1. Title

Ultrafast Magnetic Dynamics in Intercalated Transition Metal Dichalcoginides

2. Abstract

The goal of the project is to study the magnetic dynamics of intercalated dichalcogenides M_xTaS_2 (M = Fe, Ni, Co, Mn). This family of materials has a wide variety of magnetic properties that can be readily tuned as the concentration and species of the intercalant are changed. Thus, these systems can be considered as ideal testbeds on which to understand the ultrafast dynamics of magnetic systems. Our research program incorporates a variety of ultrafast x-ray techniques including femtosecond XMCD at synchrotrons and FELs, XMCD and PEEM to understand the domain structures, and finally a component for development, with external collaboration, to study ultrafast XMCD using table-top sources of soft x-rays.

3. Applicants

Safdar Abbas Malik, MSc.
Ron Tobey, PhD

4. Institute

Optical Condensed Matter Physics
Zernike Institute for Advanced Materials
University of Groningen
Nijenborgh 4, 9747 AG Groningen, the Netherlands

5. Duration of the Project

4 years, starting in september 2014

6. Personnel

6.1 Senior-scientists

Ron Tobey, supervisor, 20%

6.2 Junior-scientists

Safdar Abbas Malik, OIO full time

7. Cost Estimates

7.1 Personnel Positions

1 OIO, four years, k€ 204.000

7.2 Running Budget

4× k€ 5.000 for standard expenses

7.3 Budget Summary

	2014	2015	2016	2017	2018	
OIO	1/4	1	1	1	3/4	204.000
	2.500	10.000	10.000	10.000	7.500	40.000
Total						244.000

8. Research Programme

8.1 Introduction

Ultrafast dynamics in magnetic materials is one of the richest areas in condensed matter physics. The wide array of theories and the lack of convergence between theory and experiment nearly 20 years after subpicosecond demagnetization was first discovered[1] has continued to drive this field forward. The variety of magnetic materials and exchange interactions, plus the structural differences between many materials, has resulted in ultrafast demagnetization dynamics spanning many orders of magnitude in time constant. Seemingly the fastest that can be measured is in the 100s of femtoseconds in simple itinerant ferromagnets like nickel and iron, while much slower dynamics are seen in local moment f-orbital magnets like gadolinium and terbium in the 10s of picoseconds[2].

Fundamentally, there is one simple concept that must be understood, namely, if we are beholden to the notions of conservation of angular momentum, then what are the times scales associated with dissipation of that angular momentum from the spin system to any other coupled bath? The early experiments by Einstein and de Haas showed that the likely coupled system is that of the lattice. And so fundamentally, every experiment to date is asking how fast does the spin angular momentum transfer to the lattice?, and furthermore, through which channels does this transfer proceed?

This somewhat academic discussion is punctuated by the technological implications for faster and faster magnetic materials.

The demands for the ever-increasing speed of storage of information in magnetic media plus the intrinsic limitations that are connected with the generation of magnetic field pulses by current have triggered intense searches for ways to control magnetization by means other than magnetic fields. Femtosecond laser pulses offer the intriguing possibility to probe a magnetic system on a time scale that corresponds to the (equilibrium) exchange interaction, responsible for the existence of magnetic order, while being much faster than the time scale of spin-orbit interaction (1–10 ps) or magnetic precession (100–1000 ps). The option of femtosecond optical excitation immediately leads to the question whether it would be possible to reverse magnetization faster than within half a precessional period?
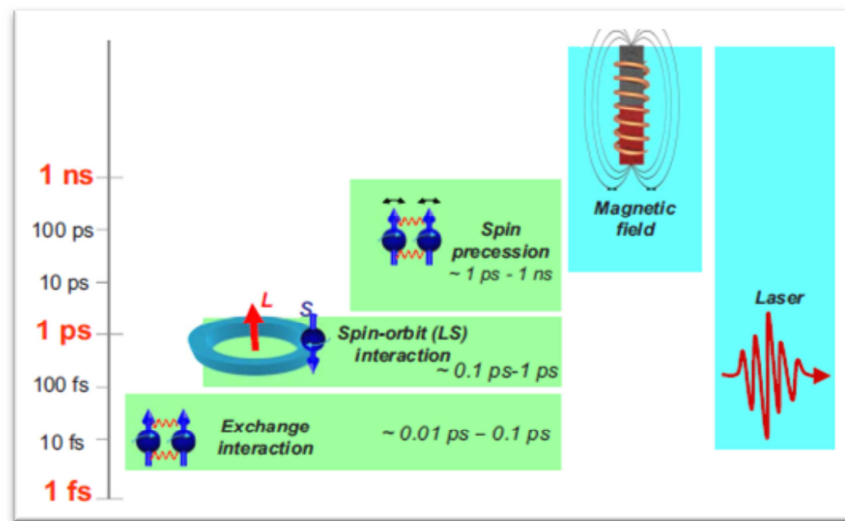

