iron atoms occupy two inequivalent sites: some are positioned within the same plane as the germanium atoms, while others are located between the germanium and tellurium layers.

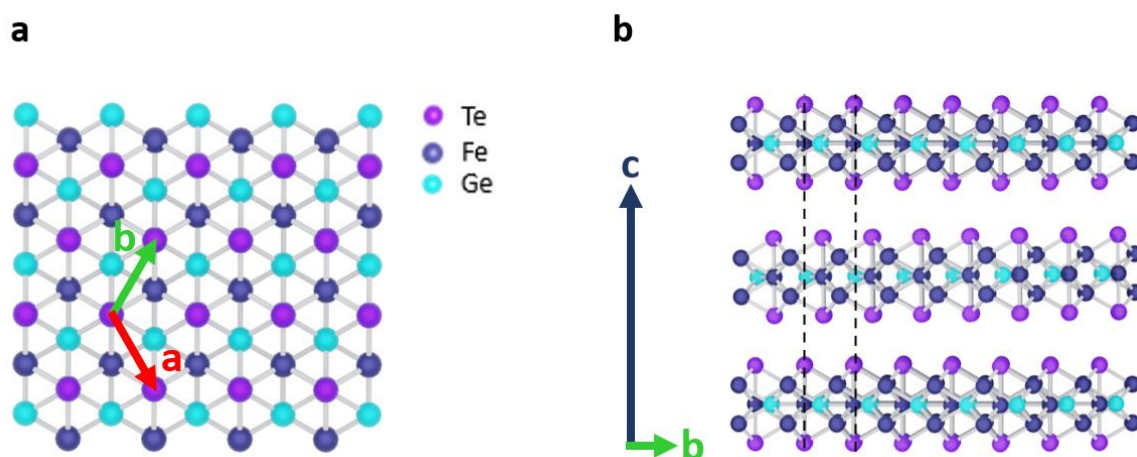


Figure 5.13: Crystal structure of Fe_3GeTe_2 . (a) Top view along the c -axis, the Te, Fe, and Ge atoms are represented by purple, blue, and cyan spheres, respectively. The in-plane lattice vectors a (red) and b (green) are indicated. (b) Side view of F3GT, illustrating the stacking of multiple layers in the crystal. The lattice vector c (blue) indicates the out-of-plane direction.

The periodic arrangement of atoms, particularly the out of plane stacking of the van der Waals material, directly influences the diffraction pattern. Out-of-plane reflections peaks provide information on the layered ordering along the c -axis, while in-plane diffraction peaks reveal details about the hexagonal lattice symmetry.

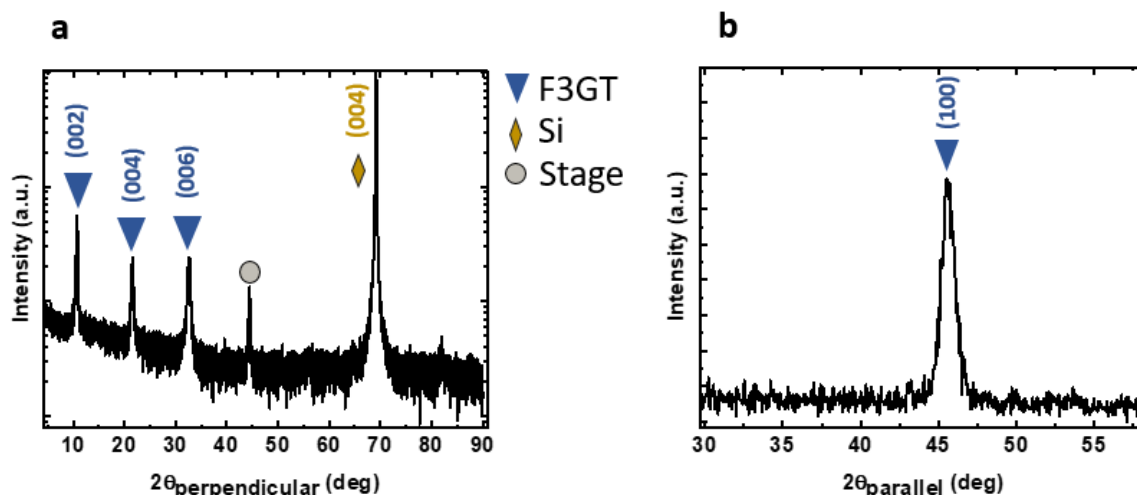


Figure 5.14: XRD measurement of F3GT crystal. (a) XRD scan with the incident X-ray beam perpendicular to the plane of the crystal. Peaks corresponding to the (002), (004), and (006) planes of F3GT are marked by blue triangles, with additional peaks corresponding to the silicon substrate (yellow diamond) and the stage (grey circle) also indicated. (b) XRD scan with the incident X-ray beam parallel to the plane of the crystal, showing (100) peaks corresponding to the in-plane crystallographic orientation of F3GT.

In Figure 5.14a, the $2\theta/\omega$ XRD spectrum is shown. Prominent is the strong Si (100) substrate peak at 69° . It has to be mentioned that the substrates are commercially available silicon substrates, which are thermally oxidised on top to form an amorphous 280 nm Silica layer. Apart from the silicon peak, peaks at lower angles can be seen. Those peaks can be attributed to F3GT. The corresponding peaks are multiple of the (002) reflection, indicating the organised structure in the out-of-plane direction (regarding the substrate surface). From the peak analysis, the c lattice parameter of $16.45(0.07)\text{\AA}$ is obtained. This value corresponds with the literature values for bulk F3GT [168]. From the $2\theta/\phi/\chi$ measurements, the in-plane lattice parameter can be deduced. From the (110) peak (Figure 5.14b), a lattice parameter of $3.99(0.01)\text{\AA}$ for F3GT is found, which is consistent with reported values [168].

5.4.3.2 Magnetic characterisation

The magnetic properties of the F3GT film were analysed using a SQUID magnetometer. The sample was mounted in an out-of-plane position inside the SQUID, and magnetic hysteresis curves were measured at 10K (Figure 5.15a) and 300K (Figure 5.15b).

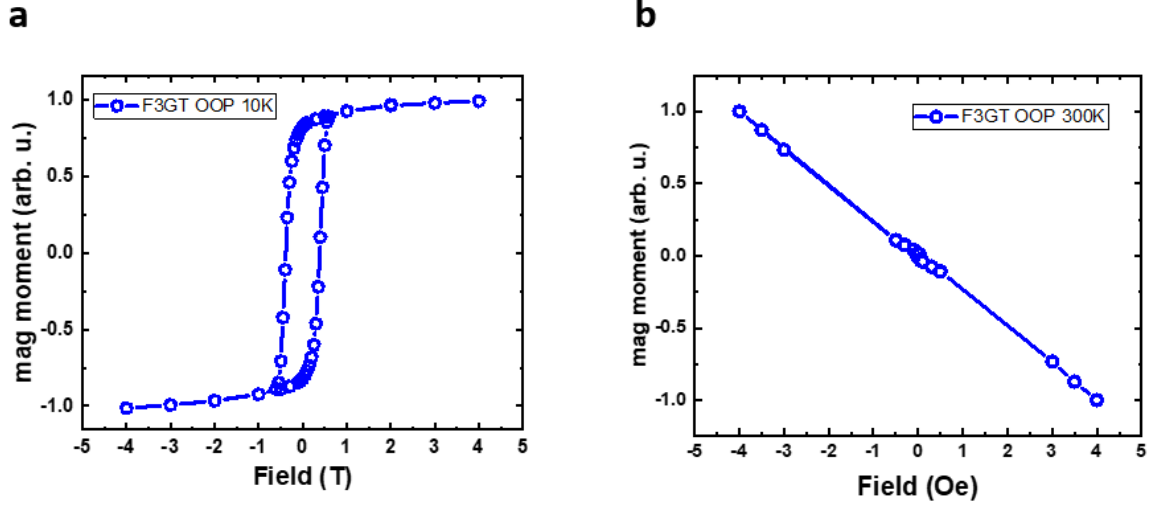


Figure 5.15: SQUID measurement of the magnetic properties of an F3GT film at 10K (a) and 300K (b) in an out-of-plane configuration. The ferromagnetic behaviour cannot be detected at high temperatures.

The ferromagnetic behaviour can be seen in the opening of the hysteresis cycle. The high coercive field, as well as the out-of-plane magnetic anisotropy, is in accordance with the literature findings [169]–[171]. No trace of magnetism can be found on the hysteresis cycles at 300°C. Only a diamagnetic contribution can be seen in the linear slope. This contribution can be attributed to the silicon substrate. The magnetism vs temperature curve was measured from 300 to 1K, indicating a magnetic transition around 170K (Figure 5.16). Regarding the resolution of the M vs T curve, the value agrees with findings from other groups for bulk F3GT. While growing a F3GT sample was successful, we decided to focus on the F4GT component, which was supposedly characterised with a higher Curie temperature than F3GT.

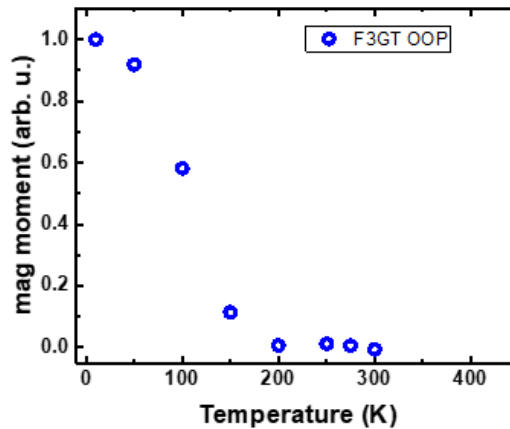


Figure 5.16: M vs T of the F3GT film from 10K to 300K. The ferromagnetic response drops rapidly around 150K, and no trace of ferromagnetism can be detected at temperatures above 200K

5.4.4 Fe_4GeTe_2

5.4.4.1 Structural characterisation

Monolayer Fe_4GeTe_2 appears along the c-axis (Figure 5.17a) like Fe_3GeTe_2 in a hexagonal arrangement of iron (blue) and germanium (cyan) atoms with the same tellurium position. However, a key difference is the stacking of F4GT layers, which changes to an ABC stacking, as indicated by the right-shifted red boxes in Figure 5.17b. Additionally, the presence of excess iron atoms in Fe_4GeTe_2 (compared to F3GT) leads to a significant rearrangement within a single layer. Unlike Fe_3GeTe_2 , where some iron atoms share the same plane as germanium, Fe_4GeTe_2 features four distinct iron planes, none of which coincide with the germanium layer.

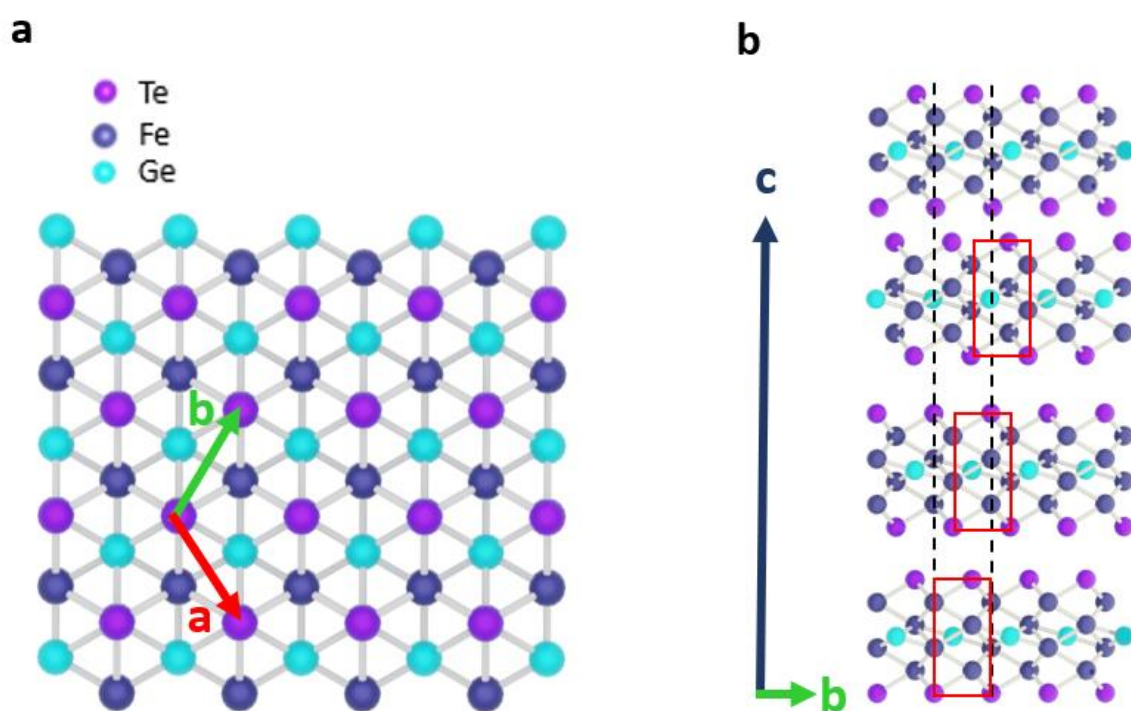


Figure 5.17: a) Top view on the atomic arrangement of the Fe_4GeTe_2 crystal with Te, Fe and Ge atoms (purple, blue and cyan, respectively). The in-plane lattice vectors a (red) and b (green) are indicated. Side view of F4GT with the stacking sequence of multiple layers in the ABC configuration. The red rectangles highlight the shift in atomic positions from one layer to the next. The lattice vector c (blue) indicates the out-of-plane direction.

The structural properties of the F4GT film were analysed using XRD, as shown in Figure 5.18. The $2\theta/\omega$ XRD spectrum is characterized by the F4GT peaks (003), (006), (009), MoS_2 (002) and silicon peaks (002),(004). The distinct peaks corresponding to the (003) multiples reflection of Fe_4GeTe_2 , indicating the layered structure of the material. From the peak analysis, a lattice c parameter of $28.6(2)\text{\AA}$ is extracted. This value is smaller than the theoretically predicted and experimentally observed values [97],[172],[173], but aligns closely with $28.6\text{\AA}$ reported in [171]. The presented sample of F4GT was capped by MoS_2 to avoid degradation. The presence of MoS_2 can be seen in the peak around

14.4° in Figure 5.18 [174]–[176]. This confirms that the capping layer did not introduce significant structural distortions to the F4GT film.

In Figure 5.18b, the diffraction pattern obtained from in-plane measurements reveals peaks corresponding to the (100), (200), (300) and (110) reflections. The in-plane lattice parameter a and b was determined to be 4.05(1)Å, which is in accordance with literature values [97],[172],[173]. The simultaneous observation of both (100) and (110) peaks suggests that while the material maintains its fundamental hexagonal order, it consists of multiple crystallographic domains rather than a single, highly oriented phase.

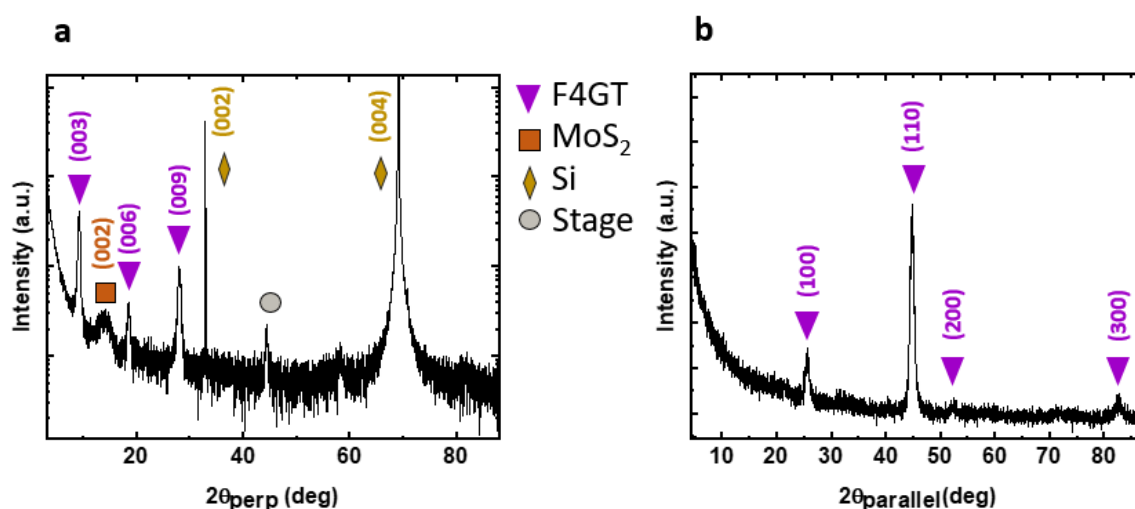


Figure 5.18: XRD measurement of (F4GT) crystal. (a) XRD scan in the perpendicular configuration showing the (003), (006), and (009) peaks of F4GT marked by purple triangles, the MoS₂ (002) peak (orange square) and additional peaks corresponding to the silicon substrate (yellow diamond) and the stage (grey circle). (b) in-plane XRD scan showing the (100), (110), (200) and (300) peaks of F4GT.

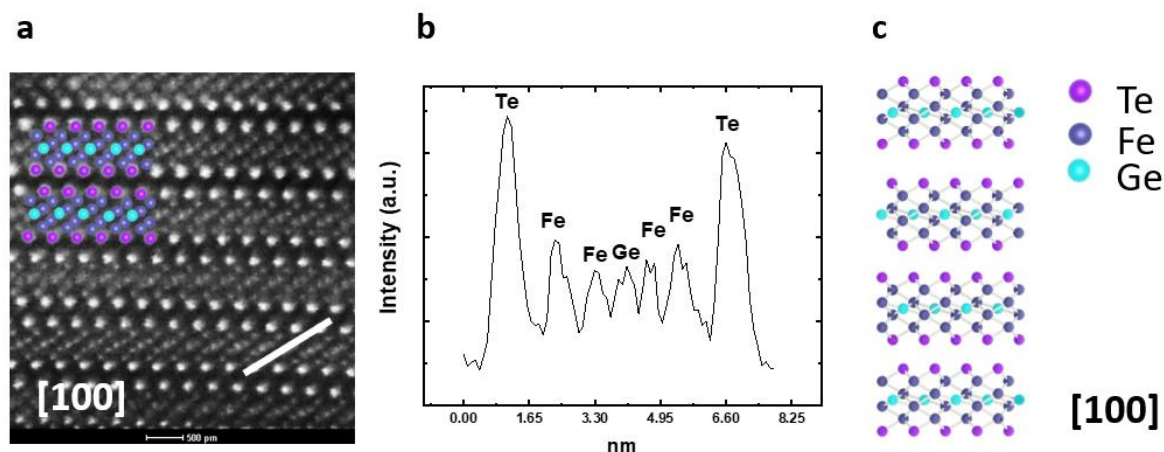


Figure 5.19: a) HAADF image of Fe_4GeTe_2 showing the crystalline arrangement corresponding to the simulated structure in (c). The white line indicates the profile line in which the intensity graph is shown in b). The different Atmos are clearly distinguishable in space.

Transition electron microscopy was performed to further verify the crystalline order of the F4GT film. The High-Angle Annular Dark Field (HAADF) image (Figure 5.19a) of F4GT shows a crystalline structure and crystal lattice arrangement (along [110]). The image reveals a clear van der Waals gap between the layers. The atomic positions are well-defined, showcasing the layered structure characteristic and high crystallinity of F4GT, agreeing with the simulated structure shown in Figure 5.19c and reported F4GT crystal structure [97],[177]. The four iron atoms are visible, separated by Germanium and capped on both sides with Tellurium. Figure 5.19b displays the intensity profile along the white line in Figure 5.19a, quantitatively showing the atomic positions. The distinct peaks correspond to the positions of Te, Fe, and Ge atoms, confirming the material's structural integrity.

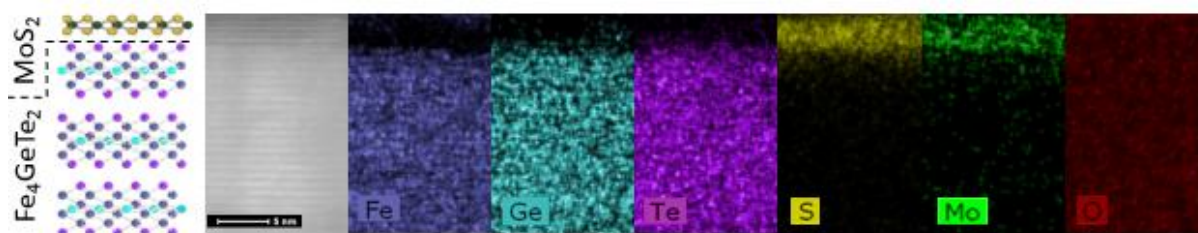


Figure 5.20: HRTEM and EDX map of the $\text{F4GT}/\text{MoS}_2$ heterostructure. A homogenous distribution of Fe, Ge and Te is visible. A distinguishable interface between F4GT and MoS_2 is present. The Oxygen EDS map does not reveal any sign of oxidised F4GT.

Energy dispersive X-ray spectroscopy (EDX) has been performed to verify the film's stoichiometry and composition. Figure 5.20 shows an HRTEM image of the $\text{F4GT}/\text{MoS}_2$ stack and EDX maps of the composites. The iron, germanium, and tellurium are equally distributed in the F4GT layer, confirming a uniform crystalline structure. Further, the stoichiometric ratio of Fe_4GeTe_2 can be deduced. The Mo and S map shows the

concentration of those elements in the top layer with a distinct interface with F4GT. The layer acts as a protective capping layer, preventing the F4GT film from oxidation, as can be seen in the Oxygen EDX map.

5.4.4.2 Magnetic characterisation

Figure 5.21a presents the magnetic hysteresis loops of F4GT capped with a 5 nm MoS₂ layer, measured at 300K using VSM magnetometry. The loop is recorded in in-plane configurations relative to the ab-plane of the F4GT film. The pronounced shape of the loop indicates an in-plane magnetic anisotropy. Figure 5.21b displays a 20x magnified optical image of the magnetic domains in the F4GT film at room temperature, captured using the magneto-optical Kerr effect (MOKE) with an external magnetic field applied parallel to the film plane.

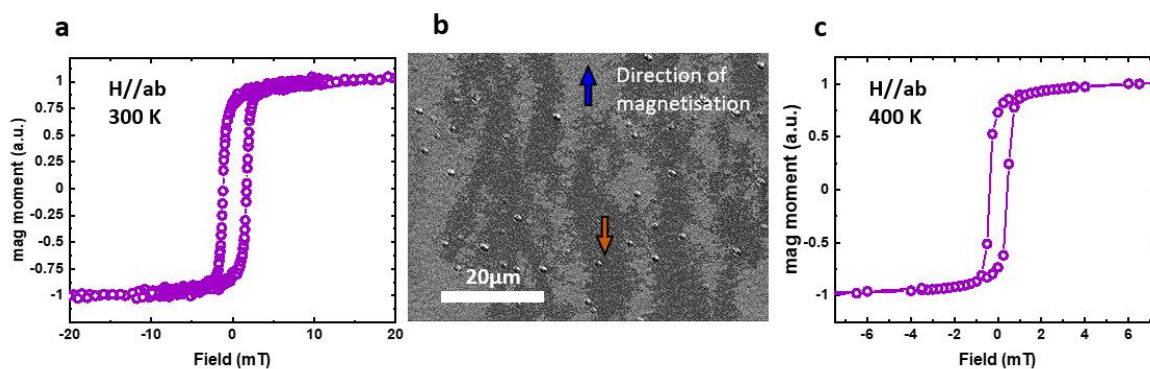


Figure 5.21: (a) In-plane VSM measurement of the F4GT/MoS₂ stack at room temperature. (b) MOKE images of the sample showing differently orientated domains at RT. (c) The magnetic hysteresis cycle survives up to 400 K, measured by SQUID.

The observed stripe-like domains are characteristic of ferromagnetic behaviour at room temperature, further solidifying the evidence of robust ferromagnetism in F4GT. The thermal stability is verified further by measuring the in-plane hysteresis loop at 400K in a SQUID (Figure 5.21c). The ferromagnetism sustains temperatures of 400K which is a crucial attribute for practical applications where the material must operate effectively at room temperature or higher. Compared to other 2D ferromagnets like CrI₃, Ce₂Ge₂Te₆ or F₃GT, which have lower T_c values [21]–[24], F4GT's high T_c extends its usability in environments without cooling mechanisms. The capping of F4GT with 5 nm MoS₂ serves a dual purpose. Primarily, it acts as a protective barrier against oxidation[140],[178], preserving the film's surface quality and preventing environmental degradation that could compromise its magnetic properties. Furthermore, the MoS₂ layer is particularly beneficial in maintaining the pristine interface essential for high-performance spintronic devices [164],[179], accessing large-scale *in situ* MTJs, thus overcoming the bottleneck of time-consuming stacking of flakes. This protective capping thereby not only extends the material's longevity but could also open avenues for novel devices.

As the T_C of our F4GT samples was found to be above the limit of our SQUID measurement system (400K), in order to be able to determine the ferromagnetic transition temperature, we had to develop a new system allowing measurements up to 600K. We built a temperature-dependent setup relying on a Linkam sealed vacuum cell and permanent magnets to obtain a magnetic field in the 20mT range (see Figure 5.22). On top of the LINKAM cell, two permanent magnets are aligned with each other to create a static in-plane magnetic field at the sample position. Below the cell a stronger magnet with opposite magnetic field direction regarding the top magnets is mounted on a linear stage, which enables to drive the magnet closer to the cell. In a retracted position the field at the sample position is governed by the top magnets, while the bottom magnet switches the field when it approaches the sample position, enabling the 20mT sweeping field range.

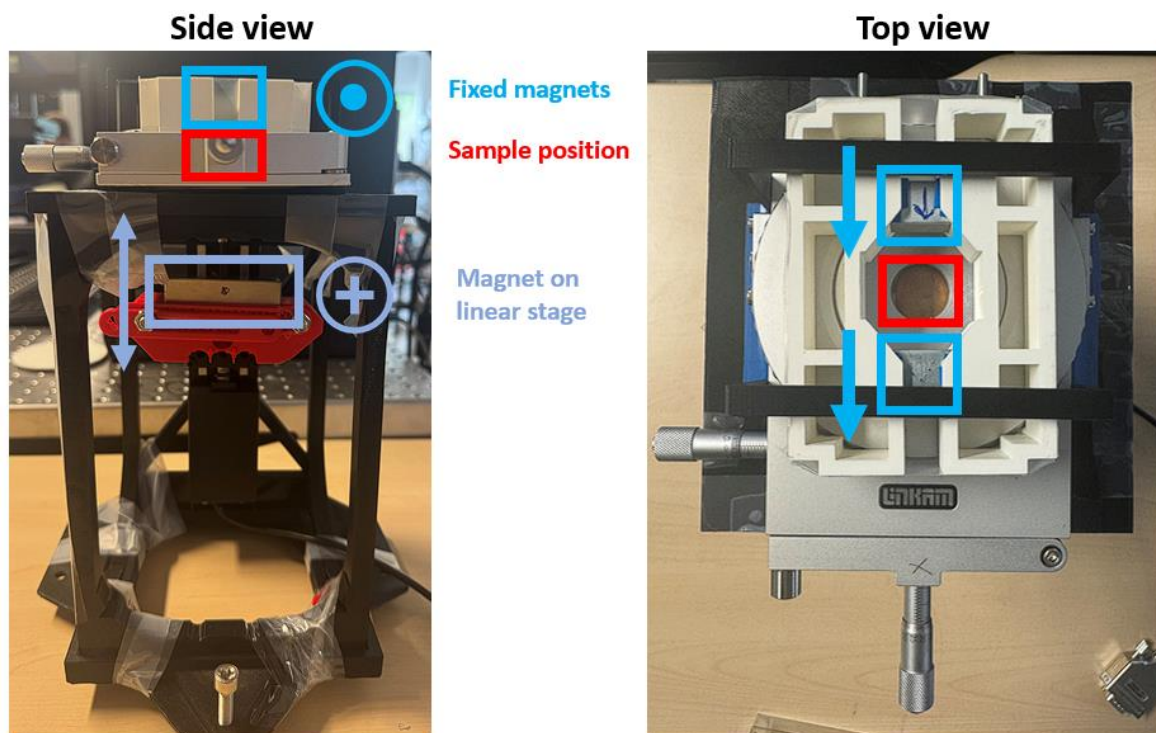


Figure 5.22: Image of the self-build heat modulated setup used for MOKE measurements. The LINKAM cell allows the sample to be sealed under vacuum and heated to temperatures up to 600K. A 3D printed holder aligns the two in-plane magnets on top of the LINKAM cell (top view), while a third magnet is placed below the chamber with its magnetic field pointing into the opposite direction. The bottom magnet is mounted on a linear stage which allows the field inversion when approaching the sample position.