FIG. 1. (Color online) Time scales in magnetism as compared to magnetic field and laser pulses. The short duration of the laser pulses makes them an attractive alternative to manipulate the magnetization[3].

8.2. Intercalated Transition Metal Dichalcoginides

Transition Metal dichalcoginides (e.g. TaS_2, $TaSe_2$, NbS_2, etc.) are systems with hexagonal layers bound by van der Waals forces. For the intercalated magnetic systems of interest, the 2H-type layer stacking results in metallic properties for the TaS_2 compound for all temperatures. The loosely bonded layers allow the incorporation of atoms and small molecules in between them (termed intercalation), resulting in additional emergent properties such as magnetism, superconductivity, and change density waves.

To elaborate the importance of these systems, we choose the example of 2H-TaS_2 with iron(Fe^{2+}) intercalated between the layers. 2H-TaS_2 has two bilayer stacking periodicity and hexagonal symmetry. In each TaS_2, layer in the structure, Ta ions are coordinated by trigonal-prismatic S^{2-} cages.

Fe_xTaS_2 exhibits interesting magnetic properties with a ferromagnetic to antiferromagnetic transition at $x \approx 0.4$[4]. In the FM region (x < 0.4), the Curie temperature T_C strongly varies with the Fe concentration x. As x increases, T_C increases to reach a maximum $T_C \approx 160$ K at x

= ¼ and then decreases to $T_C \approx 35$ K at x = 1⁄3. Interestingly, the intercalated irons were found to form 2 × 2 or √3×√3 superstructures at x = ¼ or 1/3, respectively[5, 6].
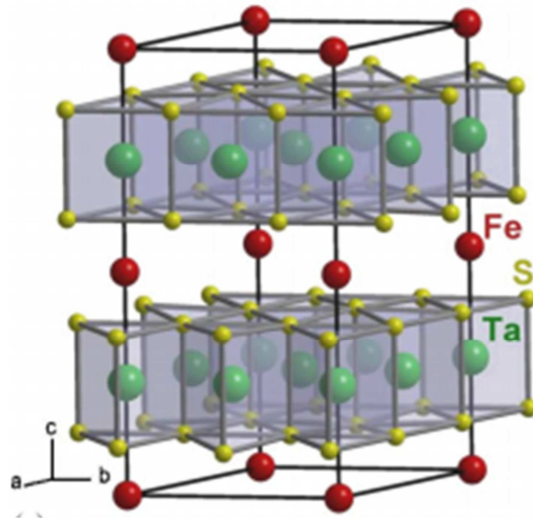

FIG.2. The crystal structure of $Fe_{1/4}TaS_2$ [5].

Due to its special crystal field environment around Fe ions, it hosts extremely large magnetic anisotropy at low temperatures, which is responsible for many anomalous physical behaviors. The density of defects (anitphase boundaries) that would pin magnetic domain walls can be controlled by annealing conditions [6]. It has a sharp switching of magnetization (H < 0.01 T)[5].