The system allows the sample to be sealed under an inert atmosphere or under vacuum to avoid oxidation during heating. Using this setup, we were able to record the magnetic response above our SQUID limit of 400K (Figure 5.23, red points) giving the first indication of a Curie temperature $>450K$.

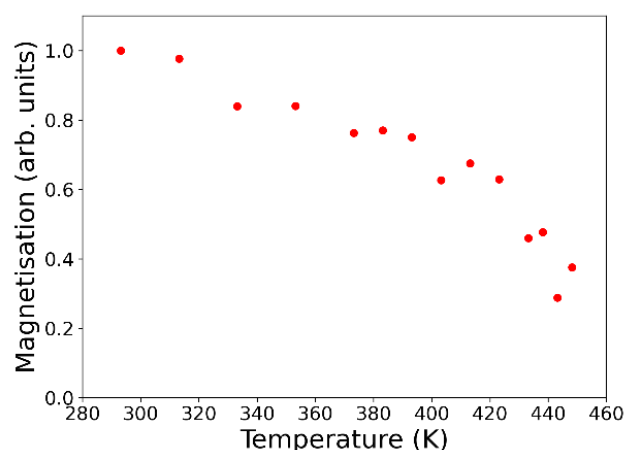


Figure 5.23: Magnetisation near remanence of F4GT measured by MOKE using the heat modulated LINKAM cell from Figure 5.22..

Another estimate of the Curie temperature was obtained plotting the intercepts of isotherms as shown in Figure 5.25b (see below for detailed explanation) on the magnetization axis as a function of temperature. This approach allowed us to estimate the Curie temperature by linear regression to be approximately 550K. The found value reinforces the conclusion that T_C lies well above room temperature.

Overall the results indicate a Curie temperature in the 450-550K range with a clear signal at room temperature and up to 400K. It is interesting to compare these results to the nascent field of FGT 2D magnets. Despite being few years old now, the magnetic properties of F4GT and F5GT compounds are currently under significant debate due to discrepancies in reported Curie temperatures (T_C) and the overall lack of consensus on the underlying magnetic behaviour and models. Our PLD-grown F4GT large-scale 2D magnet is characterised by a $T_C > 450$ K. This value differs from the T_C reported bulk F4GT crystals grown by CVT of 270K [171],[180]. Similarly, other groups reported F3GT [181] and F5GT [182],[183] with T_C above room temperature, when grown by MBE. Due to the spread of Curie temperatures regarding sample growth method and crystallinity, theoretical models try to reproduce the experimentally recorded data. Interestingly Wang *et al.* achieved unusually high T_C for F4GT when reducing the thicknesses down to 4nm attributing the high Curie temperature not to the bulk F4GT but to an interfacial effect between the Al_2O_3 and F4GT layer [177]. Above 16nm, such as our films, the T_C drops down to below 300K. Until now, the theoretical approach is under discussion, leading to a widespread of theoretically obtained T_C temperatures for F4GT from 68K[184] to 322K [185], while most models cannot reproduce all three compounds simultaneously [186]. Our own observations suggest that the high T_C values could be attributed to a reduction in the lattice c-parameter. The reduced thickness in our samples may enhance interlayer exchange coupling between the F4GT layers[187], which could be a critical factor in stabilising ferromagnetism above room temperature.

5.4.4.3 Origin of magnetism

Next, as a first hint of understanding the underlying magnetism, we attempted to fit the data using critical exponent behaviour $M \propto (T_C - T)^\beta$. Figure 5.22 shows the different simulations using the most common models used for magnetisms from 3D to 2D: mean field, 3D Heisenberg, 3D XY, 3D Ising, Tricritical mean field, 2D XY, 2D Heisenberg. One can first see that both extreme, the Mean field model ($\beta = 0.5$) and the 2D Ising model ($\beta = 0.125$) poorly reproduce the data. In contrast, the other models require a little more detailed analysis. Indeed, models with critical exponents in the range $0.231 < \beta < 0.369$ fit the experimental points more accurately, with a better fit for $0.326 < \beta < 0.369$ (3D Ising $\beta=0.326$, 3D XY $\beta=0.349$; 3D Heisenberg $\beta=0.369$), corresponding to 3D magnetism. This indeed corresponds to previous reports for FXGT for which the beta coefficient was found >0.32 and hence to depart from the Tricritical mean field ($\beta = 0.25$) [115].

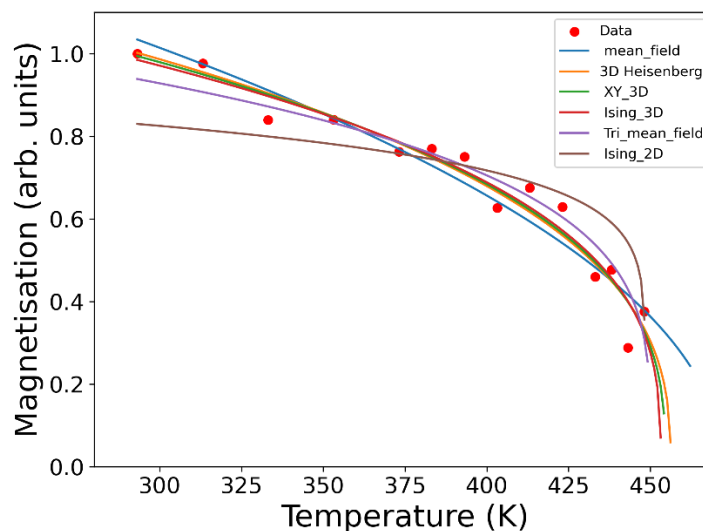


Figure 5.24: $M(T)$ of F4GT measured by MOKE (red points) in a self-built temperature-dependent setup based on a Linka, sealed vacuum cell. Various models are fitted to our data point (solid lines).

To complement the MOKE analysis, we pushed forward an analysis with regard to the critical exponent and the Curie temperature. As such, we derived Arrott-Noaks plots [188] based on the following approximate equation:

$$M^{\frac{1}{\beta}} = a \left(\frac{T - T_C}{T_C} \right) + b \left(\frac{H}{M} \right)^{\frac{1}{\gamma}} \quad (5.1)$$

with the material-dependent critical exponents β and γ , and temperature independent constants a and b . The idea is that parallel isotherms of the datasets (as seen in Figure

5.23a) should be obtained by renormalizing the data with the correct values of the critical exponents β and γ . This is expected to hold true in the vicinity of T_C (while β is normally extracted from measurements below T_C , γ is expected to be extracted from above) and at high fields when the magnetization saturates.

For this approach, we relied on SQUID measurements in the temperature range 360K–400K, and the field range 3T–4T, to warrant magnetization saturation. The curves of Figure 5.23a were obtained after subtracting the diamagnetic contribution of the silicon substrate χ_S at high fields and taking into account its temperature dependent behaviour[189]. A perfect linearity in the Arrott-Noakes plot is difficult to be achieved as the method is expected to work flawlessly in a narrow temperature window around T_C .

The shown results of Figure 5.23a, corresponding to the best agreement has been obtained for the parameter set of $\beta = 0.35$, $\gamma = 1.36$, and diamagnetic susceptibility $\chi_S = 2.2 \cdot 10^{-6}$ (in SI) with $d\chi_{SI}/dT = 0.04 \cdot 10^{-6}$. This β and γ values can be compared to the 3D Heisenberg model ($\beta = 0.369$, $\gamma = 1.396$), the 3D XY model ($\beta = 0.349$, $\gamma = 1.318$), and the 3D Ising model ($\beta = 0.326$, $\gamma = 1.237$). Physically, it is important to understand that β describes the behavior of the spontaneous magnetization as the material approaches the Curie temperature T_C from below. Hence, a smaller β (e.g., close to 0.326 for the 3D Ising model) implies a sharper increase in magnetization just below T_C , suggesting a stronger magnetic anisotropy and lower dimensionality. Similarly, γ characterizes the divergence of the magnetic susceptibility (χ) as the material approaches T_C from above. A larger value of γ indicates stronger critical fluctuations around the transition, typically related to lower-dimensionality or longer-range interactions. The given values $\beta = 0.35$ and $\gamma = 1.36$ are indicative of a 3D-like critical behavior with long-range interactions close to those predicted by the 3D XY model or a weakly anisotropic 3D Heisenberg model. Indeed, our extracted beta value of $\beta = 0.35$, lies between the theoretical values for the 3D-XY model ($\beta = 0.349$) and the 3D-Heisenberg model ($\beta = 0.369$). In addition, the $\gamma = 1.36$ values lie comparably in-between the 3D-XY model ($\gamma = 1.318$) and the 3D-Heisenberg model ($\gamma = 1.396$).

	technique	T _c	β	γ	Ref
F4GT *this work	MAP	>450	0.35	1.36	
F4GT	MAP	270.2	0.37	1.21	[171]
	KF	270.2	0.376	1.2	
F5GT	KF	273.7	0.346	1.364	[115]
F3GT	KF	215	0.322	1.063	[190]
Mean field			0.5	1	[67]
Tricritical mean field			0.25	1	[63]
3D Heisenberg			0.369	1.396	[64]
3D XY			0.349	1.318	[65]
3D Ising			0.326	1.237	[66]
2D Ising			0.125	1.75	[67]

Table 5.1: Critical exponents determined by this work and others for F3GT, F4GT and F5GT, as well as the exponents for the most common systems. MAP means modified Arrott plot, KF means Kouvel-Fisher method.

One can try to relate this to previous work on renormalization group (RG) in order to derive the range of the magnetic interaction. Indeed, we have [191]:

$$\gamma = 1 + \frac{4}{d} \left(\frac{n+2}{n+8} \right) \Delta\sigma + \frac{8(n+2)(n-4)}{d^2(n+8)^2} \left(1 + \frac{2 \left(3 - \frac{1}{4} \left(\frac{d}{2} \right)^2 \right) (7n+20)}{(n-4)(n+8)} \right) \Delta\sigma^2 \quad (5.2)$$

where $\Delta\sigma = \left(\sigma - \frac{d}{2} \right)$ and n and d are the spin and physical dimensions of the system. This formula is expected to give rise to a slight overshoot for γ vs the canonical values. Here the value of the exponent σ is closely related to the spatial decay of the magnetic interaction according to the form: $J(r) \propto r^{-(d+\sigma)}$ where d is the dimensionality of the system (most probably 3D in this case).

Ideally, the critical exponents of the 3D Heisenberg model ($\beta=0.369$, $\gamma=1.396$) are derived assuming that the interactions decrease rapidly with distance, typically with $\sigma > 2$, usually exceeding approximately 2.0–2.1. Similarly, the 3D XY model ($\beta = 0.349$, $\gamma=1.318$) is associated with a slightly different spin symmetry but also describes systems with short-range interactions. For this model, again, typically with $\sigma > 2$, around or slightly above 2.0, indicating rapid decay of interactions with distance. Hence, in practice $\sigma > 2$ indicates short-range interactions (typical of pure 3D Heisenberg and 3D XY models). On the contrary, usually $\sigma \leq 3/2$ approaches mean-field theory behaviour, indicating significantly longer-range interactions, and $3/2 < \sigma < 2$ clearly indicates a crossover region with long-range interactions.

In order to try to understand the kind of interaction present in the F4GT sample we can make use of the RG to determine σ . From previous analyses, we narrowed down the models to consider to be the 3D XY or 3D Heisenberg. Utilising the measured

$\gamma=1.36$ value of our samples, we can use $n=3, d=3$ (3D Heisenberg) or $n=2, d=3$ (3D XY) to obtain $\sigma \sim 1.915$ and $\sigma \sim 1.965$ from equation (5.2), respectively. With the scaling relation of critical exponents $\beta = \frac{\gamma}{2} \left(\frac{d}{\sigma} - 1 \right)$ [115] we can determine the related $\beta_{(n=3, d=3)} \sim 0.385$ and $\beta_{(n=2, d=3)} \sim 0.358$ critical exponents. The obtained beta value of the 3D XY model is the closest to our configuration. In fine, our best guess is achieved for $n \sim 2$ and $d \sim 2.85$ and $\sigma \sim 1.9$ giving our expected $\beta = 0.35$ and a $\gamma = 1.40$. Here, the slight overshoot of γ vs our value of 1.36 is expected from the RG equation. Finally, these values are very close to the universality class for a 3D XY model with long-range magnetic interactions, where the interaction distance decays approximately as $J(r) \sim r^{-4.9}$, signifying a nearly isotropic/weakly anisotropic, or itinerant ferromagnetic character with critical fluctuations extending over a substantial range.

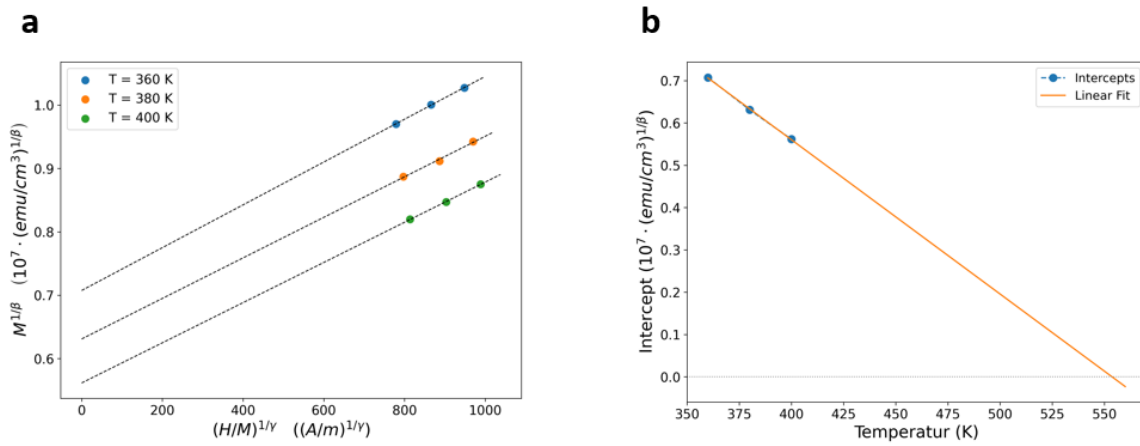


Figure 5.25: a) Arrott-Noakes plot of the measured SQUID data. Nealy parallel isotherms are achieved by subtracting a diamagnetic susceptibility of $\chi_S = 2.2e-6$ contribution from the silicon wafer, and utilising $\beta = 0.35$, $\gamma = 1.36$. b) Intercepts from a are plotted against the temperature and linearly fitted. The intercept with the x axis gives an estimation of $T_c = 550$ K.