As shown in Fig.3, the magnetic hysteresis parallel to the c-axis shows good square shape with a saturation magnetic moment $M_{sat} \approx 4\mu_B$/Fe while the moment in the plane of TaS$_2$ layers (H//a) has small magnetization even at a high magnetic field of 6T[6].
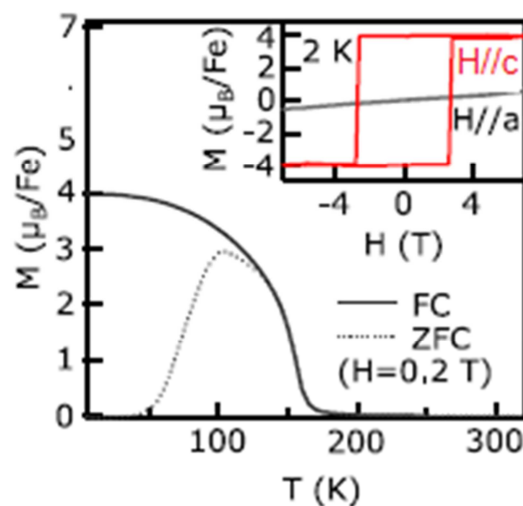

FIG.3. Field cooled (FC) and zero field cooled (ZFC) M-T curves under H = 0.2 T along the c axis. The in-plane (H // a) and out-of-plane (H // c)M-H hysteresis curves at 2 K are presented in the inset[7].

The anisotropy field is estimated to be $H_{ani} \approx 60$ T, even larger than that of the rare-earth magnetic elements. The RKKY interaction is considered to be the exchange mechanism responsible for the magnetic ordering of far separated Fe^{2+} ions in this system[8] mediated by the conduction electrons of the TaS_2 layers. However, because of lack of detailed electronic structure studies, the understanding is very primitive, and the magnetic properties and exchange mechanism are yet to be explored.

Ising-type spin states and an extremely high, unquenched orbital magnetic moment ($m_o \approx$ 1.0 µB/Fe), which persists at the intercalated Fe^{2+} ion and originates the huge magnetocrystalline anisotropy, have been reported[7].

In and of itself, this material is an interesting candidate in which to study ultrafast magnetic dynamics. Structurally and magnetically it can already be considered as a cross-over system between itinerant transition metal ferromagnetic system and those of local moment lanthanides. The magnetic moments are carried by spins in the d-manifold, but these states are localized and exchange is mediated by the conduction electrons. This is precisely the case for Gd, for example, where the local moment f-orbitals are coupled via the conduction sp electrons. The two systems, d-orbital magnetism and f-orbital local moment magnetism, already display a 2 order of magnitude difference in demagnetization timescale, and form the two 'pillars' of ultrafast magnetic measurement[2]. Our sample sits right in between the two. Structurally and magnetically, it has commonalities with both classes of materials and thus lets us study the cross-over behavior from one extreme to the other.

The true power of our material system comes when we replace Fe with another magnetic transition metal. In making such a substitution (effectively a new sample) the optical properties of the material do not change drastically, the electronic properties also do not change (remaining metallic) while the ratio of orbital to spin moment on the intercalated ion changes as well as the magneto crystalline anisotropy, due to size effects. The expectation is that we can make changes to the intercalant 'impurity' without changing the properties of the host lattice. This now allows us to study the effects of each of these parameters on the demagnetization timescales.

In the initial phase of these measurements, samples will be acquired from external sources. Currently samples of $Fe_{0.25}TaS_2$ are being supplied by the group of Sang-Wook Cheong in Rutgers University. In the future, we hope to have an in-house source of materials in collaboration with the group of Graeme Blake.

8.3 Ultrafast Laser Induced Magnetization

A typical scenario of the processes leading to a laser-induced demagnetization is the following. At optical frequencies, only electrons are able to respond to an electromagnetic excitation, absorbing or scattering the photons practically instantaneously. Thus, in the first step: 1) the laser beam hits the sample and creates electron-hole pairs(hot electrons) on a

time scale of ~ 1 fs; 2) the electronic system equilibrates at elevated temperatures $T_{elec.}$ by electron-electron interactions within 50–500 fs, depending on the system; and 3) the equilibrated electronic excitations decay via phonon cascades on a time scale given by the electron-phonon interaction time (within 100 fs–1 ps for metals) and heat up the lattice, increasing $T_{ph.}$. Thus, at the end of a picosecond, electron and lattice systems are in thermal equilibrium with each other. What happens with the spins?