Interestingly, itinerant ferromagnetism was claimed by Wang *et al.* [192] through a flat band analysis and the work of Bera *et al.* [180], who reported $\beta=0.40$ and $\gamma=1.302$ for F4GT and Rhodes-Wohlfarth ratio (RWR) of 2.35 (itinerant when $RWR > 1$). In comparison to F4GT, F3GT, which is widely accepted as an itinerant magnet, has a RWR of 3.8 [155]. This difference in RWR indicates that excessive iron in F4GT compared to F3GT reduces the itinerant character in the film [171]. Mondal *et al.* proposed that F4GT exhibits a combination of itinerant and localised magnetism [171], supported by their observed $\beta=0.37$ and $\gamma=1.21$ (see Table 5.1), which is characteristic of a 3D Heisenberg model, a model traditionally associated with localised magnetism, while measuring a RWR of 2.9, indicating itinerant magnetism. This idea is further supported by theoretical calculations from Liu *et al.* [187], which also suggests the coexistence of itinerant and localised magnetic behaviour in F4GT. These mixed results from the literature, in combination with our own critical exponents, suggest a nontrivial magnetic behaviour in F4GT. Likely in the form of a hybrid system between itinerant

and localised contributions.

In order to further deepen the understanding of the nature of the magnetism in F4GT, we asked collaborators from UC Louvain, Simon Dubois and Jean-Christophe Charlier, to perform first-principles calculations. In the unit cell of F4GT, the Fe-planes are subdivided into two distinct lattice sites: α -Fe and β -Fe (see figure 5.26). Relying on the linear response approach, they were able to determine U (on-site Coulomb repulsion values) of 2.54eV for α -Fe and 2.30eV for β -Fe. These values already provide insight into the degree of electron localisation vs itinerant magnetism contribution. In a first approximation, high Coulomb energies are associated with localised magnetism since the Coulomb repulsion restricts the hopping of the electrons to neighbouring orbitals. Inversely, low Coulomb energies favour a delocalisation of the electrons, thus itinerant magnetic moments. In F4GT, α -Fe which is expected to contribute more significantly to interlayer coupling as it belongs to the outermost iron plane of the 2D unit layer, is characterised by stronger localisation. This contrasts with the more itinerant nature of the innermost β -Fe.

Utilising the U values, the spin-resolved band structure for the two lattice sites were computed. The bands of the majority spins are pushed below the Fermi energy due to the Coulomb repulsion. These filled bands are an expression of the localised character for the majority spins. Whereas the minority bands are present at the Fermi level indicating the partial itinerancy for both α -Fe and β -Fe.

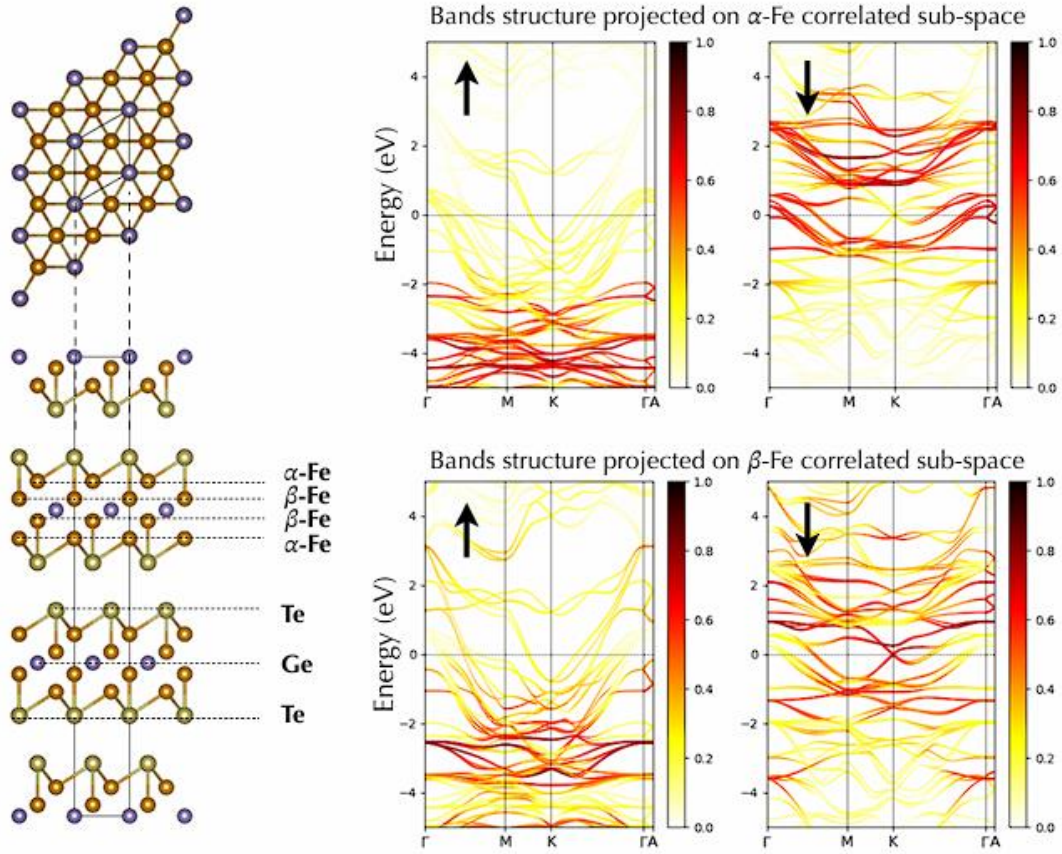


Figure 5.26: Spin-resolved band structure of F4GT for the two Fe lattice sides. The left panel shows the crystal structure of F4GT with the α -Fe and β -Fe lattices. The right panel shows the band structure for those lattice sides for majority and minority spins. The majority spin bands are pushed below the Fermi energy by the Coulomb energy U , while the minority bands are present around E_F .

It was possible to extract the exchange couplings between nearest iron atoms for various cases (see Figure 5.27). The calculation revealed that the intralayer exchange interaction in F4GT is significantly stronger than the interlayer ones. Indeed, due to the presence of the van der Waals gap, interlayer distances are generally longer, naturally reducing the exchange strength. Although α -Fe- α -Fe (α - α) distance between different layers are from comparable size to the intralayer ones (around 6Å), they yet remain weaker than α -Fe- β -Fe (α - β) intralayer exchange interactions. This picture is coherent with the critical exponent analysis for our best solution of $n \sim 2$ and $d \sim 2.85$, where the system is not fully 2D nor 3D. These findings reinforce the picture of F4GT as a quasi-2D magnetic system.

Energy wise the α - β exchange is dominating the interactions, with strong ferromagnetic coupling. Interestingly, the α - α and β - β exchange couplings exhibit sign oscillations, with noteworthy antiferromagnetic exchange, which may indicate an RKKY-like interaction mechanism (dashed lines in Figure 5.27). This behaviour aligns with the partially itinerant nature of the β -Fe moments.

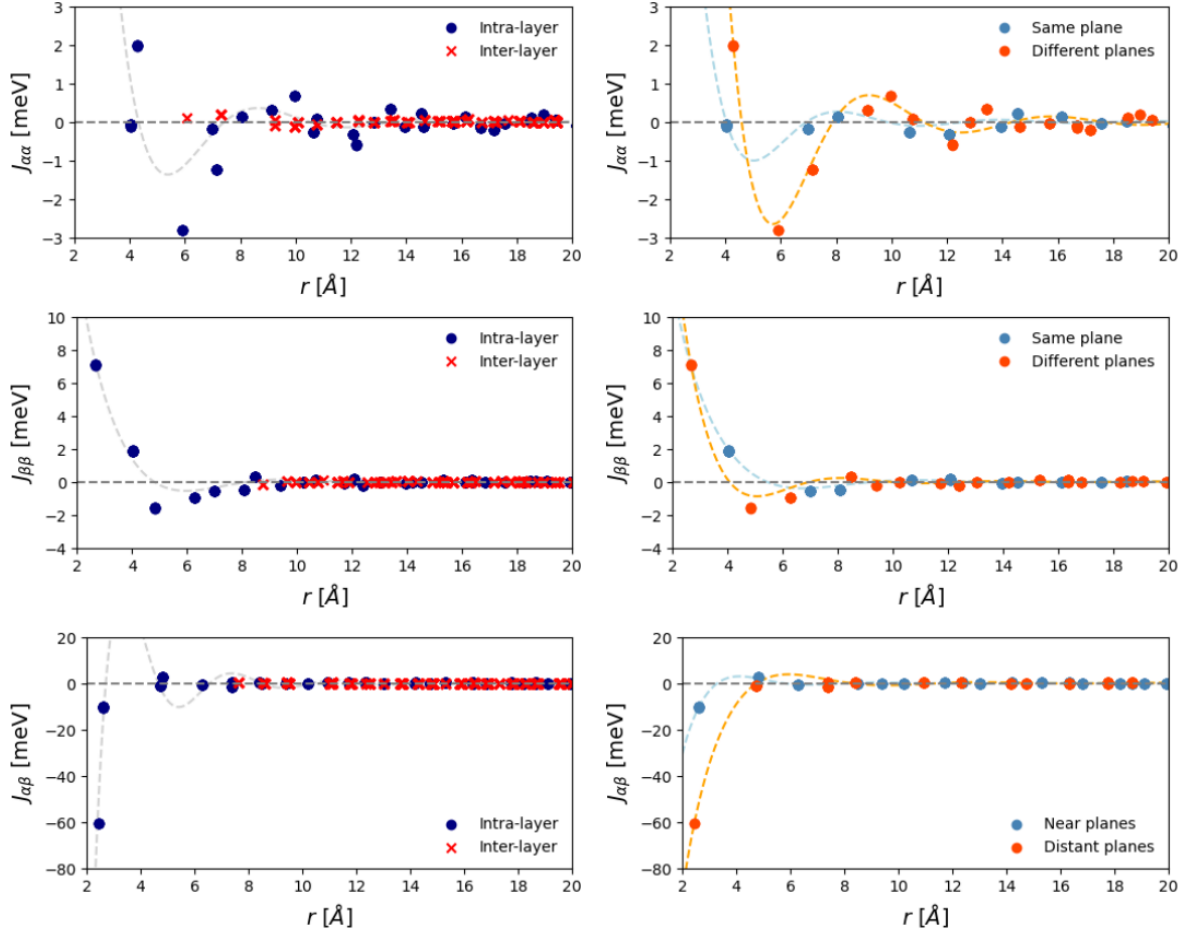


Figure 5.27: Distance-dependent exchange interaction energies in F4GT for the α - α , α - β and β - β lattice exchange interactions. Interlayer refers to interaction across the vdW gap, while intralayer refers to interaction within the same F4GT slab. The right panel shows only intralayer behaviour. The dashed lines indicate an RKKY-like behaviour.

Log-log plots of $|J(r)|$ (Figure 5.28, middle and right panels) reveal power-law behaviour with exponents close to those derived from renormalisation group (RG) analysis of experimental critical exponents ($\sigma \approx 1.9$). This supports the idea that Fe_4GeTe_2 lies in a crossover regime between localised and long-range itinerant magnetism, consistent with $\beta \approx 0.35$ and $\gamma \approx 1.36$ observed in SQUID and MOKE analyses. It can be seen through the dashed lines, which represent a system with $d=3$ and $\sigma=1.9$.

Further, our magnetocrystalline anisotropy energy (MAE) was calculated, including spin-orbit coupling (SOC) through non- and fully self-consistent SOC calculations. The non-consistent SOC leads to an in-plane MAE of about 3meV per unit cell, while a strong in-plane MAE of 26meV per unit cell was obtained for fully self-consistent SOC calculations. These results show the significant impact of spin-orbit interaction on the system, thus leading to an in-plane anisotropy known from XY like models.

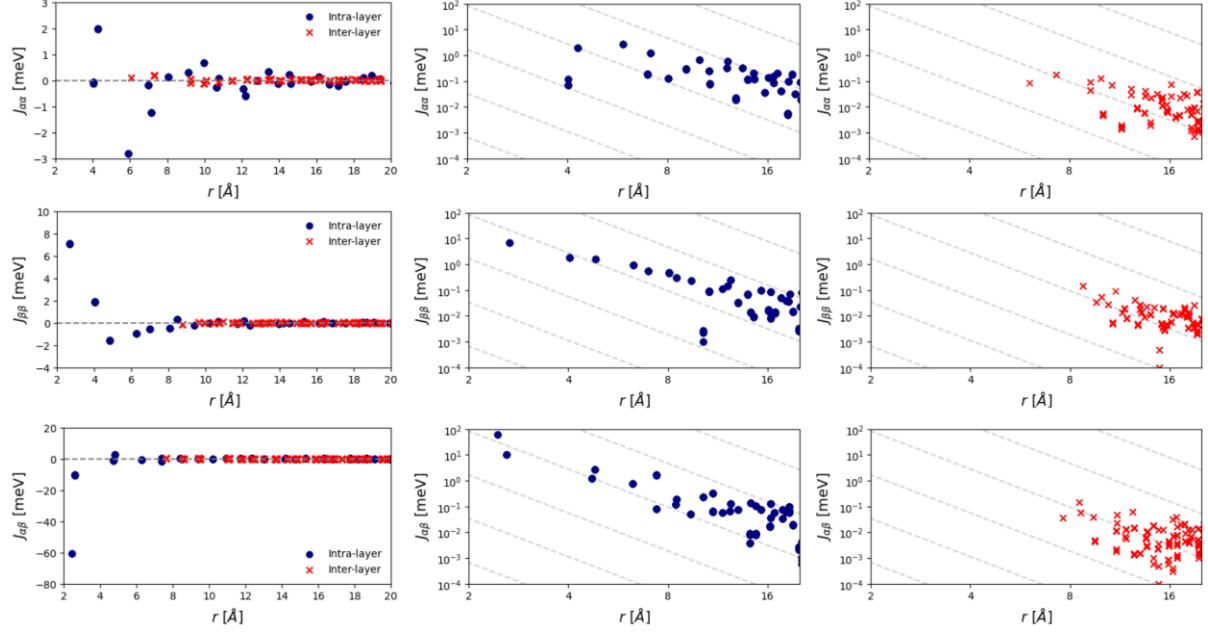


Figure 5.28: Exchange interaction energies vs distance. The left panel is identical to the left one in Figure 5.27. The middle and right panels show the exchange energies on a log-log scale. The blue points are from intralayer exchange and the red points from interlayer (across the vdW gap) exchange interactions. The dashed lines correspond to the obtained RG values from SQUID measurements (with $d=3$ and $\sigma=1.9$ and various offsets).

In conclusion, the extracted critical exponents $n \sim 2$, $d \sim 2.85$ and $\sigma \sim 1$ for our Fe_4GeTe_2 yield $\beta = 0.35$ and $\gamma = 1.40$, placing the system within the universality class of a three-dimensional 3D-XY model with long-range magnetic interactions.

The dominant magnetic couplings are ferromagnetic interactions between nearest and next-nearest α - β neighbours within the same layer. In contrast, α - α and β - β exchanges are weaker and exhibit sign oscillations, featuring notable short-range antiferromagnetic components. This oscillatory behavior, along with its distance dependence, resembles Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions, consistent with the partially itinerant nature of the β -Fe sublattice. This analysis indicates that the intra-layer exchange interactions are significantly stronger than the inter-layer ones, underscoring the quasi-two-dimensional nature of magnetism in Fe_4GeTe_2 .

This hybrid magnetic regime, characterised by long-range in-plane correlations, arises naturally from the layered van der Waals structure of Fe_4GeTe_2 , where magnetic exchange is inherently stronger within the layers than between them. The coexistence of local and itinerant magnetism extracted from critical exponents, also evident in the electronic band structure, the oscillatory exchange $J(r)$, and SOC-related in-plane MAE, points to a mixed magnetic behaviour governed by local-moment Heisenberg interactions and conduction-electron-mediated itinerant exchange.

These findings align theoretical with experimental observations, reinforcing Fe_4GeTe_2 's

classification within the 3D XY universality class with extended exchange interactions. Notably, the extracted β , being larger than the typical 3D XY value, reflects stronger interactions, and the elevated $\sigma = 1.9$ signals pronounced critical fluctuations — both consistent with the system's itinerant features and quasi-2D nature.

In this chapter, we demonstrated the successful large-scale synthesis of 2D ferromagnetic F3GT and F4GT thin films by PLD on amorphous SiO_2 at CMOS-compatible temperatures. This enables a scalable approach for fabrication of high-quality 2D ferromagnets. In particular, PLD allows growth directly on amorphous substrates without requiring epitaxy, while achieving large-area uniformity suitable for device integration. Structural characterisation by XRD, TEM, and EDX confirms the high crystalline quality and correct stoichiometry of the films, even on non-crystalline substrates.

Magnetically, PLD-grown F3GT reproduces the properties known from exfoliated flakes, validating the robustness of the growth method. For F4GT, we observed room-temperature ferromagnetism with a Curie temperature exceeding 450 K, among the highest values reported for this material system. Critical exponent analysis indicates a quasi-2D character consistent with an XY-type model, suggesting predominantly localised magnetic behaviour with signatures of itinerant contributions. These findings are supported by the analysis of the provided first-principles calculations from our collaborators at UC Louvain. The dual character of itinerant and localised magnetism is observed in the band structure, while the exchange interactions are strongly dominated by intralayer coupling with power-law behaviour corresponding to the ones found by RG analyses of SQUID measurements.

In addition, the successful *in-situ* integration of a MoS_2 capping layer during the PLD process marks a significant step toward fully integrated 2D spintronic heterostructures. Our approach demonstrates the feasibility of realising large-scale 2D magnetic systems without the need for post-processing or transfer steps, establishing a foundation for the future development of all-2D MTJs and scalable spintronic devices.

6 CONCLUSION AND PERSPECTIVE

Materials like graphene and TMDS have already shown their high potential for spin valve systems due to their unique spin transport channels, high spin polarisation, and thickness-dependent behaviour. In this direction, the recently discovered 2D ferromagnets have been the last missing material class for creating a full van der Waals MTJ. Among these, FGT arose as an outstanding candidate family due to their high intrinsic Curie temperature and metallic behaviour, making them well suited for integration as ferromagnetic electrodes in MTJs. At the beginning of this PhD, only a limited number of 2D ferromagnets were available for spintronics applications. Indeed, while pioneering studies on Fe₃GeTe₂ (F3GT) demonstrated tunnel magnetoresistance (TMR), the significant variability in measured spin polarisation underscored the challenges in achieving clean interfaces and defect-free junctions. Concurrently, although large-scale growth of 2D ferromagnets had begun, none were available on a large scale with a Curie temperature above room temperature. This called for a step forward in addressing these challenges and advancing the field of spintronics.

In a first study, we fabricated high-quality F3GT-based MTJs, carefully integrating them on a reference spin analyser to understand the origin of the tunnel current and its spin polarisation. As such, we carefully analysed F3GT's behaviour by integrating it into an asymmetric analyser junction configuration of F3GT/Al₂O₃/(Co/Pt)_n. The selection of Al₂O₃/(Co/Pt)_n was motivated by its established spin polarisation and out-of-plane anisotropy compatible with F3GT. The 2D ferromagnet was exfoliated directly on the spin analyser and subsequently passivated via atomic layer deposition ALD to prevent oxidation and preserve the pristine interfaces. Our measurements revealed a substantial tunnel magnetoresistance (TMR) of 130%. Leveraging a reference spin analyser, we could determine a negative spin polarisation for F3GT. This negative sign was attributed to the predominance of tunnelling minority spins around the gamma point, a hypothesis corroborated by ab-initio calculations conducted by our collaborators from UC Louvain (Simon Dubois, Jean-Christoph Charlier). This phenomenon can be elucidated by considering the sampling of an expanding number of spin channels away from the gamma point, where the majority of spins prevail, thereby reducing the overall spin polarisation. The Fermi surface of F3GT was found to exhibit a pronounced spin polarisation at the gamma point, predominantly occupied by minority spins, which constitutes the primary spin channel contributing to the TMR at low bias. The sharp peak at low bias could be explained by an inversion of spin polarisation through sampling over an increasing number of spin channels away from the gamma point with increasing bias, where majority spins prevail.

Another key achievement of my work was the large-scale growth of large scale F3GT and F4GT by PLD. Building upon our group's extensive experience with PLD growth of

other TMDs like MoS₂, WS₂ and WSe₂ I was able to extend our work to the ternary compounds of FGT. By precisely adjusting the growth temperature from 250°C for F3GT to 350°C for F4GT, we were able to achieve precise control over the phase stabilisation of the materials. Most importantly, we were able to grow them epitaxy-free on amorphous silica substrates. This large-scale growth process is also compatible with the industrial CMOS standards <450°C. Remarkably, a Curie temperature in the 450-550K range was determined for the synthesised F4GT, largely overcoming the requirement for room temperature operation of spintronic devices. The in-situ target exchange capability of the PLD system enabled us to directly grow MoS₂ on FGT in a single run. The top layer of TMD not only protects the FGT from degradation but also serves as a potential tunnel barrier or gate for future experimental setups. The unique ability to exchange targets *in-situ* in the PLD allowed us to demonstrate a direct growth of MoS₂ on FGT (five different elements) in a single run. Importantly, the top layer of TMD not only protects the FGT from degradation but also acts simultaneously as a tunnel barrier or gate for future experiments.

With the ability to grow both 2D ferromagnets and TMDs *in-situ*, in large-scale and in a single run we have unlocked the possibility to grow a full 2D vdW MTJ by PLD. This large-scale approach could not only allow the production of complex 2D heterostructures but also warrant the preservation of clean interfaces for future spintronics devices.

In terms of perspectives, the 2D inherited ability of the FGT family for gating, as demonstrated for F3GT [104], offers a highly promising and largely unexplored potential. A magnetic electrode with Curie temperature and Magnetic Anisotropy Energy (MAE) controllable by a gate and operating at room temperature could offer many opportunities for spintronics and MRAM applications. Indeed, since today's MRAM efficiency is guided by a compromise between stability (high MAE, T_C) and low-power switching (low MAE, T_C), gate control of magnetic properties could transform spintronics applications by enabling both low-power switching in MRAM and high retention times. Spin Transfer Torque (STT) and Spin-Orbit Torque (SOT) devices could hence see considerably improved switching efficiency and reliability, reducing power consumption. This would also include STT and SOT oscillators that could gain precise control over oscillation properties, enabling highly tunable microwave sources. In magnonics, logic devices could benefit from active control of the T_C and MAE, leading to reconfigurable logic circuits and waveguides with active control of spin wave propagation. For neuromorphic computing, shifting T_C could enable fine-tuned selection of stochastic behaviour. These advancements could unlock new possibilities in spintronics, neuromorphic, and magnonic technologies.

As such, gate control would allow for dynamic and energy-efficient manipulation of magnetic states, essential for high-speed, low-power memory devices. The ability to control magnetic properties electronically could lead to faster switching times, lower power consumption, and potentially higher storage densities through multi-level storage, paving the way for more compact and scalable memory devices. Overall, this could significantly advance the field of spintronics.

In this direction, a recent report has demonstrated F3GT gating via ferroelectric In_2Se_3 [195], observing changes in the coercive field and hysteresis loop when a gate voltage is applied. This van der Waals (vdW) heterostructure of a ferromagnetic/ferroelectric system not only validates the potential of vdW systems but also introduces direct material-based non-volatile gating, in contrast to liquid-ion gates, which are challenging to handle due to liquid control issues. This experiment highlights the strength and potential of vdW materials, which can be stacked on top of each other to create new functionalities in heterostructures through interfacial/proximity effects. However, the authors still observe strong dispersion in the impact of the ferroelectric material on the FGT, pointing to the ongoing issue of interface quality in flake transfer procedures. In this context, our PLD-grown FGT could demonstrate its strength, as 2D materials heterostructures including both FGT and ferroelectrics could be grown *in-situ*. While spintronics has been confined to magnets with fixed properties for decades, this promises to unlock unprecedented possibilities: room-temperature 2D magnets with memristive-like, non-volatile control over their Curie temperature and magnetic anisotropy energy. This direction will be pursued by two new PhD students, Jane Daniel and Samuel Vergara.

Finally, a new opportunity arises, the unique property of creating quasi-crystals by twisting layers of the same 2D materials at different angles could be made possible by the van-der-Waals nature of these materials. Twisted Graphene has shown a rich phase diagram when two layers are stacked at specific angles relative to each other. The so-called magic angle induces superconductivity in graphene due to its created Moiré pattern, and unique features such as Mott insulating states or Moiré excitons have been observed. For magnetic 2D materials, the associated spin degree of freedom combined with the possibility of creating quasi-crystals, offers a new environment for studying fundamental magnetic behaviour. Theoretical predictions of twisted ferromagnetic bilayers show an induced magnonic flatland regime on various twisting angles between two layers of CrI_3 , while the magnon band gap can be tuned [193]. Twisting the layers would allow for the breaking of symmetry, inducing Dzyaloshinskii-Moriya interaction (DMI)[194]. It has been further shown that the angle could tune the magnon valley hall and Ernst conductivity. For FGT, it was calculated that twisting layers by 180 degrees towards each other could lead to a strong impact in the spin-resolved DOS [195]. Furthermore, it was shown that FGT band structure could be strongly altered by twisting it with other 2D magnets such as CGT [196].

Interestingly, studies of twisted FGT homojunction have revealed an interesting finding: despite good electrical contact between layers, the junction does not behave like a single thicker flake. Instead, each layer retains its own distinct magnetic switching field [129]. These early results on 2D magnets show their potential for finetuning of their magnetic states well beyond conventional magnets and their alloys, thereby offering new avenues for spintronics.

- [1] M.N. Baibich, J.M. Broto, A. Fert, F.N.V. Dau, F. Petroff, P. Etienne, G. Creuzet, A. Friederich, and J. Chazelas, *Phys. Rev. Lett.* **61**, 2472 (1988).
- [2] G. Binasch, P. Grünberg, F. Saurenbach, and W. Zinn, *Phys. Rev. B* **39**, 4828 (1989).
- [3] T. Miyazaki and N. Tezuka, *J. Magn. Magn. Mater.* **139**, L231 (1995).
- [4] M. Julliere, *Phys. Lett. A* **54**, 225 (1975).
- [5] G. He, S. Qiu, Y. Cui, C. Yu, Y. Miao, G. Zhang, J. Ren, C.-K. Wang, and G. Hu, *J. Mater. Sci.* **54**, 5551 (2019).
- [6] D.A. Petukhov, *Phys. E: Low-Dimens. Syst. Nanostructures* **80**, 31 (2016).
- [7] J.S. Moodera, L.R. Kinder, T.M. Wong, and R. Meservey, *Phys. Rev. Lett.* **74**, 3273 (1995).
- [8] J. Nowak and J. Rauluszkiwicz, *J. Magn. Magn. Mater.* **109**, 79 (1992).
- [9] T. Yaoi, S. Ishio, and T. Miyazaki, *IEEE Transl. J. Magn. Jpn.* **8**, 498 (1993).
- [10] H.X. Wei, Q.H. Qin, M. Ma, R. Sharif, and X.F. Han, *J. Appl. Phys.* **101**, 09B501 (2007).
- [11] J.M.D. Teresa, A. Barthélémy, A. Fert, J.P. Contour, F. Montaigne, and P. Seneor, *Science* **286**, 507 (1999).
- [12] W.H. Butler, X.-G. Zhang, T.C. Schulthess, and J.M. MacLaren, *Phys. Rev. B* **63**, 054416 (2001).
- [13] S.S.P. Parkin, C. Kaiser, A. Panchula, P.M. Rice, B. Hughes, M. Samant, and S.-H. Yang, *Nat. Mater.* **3**, 862 (2004).
- [14] S. Ikeda, J. Hayakawa, Y. Ashizawa, Y.M. Lee, K. Miura, H. Hasegawa, M. Tsunoda, F. Matsukura, and H. Ohno, *Appl. Phys. Lett.* **93**, 082508 (2008).
- [15] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, and A.A. Firsov, *Science* **306**, 666 (2004).
- [16] K.I. Bolotin, K.J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, and H.L. Stormer, *Solid State Commun.* **146**, 351 (2008).
- [17] K.S. Novoselov, Z. Jiang, Y. Zhang, S.V. Morozov, H.L. Stormer, U. Zeitler, J.C. Maan, G.S. Boebinger, P. Kim, and A.K. Geim, *Science* **315**, 1379 (2007).