Generally speaking, both the electron system and the lattice should be able to absorb this angular momentum, even if only temporarily. The spin-lattice interaction time is expected to be quite long, especially when there is orbital quenching e.g., 300 ps in Ni. However, after the demonstration of femtosecond demagnetization, mechanisms of an effective electron-spin or spin-lattice interaction responsible for demagnetization faster than 100 fs are the subject of current research[3]. Bigot et al. proposed that the laser-induced demagnetization of Ni could be caused by a direct coupling between photons and spins. A novel relativistic quantum mechanical mechanism was said to be the reason for the ultrafast change in magnetization[9]. It has been shown that the electron orbitals do not contribute to these fast processes. Since the spin-lattice interaction is weak, interactions via virtual states have been considered to be responsible for enhancement of the interaction energy, and hence shorter timescale [10, 11].

The experiments we will undertake involve a series of element specific x-ray absorption studies. In all cases, the measurements will be done in a pump-probe geometry, where an excitation laser is used to perturb the magnetic orientation of the sample and an x-ray pulse is used to assess the magnetic properties. These measurements naturally rely on the use of external large-scale facilities such as femtosecond slicing sources at BESSY and x-ray FELs such as LCLS, XFEL and swissFEL when operable. We also propose as a portion of the work package that we develop table-top XMCD measurements based on high harmonic generation of soft x-rays. Each of these is detailed below.

8.4 TR-XMCD (Time Resolved X-ray Magnetic Circular Dichroism)

X-rays are commonly used to probe magnetic materials. When tuned to atom-specific absorption edges, x-rays are unparalleled in measuring site-specific magnetism. X-ray Magnetic Circular Dichroism (XMCD) is the difference in absorption coefficient for two different helicities of light in a ferromagnetic material and has been used for decades to probe the static magnetization. In recent years, the ability to make time resolved measurements using the XMCD technique has become available. In order to do this, the natural time structure of x-ray sources such as synchrotron and FELs can be synchronized to external pump lasers and 'standard' pump-probe spectroscopy can now be performed at large-scale facilities. In order to understand how the magnetic dynamics evolve, we monitor

the edge absorption profile (in transmission or reflection) as a function of x-ray helicity and time delay after the sample is perturbed by the laser.

We can identify a few facilities at which we can perform such measurements. For slow dynamics (picosecond to nanosecond recovery of magnetization) a host of facilities are available for use. These include Diamond Light Source, Synchrotron Soleil, and BESSY II to name a few. For faster dynamics (femtosecond to picosecond demagnetization) we need to concentration our efforts either on x-ray slicing source (slicing is a method to make synchrotron x-rays have 100fs pulse length) such as BESSY II, Synchrotron Soleil (in the coming upgrade) or FELs such as LCLS and XFEL (photon helicity is not present at LCLS at the moment). All these user facilities provide support for achieving these measurements and local expertise in running the experiments.

The utility of XMCD in studying magnetic materials is that they allow us to extract both the orbital and spin contribution to the total magnetic moment. In our systems, where the orbital magnetism is unquenched, a large portion of the moment is contributed by the orbital moment. The temporal dynamics of the orbital and spin moment can evolve on different timescales and this provides a direct measure of the mechanisms involved in demagnetization. This was clearly seen in the measurements performed at BESSY some years ago [12] where they showed the evolution of orbital and spin moments in nickel.

The selection rules for a mono-photonic transition under a magnetic field are:

$\Delta \ell = \pm 1$; $\Delta s = 0$; $\Delta J = 0, \pm 1$; $\Delta m = \pm 1$

with $\Delta m = +1$ for a right-handed circularly polarised light, $\Delta m = -1$ for a left-handed light. The interactions (absorption and emission of a photon) for which $\Delta l = +1$ are much more probable, by one order of magnitude. For example, if we have six electrons in the following configuration:
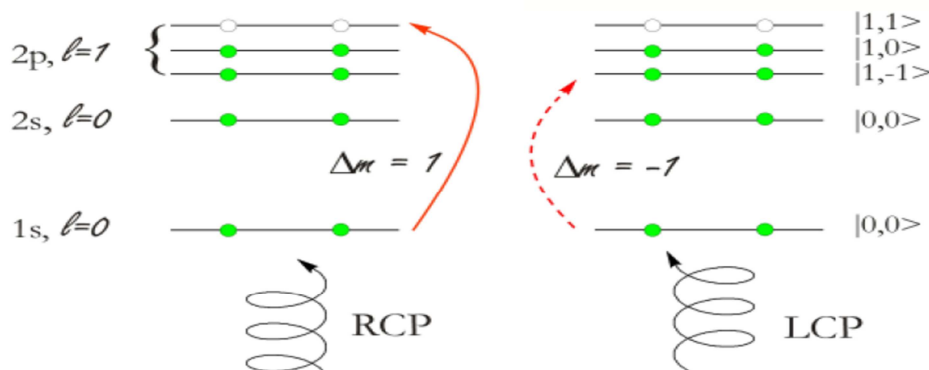

FIG.4.

Now we come to the sum rules which give us the access to the spin and orbit moments of the element under study. For this analysis, all that is needed is: 1) the absorption signal at zero-field (XAS spectrum) and its integral, which gives the "**r**" parameter, 2) the difference between the signals recorded for the two light helicities, the XMCD signal (in green and blue

in the figure below). The complete integral of this signal gives the "**q**" parameter, the integral of the XMCD signal limited to the first edge gives the "**p**" parameter.

FIG.5. The sum rules for a 3d-element are:

$$m_{orb}\,[\mu_B/atom] = \frac{-4q(10-n_{3d})}{r}$$

$$m_{spin}\,[\mu_B/atom] \approx \frac{-(6p-4q)(10-n_{3d})}{r}$$
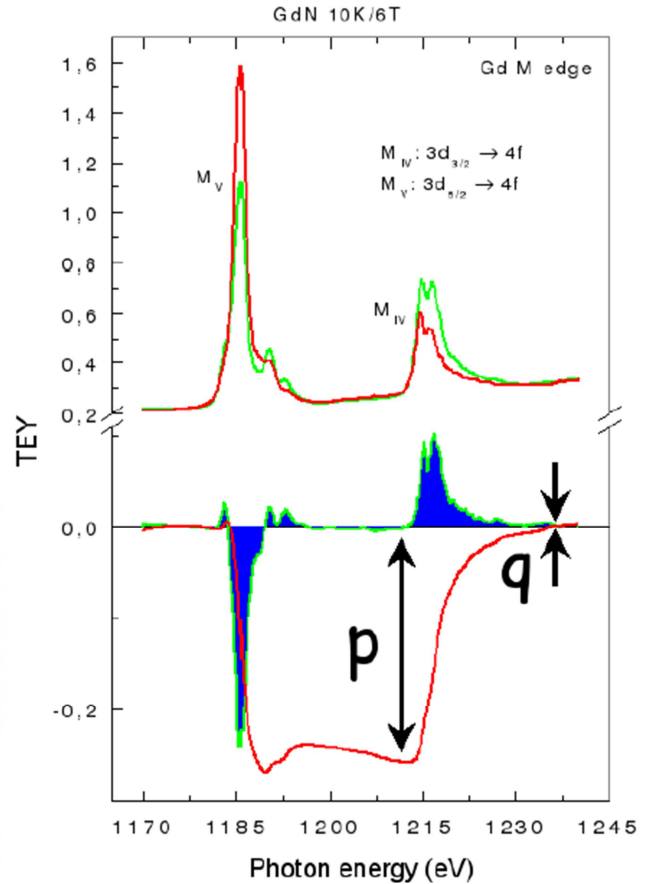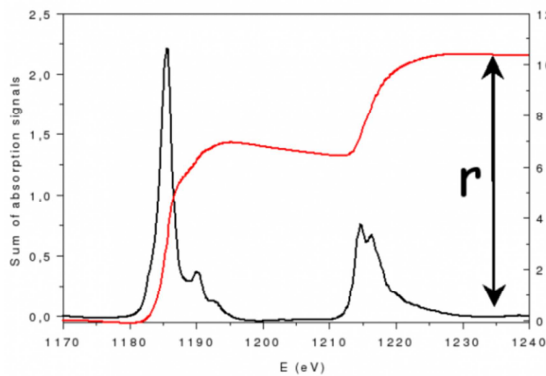
If the **q** parameter is zero, as in the example above, the orbit moment of the element is zero. The sign of the XMCD signal and that of its integral give the orientation of the spin and orbit moments relative to each other and to the applied magnetic field.

8.5. Tabletop XMCD

Recent developments in laboratory-scale high harmonic generation have opened the door to conducting XMCD on a table-top. These developments include the extension of harmonic radiation into the soft x-rays with considerable flux rates and more recently, the generation of fully circularly polarized harmonic radiation. At present the harmonic radiation that can be made circular is limited in photon energy to the extreme UV, up to about 100eV. Nonetheless, these photon energies overlap several atomic edges that could be useful for XMCD measurements. In particular, the iron M-edge (3p – 3d) at 52eV has been used in the past to measure magnetic contrast.

In collaboration with the group of Margaret Murnane and Henry Kapteyn at the University of Colorado we will attempt to make TR XMCD measurements using this one of a kind source of circularly polarized soft x-ray photons. The experimental procedure is much the same as detailed above for the synchrotron sources but now undertaken at a much smaller source,

with potentially more time availability, and importantly, better time resolution. At an HHG source, we can readily expect to get temporal resolutions of under 30 fs, allowing us to measure the fastest possible dynamics in magnetic systems[13].

8.6 X-ray Photoemission Electron Microscopy (X-PEEM)

X-ray magnetic imaging offers elemental and chemical state specificity, variable sampling depth, and the capability to follow ultrafast processes on the picosecond scale although it does not give the best spatial resolution.

When the photon energy is tuned to a prominent resonance in the X-ray absorption spectrum, like the L_3 or L_2 edges of a transition metal, a large dichroism effect is evident. Because of this effect, in an electron yield experiment, the number of photoelectrons coming from regions of different magnetic orientations will be different. The different signal strength can therefore be used as a contrast mechanism for microscopy.

In the X-ray photoemission electron microscopy (X-PEEM), the sample is illuminated by a monochromatic X-ray beam that is only moderately focused, typically to tens of micrometers, so that it matches the maximum field of view of a photoelectron microscope. The energy resolution is determined by the X-ray monochromator in the beam line and the spatial resolution is determined by the electron optics in the X-PEEM[14].
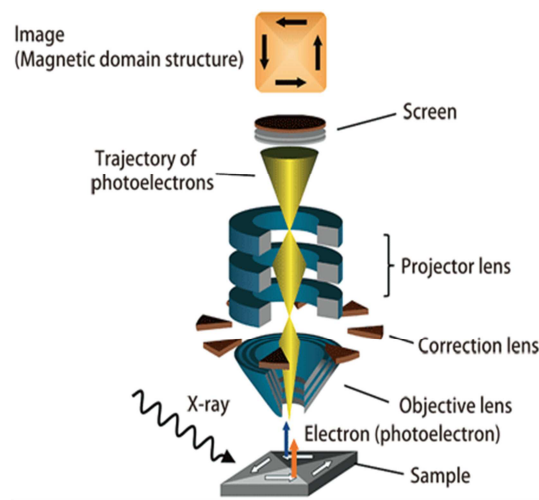

FIG. 6. Schematic of X-ray photoemission electron microscopy, XPEEM. The X-rays are focused by a shaped mirror to match the field of view of an electron microscope (1–50µm). Electrons emitted from the sample are imaged by an assembly of electrostatic or magnetic lenses with magnification onto a phosphor screen, and the image can be viewed in real time at video rates. The spatial resolution is determined by the electron optics within the microscope, the size of the aperture, and the operation voltage. In advanced designs an energy filter is employed to minimize chromatic aberration effects and such effects are further reduced by aberration correcting optics.