- [18] M.I. Katsnelson, K.S. Novoselov, and A.K. Geim, *Nat. Phys.* **2**, 620 (2006).
- [19] Q. Wilmarth, S. Berrada, D. Torrin, V.H. Nguyen, G. Fève, J.-M. Berroir, P. Dollfus, and B. Plaïs, *2D Mater.* **1**, 011006 (2014).
- [20] S. Choi, C.-H. Park, and S.G. Louie, *Phys. Rev. Lett.* **113**, 026802 (2014).
- [21] Z. Ye, T. Cao, K. O'Brien, H. Zhu, X. Yin, Y. Wang, S.G. Louie, and X. Zhang, *Nature* **513**, 214 (2014).
- [22] R. Bistritzer and A.H. MacDonald, *Proc. Natl. Acad. Sci.* **108**, 12233 (2011).
- [23] Y. Cao, V. Fatemi, A. Demir, S. Fang, S.L. Tomarken, J.Y. Luo, J.D. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, E. Kaxiras, R.C. Ashoori, and P. Jarillo-Herrero, *Nature* **556**, 80 (2018).
- [24] Y. Cao, V. Fatemi, S. Fang, K. Watanabe, T. Taniguchi, E. Kaxiras, and P. Jarillo-Herrero, *Nature* **556**, 43 (2018).
- [25] S.P. Milovanovic and F.M. Peeters, *ArXiv* (2017).
- [26] A.H.C. Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, and A.K. Geim, *Rev. Mod. Phys.* **81**, 109 (2009).
- [27] J. Wang, F. Ma, W. Liang, R. Wang, and M. Sun, *Nanophotonics* **6**, 943 (2017).
- [28] M.N. Hasan, M. Nafiujjaman, and Y.-K. Lee, *87* (2019).
- [29] M. Salavati, A. Mojahedin, and A.H.N. Shirazi, *Front. Struct. Civ. Eng.* **14**, 623 (2020).
- [30] S.M. Kim, A. Hsu, M.H. Park, S.H. Chae, S.J. Yun, J.S. Lee, D.-H. Cho, W. Fang, C. Lee, T. Palacios, M. Dresselhaus, K.K. Kim, Y.H. Lee, and J. Kong, *Nat. Commun.* **6**, 8662 (2015).
- [31] C. Elias, P. Valvin, T. Pelini, A. Summerfield, C.J. Mellor, T.S. Cheng, L. Eaves, C.T. Foxon, P.H. Beton, S.V. Novikov, B. Gil, and G. Cassabois, *Nat. Commun.* **10**, 2639 (2019).
- [32] H. Yang, X. Wang, and X.-Z. Li, *ArXiv* (2021).
- [33] S. Manzeli, D. Ovchinnikov, D. Pasquier, O.V. Yazyev, and A. Kis, *Nat. Rev. Mater.* **2**, 17033 (2017).

- [34] C. Gong, H. Zhang, W. Wang, L. Colombo, R.M. Wallace, and K. Cho, *Appl. Phys. Lett.* **103**, 053513 (2013).
- [35] K.F. Mak, C. Lee, J. Hone, J. Shan, and T.F. Heinz, *Phys. Rev. Lett.* **105**, 136805 (2010).
- [36] J.E. Padilha, H. Peelaers, A. Janotti, and C.G.V. de Walle, *Phys. Rev. B* **90**, 205420 (2014).
- [37] J. Ryou, Y.-S. Kim, S. KC, and K. Cho, *Sci. Rep.* **6**, 29184 (2016).
- [38] B. Ouyang, Z. Mi, and J. Song, *J. Phys. Chem. C* **120**, 8927 (2016).
- [39] A. Chaves, J.G. Azadani, H. Alsalman, D.R. da Costa, R. Frisenda, A.J. Chaves, S.H. Song, Y.D. Kim, D. He, J. Zhou, A. Castellanos-Gomez, F.M. Peeters, Z. Liu, C.L. Hinkle, S.-H. Oh, P.D. Ye, S.J. Koester, Y.H. Lee, Ph. Avouris, X. Wang, and T. Low, *Npj 2D Mater. Appl.* **4**, 29 (2020).
- [40] V.M. Karpan, G. Giovannetti, P.A. Khomyakov, M. Talanana, A.A. Starikov, M. Zwierzycki, J. van den Brink, G. Brocks, and P.J. Kelly, *Phys. Rev. Lett.* **99**, 176602 (2007).
- [41] M.-B. Martin, B. Dlubak, R.S. Weatherup, H. Yang, C. Deranlot, K. Bouzehouane, F. Petroff, A. Anane, S. Hofmann, J. Robertson, A. Fert, and P. Seneor, *ACS Nano* **8**, 7890 (2014).
- [42] T.M.G. Mohiuddin, E. Hill, D. Elias, A. Zhukov, K. Novoselov, and A. Geim, *IEEE Trans. Magn.* **44**, 2624 (2008).
- [43] B. Dlubak, M.-B. Martin, R.S. Weatherup, H. Yang, C. Deranlot, R. Blume, R. Schloegl, A. Fert, A. Anane, S. Hofmann, P. Seneor, and J. Robertson, *ACS Nano* **6**, 10930 (2012).
- [44] R.S. Weatherup, L. D'Arsié, A. Cabrero-Vilatela, S. Caneva, R. Blume, J. Robertson, R. Schloegl, and S. Hofmann, *J. Am. Chem. Soc.* **137**, 14358 (2015).
- [45] M. Piquemal-Banci, R. Galceran, S.M.-M. Dubois, V. Zatzko, M. Galbiati, F. Godel, M.-B. Martin, R.S. Weatherup, F. Petroff, A. Fert, J.-C. Charlier, J. Robertson, S. Hofmann, B. Dlubak, and P. Seneor, *Nat. Commun.* **11**, 5670 (2020).
- [46] M. Piquemal-Banci, R. Galceran, S. Caneva, M.-B. Martin, R.S. Weatherup, P.R. Kidambi, K. Bouzehouane, S. Xavier, A. Anane, F. Petroff, A. Fert, J. Robertson, S. Hofmann, B. Dlubak, and P. Seneor, *Appl. Phys. Lett.* **108**, 102404 (2016).

- [47] H.-C. Wu, C.Ó. Coileáin, M. Abid, O. Mauit, A. Syrlybekov, A. Khalid, H. Xu, R. Gatensby, J.J. Wang, H. Liu, L. Yang, G.S. Duesberg, H.-Z. Zhang, M. Abid, and I.V. Shvets, *Sci. Rep.* **5**, 15984 (2015).
- [48] M.Z. Iqbal, M.W. Iqbal, S. Siddique, M.F. Khan, and S.M. Ramay, *Sci. Rep.* **6**, 21038 (2016).
- [49] A. Dankert, M.V. Kamalakar, A. Wajid, R.S. Patel, and S.P. Dash, *Nano Res.* **8**, 1357 (2015).
- [50] M. Piquemal-Banci, R. Galceran, S. Caneva, M.-B. Martin, R.S. Weatherup, P.R. Kidambi, K. Bouzehouane, S. Xavier, A. Anane, F. Petroff, A. Fert, J. Robertson, S. Hofmann, B. Dlubak, and P. Seneor, *Appl. Phys. Lett.* **108**, 102404 (2016).
- [51] P.U. Asshoff, J.L. Sambricio, A.P. Rooney, S. Slizovskiy, A. Mishchenko, A.M. Rakowski, E.W. Hill, A.K. Geim, S.J. Haigh, V.I. Fal'ko, I.J. Vera-Marun, and I.V. Grigorieva, *2D Mater.* **4**, 031004 (2017).
- [52] M. Piquemal-Banci, R. Galceran, F. Godel, S. Caneva, M.-B. Martin, R.S. Weatherup, P.R. Kidambi, K. Bouzehouane, S. Xavier, A. Anane, F. Petroff, A. Fert, S.M.-M. Dubois, J.-C. Charlier, J. Robertson, S. Hofmann, B. Dlubak, and P. Seneor, *ACS Nano* **12**, 4712 (2018).
- [53] W. Wang, A. Narayan, L. Tang, K. Dolui, Y. Liu, X. Yuan, Y. Jin, Y. Wu, I. Rungger, S. Sanvito, and F. Xiu, *Nano Lett.* **15**, 5261 (2015).
- [54] A. Dankert, P. Pashaei, M.V. Kamalakar, A.P.S. Gaur, S. Sahoo, I. Rungger, A. Narayan, K. Dolui, Md.A. Hoque, R.S. Patel, M.P. de Jong, R.S. Katiyar, S. Sanvito, and S.P. Dash, *ACS Nano* **11**, 6389 (2017).
- [55] M.F. Khan, H. Kim, G. Nazir, S. Jung, and J. Eom, *Nanoscale* **10**, 16703 (2018).
- [56] H. Zhang, M. Ye, Y. Wang, R. Quhe, Y. Pan, Y. Guo, Z. Song, J. Yang, W. Guo, and J. Lu, *Phys. Chem. Chem. Phys.* **18**, 16367 (2016).
- [57] K. Dolui, A. Narayan, I. Rungger, and S. Sanvito, *Phys. Rev. B* **90**, 041401 (2014).
- [58] M. Galbiati, A. Vecchiola, S. Mañas-Valero, J. Canet-Ferrer, R. Galceran, M. Piquemal-Banci, F. Godel, A. Forment-Aliaga, B. Dlubak, P. Seneor, and E. Coronado, *ACS Appl. Mater. Interfaces* **10**, 30017 (2018).

- [59] M. Galbiati, S. Tatay, S.M.-M. Dubois, F. Godel, R. Galceran, S. Mañas-Valero, M. Piquemal-Banci, A. Vecchiola, J.-C. Charlier, A. Forment-Aliaga, E. Coronado, B. Dlubak, and P. Seneor, *Phys. Rev. Appl.* **12**, 044022 (2019).
- [60] D.L. Cortie, G.L. Causer, K.C. Rule, H. Fritzsche, W. Kreuzpaintner, and F. Klose, *Adv. Funct. Mater.* **30**, (2020).
- [61] J. Kohlhepp, H.J. Elmers, S. Cordes, and U. Gradmann, *Phys. Rev. B* **45**, 12287 (1992).
- [62] Q.H. Wang, A. Bedoya-Pinto, M. Blei, A.H. Dismukes, A. Hamo, S. Jenkins, M. Koperski, Y. Liu, Q.-C. Sun, E.J. Telford, H.H. Kim, M. Augustin, U. Vool, J.-X. Yin, L.H. Li, A. Falin, C.R. Dean, F. Casanova, R.F.L. Evans, M. Chshiev, A. Mishchenko, C. Petrovic, R. He, L. Zhao, A.W. Tsen, B.D. Gerardot, M. Brotons-Gisbert, Z. Guguchia, X. Roy, S. Tongay, Z. Wang, M.Z. Hasan, J. Wrachtrup, A. Yacoby, A. Fert, S. Parkin, K.S. Novoselov, P. Dai, L. Balicas, and E.J.G. Santos, *ACS Nano* **16**, 6960 (2022).
- [63] H.E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, New York, 1971).
- [64] M. Campostrini, M. Hasenbusch, A. Pelissetto, P. Rossi, and E. Vicari, *Phys. Rev. B* **65**, 144520 (2002).
- [65] M. Campostrini, A. Pelissetto, P. Rossi, and E. Vicari, *Phys. Rev. B* **61**, 5905 (2000).
- [66] M. Campostrini, A. Pelissetto, P. Rossi, and E. Vicari, *Phys. Rev. E* **60**, 3526 (1999).
- [67] J.M. Yeomans, 67 (1992).
- [68] C.-T. Kuo, M. Neumann, K. Balamurugan, H.J. Park, S. Kang, H.W. Shiu, J.H. Kang, B.H. Hong, M. Han, T.W. Noh, and J.-G. Park, *Sci. Rep.* **6**, 20904 (2016).
- [69] S. Lee, K.-Y. Choi, S. Lee, B.H. Park, and J.-G. Park, *APL Mater.* **4**, 086108 (2016).
- [70] K. Du, X. Wang, Y. Liu, P. Hu, M.I.B. Utama, C.K. Gan, Q. Xiong, and C. Kloc, *ACS Nano* **10**, 1738 (2016).
- [71] M.-W. Lin, H.L. Zhuang, J. Yan, T.Z. Ward, A.A. Puretzky, C.M. Rouleau, Z. Gai, L. Liang, V. Meunier, B.G. Sumpter, P. Ganesh, P.R.C. Kent, D.B. Geohegan, D.G. Mandrus, and K. Xiao, *J. Mater. Chem. C* **4**, 315 (2015).
- [72] J.-U. Lee, S. Lee, J.H. Ryoo, S. Kang, T.Y. Kim, P. Kim, C.-H. Park, J.-G. Park, and H. Cheong, *Nano Lett.* **16**, 7433 (2016).