Vannette, M. D. *et al*., studied the single crystals of $Fe_{0.25}TaS_2$ using magneto-optical imaging and radio-frequency(rf) magnetic susceptibility

and concluded that this material is a local-moment ferromagnet with very large magnetocrystalline anisotropy that increases upon cooling. The magneto-optic study reveals unusual slow domain formation and sensitivity of the domain structure on the magnetic and thermal history.

Fig. 7 shows the appearance of ferromagnetic domains after the sample was cooled to 5 K in H=−1000 Oe magnetic field and the field was slowly increased. In these and all other MO images presented herein, the c axis of the crystal is pointing out of the page. Field cooling resulted in a monodomain state for the crystal. In order to nucleate a domain wall, a positive field of H ≈ 450 Oe was necessary. The persistence of a monodomain state at 5 K in an oppositely oriented field suggests a very high anisotropy for this compound.
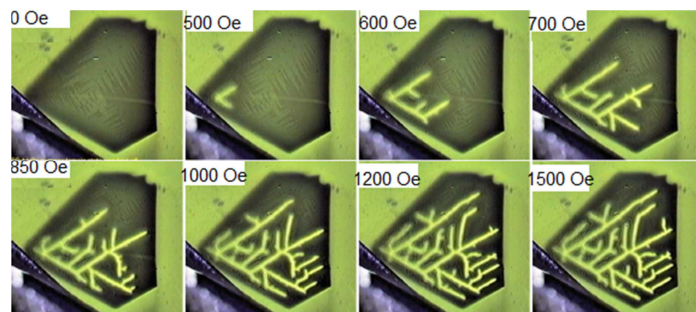

FIG. 7. Applying positive magnetic field at T=5 K after cooling in negative H=−1000 Oe and turning the field off.

Field cooling to a higher temperature (T=50 K) shows that the monodomain state is broken by lowering the applied field without changing the field direction(Fig. 8).
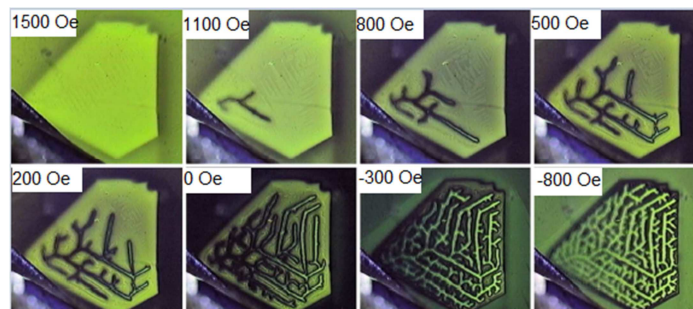

FIG. 8. Turning a magnetic field down after field cooling in 1500 Oe to T=50 K.

Again, the unusual, dendritic domains form in much the same way as at the lower temperature.

Fig. 9 shows how temperature variation affects domain formation. The sample was cooled to T=5 K in an applied field of 1500 Oe. The field was lowered to zero and the temperature was slowly warmed. No domains were observed until T ≈ 50 K, at which temperature the domains grew in a dendritic fashion similar to that observed for the constant-temperature field sweeps.
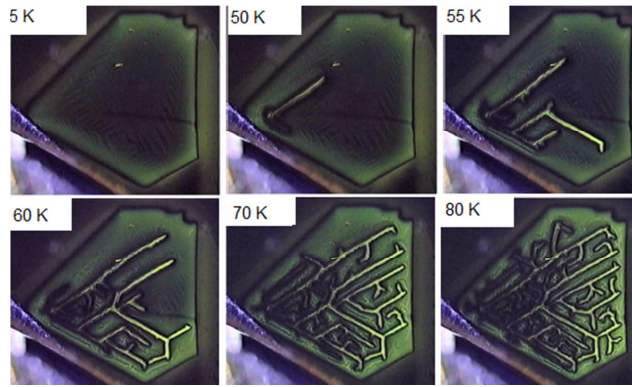
FIG. 9. Warming up after cooling in 1.5 kOe field and turning field off at 5 K.