- [73] M.A. McGuire, G. Clark, S. KC, W.M. Chance, G.E. Jellison, V.R. Cooper, X. Xu, and B.C. Sales, *Phys. Rev. Mater.* **1**, 014001 (2017).
- [74] B. Morosin and A. Narath, *J. Chem. Phys.* **40**, 1958 (1964).
- [75] T. Li, S. Jiang, N. Sivadas, Z. Wang, Y. Xu, D. Weber, J.E. Goldberger, K. Watanabe, T. Taniguchi, C.J. Fennie, K.F. Mak, and J. Shan, *Nat. Mater.* **18**, 1303 (2019).
- [76] B. Huang, G. Clark, E. Navarro-Moratalla, D.R. Klein, R. Cheng, K.L. Seyler, D. Zhong, E. Schmidgall, M.A. McGuire, D.H. Cobden, W. Yao, D. Xiao, P. Jarillo-Herrero, and X. Xu, *Nature* **546**, 270 (2017).
- [77] N. Sivadas, S. Okamoto, X. Xu, Craig.J. Fennie, and D. Xiao, *Nano Lett.* **18**, 7658 (2018).
- [78] N. Sivadas, S. Okamoto, X. Xu, Craig.J. Fennie, and D. Xiao, *Nano Lett.* **18**, 7658 (2018).
- [79] N. Wooster, *Z. Für Krist. - Cryst. Mater.* **74**, 363 (1930).
- [80] C. Starr, F. Bitter, and A.R. Kaufmann, *Phys. Rev.* **58**, 977 (1940).
- [81] J.W. Cable, M.K. Wilkinson, and E.O. Wollan, *J. Phys. Chem. Solids* **19**, 29 (1961).
- [82] A. Narath, *Phys. Rev.* **131**, 1929 (1963).
- [83] Z. Wang, M. Gibertini, D. Dumcenco, T. Taniguchi, K. Watanabe, E. Giannini, and A.F. Morpurgo, *Nat. Nanotechnol.* **14**, 1116 (2019).
- [84] I. Tsubokawa, *J. Phys. Soc. Jpn.* **15**, 1664 (1960).
- [85] Z. Zhang, J. Shang, C. Jiang, A. Rasmita, W. Gao, and T. Yu, *Nano Lett.* **19**, 3138 (2019).
- [86] H.H. Kim, B. Yang, S. Li, S. Jiang, C. Jin, Z. Tao, G. Nichols, F. Sfigakis, S. Zhong, C. Li, S. Tian, D.G. Cory, G.-X. Miao, J. Shan, K.F. Mak, H. Lei, K. Sun, L. Zhao, and A.W. Tsen, *Proc. Natl. Acad. Sci.* **116**, 11131 (2019).
- [87] W. Xing, Y. Chen, P.M. Odenthal, X. Zhang, W. Yuan, T. Su, Q. Song, T. Wang, J. Zhong, S. Jia, X.C. Xie, Y. Li, and W. Han, *2D Mater.* **4**, 024009 (2017).
- [88] C. Gong, L. Li, Z. Li, H. Ji, A. Stern, Y. Xia, T. Cao, W. Bao, C. Wang, Y. Wang, Z.Q. Qiu, R.J. Cava, S.G. Louie, J. Xia, and X. Zhang, *Nature* **546**, 265 (2017).

- [89] V. Carteaux, D. Brunet, G. Ouvrard, and G. Andre, *J. Phys.: Condens. Matter* **7**, 69 (1995).
- [90] M. Bonilla, S. Kolekar, Y. Ma, H.C. Diaz, V. Kalappattil, R. Das, T. Eggers, H.R. Gutierrez, M.-H. Phan, and M. Batzill, *Nat. Nanotechnol.* **13**, 289 (2018).
- [91] W. Yu, J. Li, T.S. Herng, Z. Wang, X. Zhao, X. Chi, W. Fu, I. Abdelwahab, J. Zhou, J. Dan, Z. Chen, Z. Chen, Z. Li, J. Lu, S.J. Pennycook, Y.P. Feng, J. Ding, and K.P. Loh, *Adv. Mater.* **31**, e1903779 (2019).
- [92] J. Feng, D. Biswas, A. Rajan, M.D. Watson, F. Mazzola, O.J. Clark, K. Underwood, I. Marković, M. McLaren, A. Hunter, D.M. Burn, L.B. Duffy, S. Barua, G. Balakrishnan, F. Bertran, P.L. Fèvre, T.K. Kim, G. van der Laan, T. Hesjedal, P. Wahl, and P.D.C. King, *Nano Lett.* **18**, 4493 (2018).
- [93] P.M. Coelho, K.N. Cong, M. Bonilla, S. Kolekar, M.-H. Phan, J. Avila, M.C. Asensio, I.I. Oleynik, and M. Batzill, *J. Phys. Chem. C* **123**, 14089 (2019).
- [94] A.O. Fumega, M. Gobbi, P. Dreher, W. Wan, C. González-Orellana, M. Peña-Díaz, C. Rogero, J. Herrero-Martín, P. Gargiani, M. Ilyn, M.M. Ugeda, V. Pardo, and S. Blanco-Canosa, *J. Phys. Chem. C* **123**, 27802 (2019).
- [95] M. Joe, P.K. Srivastava, B. Singh, H. Ahn, and C. Lee, *J. Phys. D: Appl. Phys.* **54**, 473002 (2021).
- [96] H. Deiseroth, K. Aleksandrov, C. Reiner, L. Kienle, and R.K. Kremer, *Eur. J. Inorg. Chem.* **2006**, 1561 (2006).
- [97] J. Seo, D.Y. Kim, E.S. An, K. Kim, G.-Y. Kim, S.-Y. Hwang, D.W. Kim, B.G. Jang, H. Kim, G. Eom, S.Y. Seo, R. Stania, M. Muntwiler, J. Lee, K. Watanabe, T. Taniguchi, Y.J. Jo, J. Lee, B.I. Min, M.H. Jo, H.W. Yeom, S.-Y. Choi, J.H. Shim, and J.S. Kim, *Sci. Adv.* **6**, eaay8912 (2020).
- [98] J. Stahl, E. Shlaen, and D. Johrendt, *Zeitschrift Für Anorganische Und Allgemeine Chemie* **644**, 1923 (2018).
- [99] D.A. Mayoh, G.D.A. Wood, S.J.R. Holt, G. Beckett, E.J.L. Dekker, M.R. Lees, and G. Balakrishnan, *Cryst. Growth Des.* **21**, 6786 (2021).
- [100] A.F. May, D. Ovchinnikov, Q. Zheng, R. Hermann, S. Calder, B. Huang, Z. Fei, Y. Liu, X. Xu, and M.A. McGuire, *ACS Nano* **13**, 4436 (2019).

- [101] A.F. May, S. Calder, C. Cantoni, H. Cao, and M.A. McGuire, *Phys. Rev. B* **93**, 014411 (2016).
- [102] S. Liu, X. Yuan, Y. Zou, Y. Sheng, C. Huang, E. Zhang, J. Ling, Y. Liu, W. Wang, C. Zhang, J. Zou, K. Wang, and F. Xiu, *Npj 2D Mater. Appl.* **1**, 30 (2017).
- [103] Z. Fei, B. Huang, P. Malinowski, W. Wang, T. Song, J. Sanchez, W. Yao, D. Xiao, X. Zhu, A.F. May, W. Wu, D.H. Cobden, J.-H. Chu, and X. Xu, *Nat. Mater.* **17**, 778 (2018).
- [104] Y. Deng, Y. Yu, Y. Song, J. Zhang, N.Z. Wang, Z. Sun, Y. Yi, Y.Z. Wu, S. Wu, J. Zhu, J. Wang, X.H. Chen, and Y. Zhang, *Nature* **563**, 94 (2018).
- [105] H.L. Zhuang, P.R.C. Kent, and R.G. Hennig, *Phys. Rev. B* **93**, 134407 (2016).
- [106] R. Roemer, C. Liu, and K. Zou, *Npj 2D Mater. Appl.* **4**, 33 (2020).
- [107] H. Wang, Y. Liu, P. Wu, W. Hou, Y. Jiang, X. Li, C. Pandey, D. Chen, Q. Yang, H. Wang, D. Wei, N. Lei, W. Kang, L. Wen, T. Nie, W. Zhao, and K.L. Wang, *ACS Nano* **14**, 10045 (2020).
- [108] J. Stahl, E. Shlaen, and D. Johrendt, *Z. Für Anorg. Allg. Chem.* **644**, 1923 (2018).
- [109] A.F. May, C.A. Bridges, and M.A. McGuire, *Phys. Rev. Mater.* **3**, 104401 (2019).
- [110] A.F. May, D. Ovchinnikov, Q. Zheng, R. Hermann, S. Calder, B. Huang, Z. Fei, Y. Liu, X. Xu, and M.A. McGuire, *ACS Nano* **13**, 4436 (2019).
- [111] T. Ohta, K. Sakai, H. Taniguchi, B. Driesen, Y. Okada, K. Kobayashi, and Y. Niimi, *Appl. Phys. Express* **13**, 043005 (2020).
- [112] C. Tian, F. Pan, S. Xu, K. Ai, T. Xia, and P. Cheng, *Appl. Phys. Lett.* **116**, 202402 (2020).
- [113] M.A. McGuire, H. Dixit, V.R. Cooper, and B.C. Sales, *Chem. Mater.* **27**, 612 (2015).
- [114] H. Deiseroth, K. Aleksandrov, C. Reiner, L. Kienle, and R.K. Kremer, *European Journal of Inorganic Chemistry* **2006**, 1561 (2006).
- [115] Z. Li, W. Xia, H. Su, Z. Yu, Y. Fu, L. Chen, X. Wang, N. Yu, Z. Zou, and Y. Guo, *Sci. Rep.* **10**, 15345 (2020).
- [116] P.A. Joy and S. Vasudevan, *Phys. Rev. B* **46**, 5425 (1992).

- [117] K. Kim, S.Y. Lim, J.-U. Lee, S. Lee, T.Y. Kim, K. Park, G.S. Jeon, C.-H. Park, J.-G. Park, and H. Cheong, *Nat. Commun.* **10**, 345 (2019).
- [118] A.R. Wildes, V. Simonet, E. Ressouche, R. Ballou, and G.J. McIntyre, *J. Phys.: Condens. Matter* **29**, 455801 (2017).
- [119] D. Ghazaryan, M.T. Greenaway, Z. Wang, V.H. Guarochico-Moreira, I.J. Vera-Marun, J. Yin, Y. Liao, S.V. Morozov, O. Kristanovski, A.I. Lichtenstein, M.I. Katsnelson, F. Withers, A. Mishchenko, L. Eaves, A.K. Geim, K.S. Novoselov, and A. Misra, *Nat. Electron.* **1**, 344 (2018).
- [120] X. Cai, T. Song, N.P. Wilson, G. Clark, M. He, X. Zhang, T. Taniguchi, K. Watanabe, W. Yao, D. Xiao, M.A. McGuire, D.H. Cobden, and X. Xu, *Nano Lett.* **19**, 3993 (2019).
- [121] T. Song, X. Cai, M.W.-Y. Tu, X. Zhang, B. Huang, N.P. Wilson, K.L. Seyler, L. Zhu, T. Taniguchi, K. Watanabe, M.A. McGuire, D.H. Cobden, D. Xiao, W. Yao, and X. Xu, *Science* **360**, 1214 (2018).
- [122] H.H. Kim, B. Yang, T. Patel, F. Sfigakis, C. Li, S. Tian, H. Lei, and A.W. Tsen, *Nano Lett.* **18**, 4885 (2018).
- [123] D.R. Klein, D. MacNeill, J.L. Lado, D. Soriano, E. Navarro-Moratalla, K. Watanabe, T. Taniguchi, S. Manni, P. Canfield, J. Fernández-Rossier, and P. Jarillo-Herrero, *Science* **360**, 1218 (2018).
- [124] Z. Wang, I. Gutiérrez-Lezama, N. Ubrig, M. Kroner, M. Gibertini, T. Taniguchi, K. Watanabe, A. Imamoğlu, E. Giannini, and A.F. Morpurgo, *Nat. Commun.* **9**, 2516 (2018).
- [125] T. Song, M.W.-Y. Tu, C. Carnahan, X. Cai, T. Taniguchi, K. Watanabe, M.A. McGuire, D.H. Cobden, D. Xiao, W. Yao, and X. Xu, *Nano Lett.* **19**, 915 (2019).
- [126] Z. Wang, D. Sapkota, T. Taniguchi, K. Watanabe, D. Mandrus, and A.F. Morpurgo, *Nano Lett.* **18**, 4303 (2018).
- [127] H. Lin, F. Yan, C. Hu, Q. Lv, W. Zhu, Z. Wang, Z. Wei, K. Chang, and K. Wang, *ACS Appl. Mater. Interfaces* **12**, 43921 (2020).
- [128] S. Albarakati, C. Tan, Z.-J. Chen, J.G. Partridge, G. Zheng, L. Farrar, E.L.H. Mayes, M.R. Field, C. Lee, Y. Wang, Y. Xiong, M. Tian, F. Xiang, A.R. Hamilton, O.A. Tretiakov, D. Culcer, Y.-J. Zhao, and L. Wang, *Sci. Adv.* **5**, eaaw0409 (2019).

- [129] J. Kim, S. Son, M.J. Coak, I. Hwang, Y. Lee, K. Zhang, and J.-G. Park, *J. Appl. Phys.* **128**, 093901 (2020).
- [130] X. Li, J.-T. Lü, J. Zhang, L. You, Y. Su, and E.Y. Tsymbal, *Nano Lett.* **19**, 5133 (2019).
- [131] Z. Lin and X. Chen, *Adv. Electron. Mater.* **6**, (2020).
- [132] L. Zhang, T. Li, J. Li, Y. Jiang, J. Yuan, and H. Li, *J. Phys. Chem. C* **124**, 27429 (2020).
- [133] Y. Wang, C. Xian, J. Wang, B. Liu, L. Ling, L. Zhang, L. Cao, Z. Qu, and Y. Xiong, *Phys. Rev. B* **96**, 134428 (2017).
- [134] J.-X. Zhu, M. Janoschek, D.S. Chaves, J.C. Cezar, T. Durakiewicz, F. Ronning, Y. Sassa, M. Mansson, B.L. Scott, N. Wakeham, E.D. Bauer, and J.D. Thompson, *Phys. Rev. B* **93**, 144404 (2016).
- [135] C.-J. Lin, G.L. Gorman, C.H. Lee, R.F.C. Farrow, E.E. Marinero, H.V. Do, H. Notarys, and C.J. Chien, *J. Magn. Magn. Mater.* **93**, 194 (1991).
- [136] T. da C.S.C. Gomes, T. Bhatnagar-Schöffmann, S. Krishnia, Y. Sassi, D. Sanz-Hernández, N. Reyren, M.-B. Martin, F. Brunnett, S. Collin, F. Godel, S. Ono, D. Querlioz, D. Ravelosona, V. Cros, J. Grollier, P. Seneor, and L.H. Diez, *Phys. Rev. Appl.* **21**, 024010 (2024).
- [137] Y.-C. Lau, Z. Chi, T. Taniguchi, M. Kawaguchi, G. Shibata, N. Kawamura, M. Suzuki, S. Fukami, A. Fujimori, H. Ohno, and M. Hayashi, *Phys. Rev. Mater.* **3**, 104419 (2019).
- [138] Y. Li, X. Hu, A. Fereidouni, R. Basnet, K. Pandey, J. Wen, Y. Liu, H. Zheng, H.O.H. Churchill, J. Hu, A.K. Petford-Long, and C. Phatak, *ACS Appl. Nano Mater.* **6**, 4390 (2023).
- [139] R. Zhao, W. Xu, Y. Wu, X. Liu, Z. Zhang, M. Zhu, L. Zhang, J. Shen, S. Shen, H. Huang, J. Zhang, X. Zheng, and S. Wang, *ACS Appl. Nano Mater.* **6**, 20982 (2023).
- [140] A.P. Balan, A. Kumar, T. Scholz, Z. Lin, A. Shahee, S. Fu, T. Denneulin, J. Vas, A. Kovács, R.E. Dunin-Borkowski, H.I. Wang, J. Yang, B.V. Lotsch, U. Nowak, and M. Kläui, *ACS Nano* **18**, 8383 (2024).
- [141] X. Zhang, Y. Li, W. Mu, W. Bai, X. Sun, M. Zhao, Z. Zhang, F. Shan, and Z. Yang, *2D Mater.* **8**, 032002 (2021).

- [142] D. Bing, Y. Wang, J. Bai, R. Du, G. Wu, and L. Liu, *Opt. Commun.* **406**, 128 (2018).
- [143] L. Du, J. Tang, Y. Zhao, X. Li, R. Yang, X. Hu, X. Bai, X. Wang, K. Watanabe, T. Taniguchi, D. Shi, G. Yu, X. Bai, T. Hasan, G. Zhang, and Z. Sun, *Adv. Funct. Mater.* **29**, 1904734 (2019).
- [144] X. Kong, T. Berlijn, and L. Liang, *Adv. Electron. Mater.* **7**, 2001159 (2021).
- [145] L.-M. Kern, R. Galceran, V. Zatzko, M. Galbiati, F. Godel, D. Perconte, F. Bouamrane, E. Gaufrès, A. Loiseau, P. Brus, O. Bezencenet, M.-B. Martin, B. Servet, F. Petroff, B. Dlubak, and P. Seneor, *Appl. Phys. Lett.* **114**, 053107 (2019).
- [146] H.-H. Yang, N. Bansal, P. Rüßmann, M. Hoffmann, L. Zhang, D. Go, Q. Li, A.-A. Haghighirad, K. Sen, S. Blügel, M.L. Tacon, Y. Mokrousov, and W. Wulfhekkel, *2D Mater.* **9**, 025022 (2022).
- [147] C. Trainer, O.R. Armitage, H. Lane, L.C. Rhodes, E. Chan, I. Benedičič, J.A. Rodriguez-Rivera, O. Fabelo, C. Stock, and P. Wahl, *Phys. Rev. B* **106**, L081405 (2022).
- [148] Y. Zhang, H. Lu, X. Zhu, S. Tan, W. Feng, Q. Liu, W. Zhang, Q. Chen, Y. Liu, X. Luo, D. Xie, L. Luo, Z. Zhang, and X. Lai, *Sci. Adv.* **4**, eaao6791 (2018).
- [149] M. Zhao, B.-B. Chen, Y. Xi, Y. Zhao, H. Xu, H. Zhang, N. Cheng, H. Feng, J. Zhuang, F. Pan, X. Xu, W. Hao, W. Li, S. Zhou, S.X. Dou, and Y. Du, *Nano Lett.* **21**, 6117 (2021).
- [150] J.M.D. Teresa, A. Barthélémy, A. Fert, J.P. Contour, R. Lyonnet, F. Montaigne, P. Seneor, and A. Vaurès, *Phys. Rev. Lett.* **82**, 4288 (1998).
- [151] J.S. Moodera and G. Mathon, *J. Magn. Magn. Mater.* **200**, 248 (1999).
- [152] W. Zhu, Y. Zhu, T. Zhou, X. Zhang, H. Lin, Q. Cui, F. Yan, Z. Wang, Y. Deng, H. Yang, L. Zhao, I. Žutić, K.D. Belashchenko, and K. Wang, *Nat. Commun.* **14**, 5371 (2023).
- [153] X. Yu, X. Zhang, Q. Shi, S. Tian, H. Lei, K. Xu, and H. Hosono, *Front. Phys.* **14**, 43501 (2019).
- [154] J. Yi, H. Zhuang, Q. Zou, Z. Wu, G. Cao, S. Tang, S.A. Calder, P.R.C. Kent, D. Mandrus, and Z. Gai, *2D Mater.* **4**, 011005 (2016).
- [155] B. Chen, J. Yang, H. Wang, M. Imai, H. Ohta, C. Michioka, K. Yoshimura, and M. Fang, *J. Phys. Soc. Jpn.* **82**, 124711 (2013).

- [156] S. Liu, K. Yang, W. Liu, E. Zhang, Z. Li, X. Zhang, Z. Liao, W. Zhang, J. Sun, Y. Yang, H. Gao, C. Huang, L. Ai, P.K.J. Wong, A.T.S. Wee, A.T. N'Diaye, S.A. Morton, X. Kou, J. Zou, Y. Xu, H. Wu, and F. Xiu, *Natl. Sci. Rev.* **7**, 745 (2019).
- [157] O. Paull, C. Xu, X. Cheng, Y. Zhang, B. Xu, K. Kelley, L. Collins, A. de Marco, R.K. Vasudevan, L. Bellaiche, V. Nagarajan, and D. Sando, *Nat. Mater.* **21**, 74 (2022).
- [158] D. Gouéré, H. Merbouche, A.E. Kanj, F. Kohl, C. Carrétéro, I. Boverter, R. Lebrun, P. Bortolotti, V. Cros, J.B. Youssef, and A. Anane, *Phys. Rev. Mater.* **6**, 114402 (2022).
- [159] J.G. Lunney, *Appl. Surf. Sci.* **86**, 79 (1995).
- [160] N.R. Glavin, M.L. Jespersen, M.H. Check, J. Hu, A.M. Hilton, T.S. Fisher, and A.A. Voevodin, *Thin Solid Films* **572**, 245 (2014).
- [161] Y. Ho, C. Ma, T. Luong, L. Wei, T. Yen, W. Hsu, W. Chang, Y. Chu, Y. Tu, K.P. Pande, and E.Y. Chang, *Phys. Status Solidi (RRL) Rapid Res. Lett.* **9**, 187 (2015).
- [162] F. Godel, V. Zatko, C. Carrétéro, A. Sander, M. Galbiati, A. Vecchiola, P. Brus, O. Bezencenet, B. Servet, M.-B. Martin, B. Dlubak, and P. Seneor, *ACS Appl. Nano Mater.* **3**, 7908 (2020).
- [163] Z. Yang, J. Hao, S. Yuan, S. Lin, H.M. Yau, J. Dai, and S.P. Lau, *Adv. Mater.* **27**, 3748 (2015).
- [164] V. Zatko, S.M.-M. Dubois, F. Godel, C. Carrétéro, A. Sander, S. Collin, M. Galbiati, J. Peiro, F. Panciera, G. Patriarche, P. Brus, B. Servet, J.-C. Charlier, M.-B. Martin, B. Dlubak, and P. Seneor, *ACS Nano* **15**, 7279 (2021).
- [165] A. Dittrich, C. Eberl, S. Schlenkrich, F. Schlenkrich, F. Döring, and H.-U. Krebs, *Appl. Phys. A* **122**, 301 (2016).
- [166] S. Acquaviva, E. D'Anna, M.L.D. Giorgi, M. Fernandez, A. Luches, G. Majni, S. Luby, and E. Majkova, *Appl. Surf. Sci.* **248**, 286 (2005).
- [167] K. Sturm, S. Fähler, and H.-U. Krebs, *Appl. Surf. Sci.* **154**, 462 (2000).
- [168] S. Liu, X. Yuan, Y. Zou, Y. Sheng, C. Huang, E. Zhang, J. Ling, Y. Liu, W. Wang, C. Zhang, J. Zou, K. Wang, and F. Xiu, *Npj 2D Mater. Appl.* **1**, 30 (2017).
- [169] Z. Fei, B. Huang, P. Malinowski, W. Wang, T. Song, J. Sanchez, W. Yao, D. Xiao, X. Zhu, A.F. May, W. Wu, D.H. Cobden, J.-H. Chu, and X. Xu, *Nat. Mater.* **17**, 778 (2018).

- [170] C. Tan, J. Lee, S.-G. Jung, T. Park, S. Albarakati, J. Partridge, M.R. Field, D.G. McCulloch, L. Wang, and C. Lee, *Nat. Commun.* **9**, 1554 (2018).
- [171] S. Mondal, N. Khan, S.M. Mishra, B. Satpati, and P. Mandal, *Phys. Rev. B* **104**, 094405 (2021).
- [172] J. Seo, E.S. An, T. Park, S.-Y. Hwang, G.-Y. Kim, K. Song, W. Noh, J.Y. Kim, G.S. Choi, M. Choi, E. Oh, K. Watanabe, T. Taniguchi, J.-H. Park, Y.J. Jo, H.W. Yeom, S.-Y. Choi, J.H. Shim, and J.S. Kim, *Nat. Commun.* **12**, 2844 (2021).
- [173] G.K.R. Nair, Z. Zhang, F. Hou, A. Abdelaziem, X. Xu, S.W.Q. Yang, N. Zhang, W. Li, C. Zhu, Y. Wu, H. Weiling, L. Kang, T. Salim, J. Zhou, L. Ke, J. Lin, X. Li, W. Gao, and Z. Liu, *Nano Res.* **15**, 457 (2022).
- [174] C.D. Quilty, L.M. Housel, D.C. Bock, M.R. Dunkin, L. Wang, D.M. Lutz, A. Abraham, A.M. Bruck, E.S. Takeuchi, K.J. Takeuchi, and A.C. Marschilok, *ACS Appl. Energy Mater.* **2**, 7635 (2019).
- [175] S.V.P. Vattikuti and C. Byon, *J. Nanomater.* **2015**, (2015).
- [176] K.C. Lalithambika, K. Shanmugapriya, and S. Sriram, *Appl. Phys. A* **125**, 817 (2019).
- [177] H. Wang, H. Lu, Z. Guo, A. Li, P. Wu, J. Li, W. Xie, Z. Sun, P. Li, H. Damas, A.M. Friedel, S. Migot, J. Ghanbaja, L. Moreau, Y. Fagot-Revurat, S. Petit-Watelot, T. Hauet, J. Robertson, S. Mangin, W. Zhao, and T. Nie, *Nat. Commun.* **14**, 2483 (2023).
- [178] W. Xie, J. Zhang, Y. Bai, Y. Liu, H. Wang, P. Yu, J. Li, H. Chang, Z. Wang, F. Gao, G. Wei, W. Zhao, and T. Nie, *APL Mater.* **12**, 031102 (2024).
- [179] V. Zatkan, S.M.-M. Dubois, F. Godel, M. Galbiati, J. Peiro, A. Sander, C. Carretero, A. Vecchiola, S. Collin, K. Bouzehouane, B. Servet, F. Petroff, J.-C. Charlier, M.-B. Martin, B. Dlubak, and P. Seneor, *ACS Nano* **16**, 14007 (2022).
- [180] S. Bera, S.K. Pradhan, M.S. Khan, R. Pal, B. Pal, S. Kalimuddin, A. Bera, B. Das, A.N. Pal, and M. Mondal, *J. Magn. Magn. Mater.* **565**, 170257 (2023).
- [181] S. Liu, Z. Li, K. Yang, E. Zhang, A. Narayan, X. Zhang, J. Zhu, W. Liu, Z. Liao, M. Kudo, T. Toriyama, Y. Yang, Q. Li, L. Ai, C. Huang, J. Sun, X. Guo, W. Bao, Q. Deng, Y. Chen, L. Yin, J. Shen, X. Han, S. Matsumura, J. Zou, Y. Xu, X. Xu, H. Wu, and F. Xiu, *Natl. Sci. Rev.* **9**, nwab117 (2021).

- [182] H. Lv, A. da Silva, A.I. Figueroa, C. Guillemard, I.F. Aguirre, L. Camosi, L. Aballe, M. Valvidares, S.O. Valenzuela, J. Schubert, M. Schmidbauer, J. Herfort, M. Hanke, A. Trampert, R. Engel-Herbert, M. Ramsteiner, and J.M.J. Lopes, *Small* **19**, e2302387 (2023).
- [183] E. Georgopoulou-Kotsaki, P. Pappas, A. Lintzeris, P. Tsipas, S. Fragkos, A. Markou, C. Felser, E. Longo, M. Fanciulli, R. Mantovan, F. Mahfouzi, N. Kioussis, and A. Dimoulas, *Nanoscale* **15**, 2223 (2023).
- [184] X. Yang, X. Zhou, W. Feng, and Y. Yao, *Phys. Rev. B* **104**, 104427 (2021).
- [185] Y. Zhao, Y. Guo, S. Zhou, and J. Zhao, *Phys. Rev. Mater.* **6**, 044005 (2022).
- [186] S. Ghosh, S. Ershadrad, V. Borisov, and B. Sanyal, *Npj Comput. Mater.* **9**, 86 (2023).
- [187] Q. Liu, J. Xing, Z. Jiang, Y. Guo, X. Jiang, Y. Qi, and J. Zhao, *Commun. Phys.* **5**, 140 (2022).
- [188] A. Arrott and J.E. Noakes, *Phys. Rev. Lett.* **19**, 786 (1967).
- [189] E. Sonder and D.K. Stevens, *Phys. Rev.* **110**, 1027 (1958).
- [190] B. Liu, Y. Zou, S. Zhou, L. Zhang, Z. Wang, H. Li, Z. Qu, and Y. Zhang, *Sci. Rep.* **7**, 6184 (2017).
- [191] M.E. Fisher, S. Ma, and B.G. Nickel, *Phys. Rev. Lett.* **29**, 917 (1972).
- [192] F. Wang and H. Zhang, *Phys. Rev. B* **108**, 195140 (2023).
- [193] D. Ghader, *Sci. Rep.* **10**, 15069 (2020).
- [194] Q. Tong, F. Liu, J. Xiao, and W. Yao, *Nano Lett.* **18**, 7194 (2018).
- [195] D. Chen, (n.d.).
- [196] E. Ko, *Sci. Rep.* **12**, 5101 (2022).