The overall domain structure observed under different conditions is different so there is no one-to-one correlation between the distribution of the domains and the structural features of the crystal. This indicates that, in addition to the large c-axis magnetic anisotropy, there exists significant in-plane anisotropy with respect to domain-wall motion[15].

The work of Vannette *et al*. has some drawbacks. The spatial resolution of the images is in microns and they did not study the temporal profile of the domain formation. X-PEEM offers nanometer spatial resolution as well as temporal resolution.

In our project, we want to do X-PEEM measurements on these systems and a comparison of the results with this data and data from the other ferromagnetic members of this family may offer clues regarding to how the crossover between local-moment and itinerant ferromagnetism proceeds?

9. The Experimental Plan

The three objectives are as follows. All will need to be distributed amongst the several sources that we intend to use, and beamtime proposals need to be applied for:-

1. TR-XMCD – (Diamond Light Source, BESSY II, Soleil, LCLS, XFEL) –

2. TR-XMCD/PEEM – (Diamond Light Source, BESSY II)

3. TR-XMCD HHG – (JILA and University of Colorado)

Additionally, we need to acquire samples from the following sources:-

1. Sang-Wook Cheong (Rutgers University) - Ongoing collaboration is supplying samples presently.

2. Graeme Blake (Groningen) – Needs to get his operation up and running, but potentially a great source for samples.

3. Several other groups that have not been contacted yet (Cava – Princeton, Morosan – Rice)

References

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SAFDAR ABBAS MALIK

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STATEMENT OF PURPOSE

I intend to be trained in research in Optical Condensed Matter Physics, in an environment that allows me to explore my potential and to exercise my mental and intellectual faculties.

EDUCATION HISTORY

DEGREE CURRENTLY PURSUING

2012 – 2014　　　　**University of Groningen**
Zernike Institute for Advance Materials
Top Master Nanoscience

Master Thesis:　　Effects of Doping on the Thermoelectric Power of TAGS
Solid State Materials for Electronics (SSME) Group
Zernike Institute for Advanced Materials

Small Project:　　DFT Calculations on Möbius Aromaticity in Metallacycles
Theoretical Chemistry Group
Zernike Institute for Advanced Materials

Research Interests:　　Optical Condensed matter Physics
Experimental Condensed Matter Physics
Magnetism of Materials

2009 – 2011　　　　**Quaid-i-Azam University**
MSc Physics

2002 – 2005　　　　**University of the Punjab**
BSc (Hons.) Physics

1999 – 2001　　　　**Higher Secondary School Certificate**

1997 – 1999　　　　**Secondary School Certificate**

university of groningen

faculty of mathematics and
natural sciences

zernike institute for
advanced materials

Version 3 Dec. 2013

Declaration of hospitality and financial support for research costs

Appendix to the Proposal for a PhD research position
in the NWO Graduate Programme Advanced Materials, deadline 2 Feb. 2014
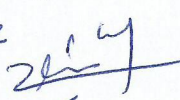
Name of the applicant: *Safdar Abbas Malik*

Title of the proposal: *Ultrafast Magnetic Dynamics in Intercalated Transition Metal Dichalcogenides*

By signing this document the staff member declares that she/he is willing to host and supervise the PhD research project that is mentioned above. In addition, the staff member declares that she/he has and makes available the materials, infrastructure and the funding that is needed for covering the research costs (the costs in addition to the salary of the PhD student some funding for travel and training), as described in the proposal.
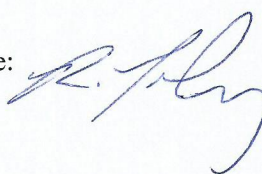
The signing staff members must be affiliated with the Zernike Institute for Advanced Materials (including the associate members).

Signatures

Applicant (the student applying for the PhD grant)

Date: *Jan 31, 2014*   Name: *Safdar Abbas Malik*   Signature:

Daily PhD supervisor (only needed if applicable, in case of supervision by an assistant professor or UD/UHD without ius promovendi)

Date: *Jan 31, 2014*   Name: *R. Tobey*   Signature:

1ˢᵗ Promotor (staff member with ius promovendi)

Date: Name: Signature: