Ultrafast magnetization and structural dynamics in the intercalated transition metal dichalcogenides Fe$_{0.25}$TaS$_2$ and Mn$_{0.25}$TaS$_2$

Q Liu$^1$, X D Zhu$^2$, L H Wang$^3$, S-W Cheong$^{3,4}$ and R I Tobey$^1$

$^1$ Zernike Institute for Advanced Materials, University of Groningen, Groningen 9747AG, The Netherlands
$^2$ High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, People’s Republic of China
$^3$ Laboratory for Pohang Emergent Materials and Max Plank POSTECH Center for Complex Phase Materials, Pohang University of Science and Technology, Pohang 790-784, Korea
$^4$ Rutgers Center for Emergent Materials and Department of Physics and Astronomy, Piscataway, NJ 08854, USA

E-mail: r.i.tobey@rug.nl

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Abstract

We measure magnetization and structural dynamics in two intercalant-ordered transition metal dichalcogenides: Fe$_{0.25}$TaS$_2$ and Mn$_{0.25}$TaS$_2$. The structurally equivalent materials allow us to probe the effect of orbital angular momentum which is active in Fe$_{0.25}$TaS$_2$ and absent in Mn$_{0.25}$TaS$_2$. Interestingly, we find that the magnetooptics dynamics are nearly indistinguishable in these two materials, in contradiction to conventional explanations of a spin–lattice mechanism. We compare our results to other materials where spin–lattice demagnetization has been put forth as a demagnetization channel.

Keywords: ultrafast magnetooptics, intercalated transition metal dichalcogenides, ultrafast dynamics

(Some figures may appear in colour only in the online journal)

1. Introduction

Two dimensional materials have come to the fore of the condensed matter research landscape, promising to revolutionize electronics and photonics capabilities [1, 2], and heralding new device architectures for increased speed and efficiency of information processing [3]. Endearing these materials to the research community are their tunability in electronic properties that can be affected by sample composition and thickness, all while maintaining nearly atomically thin active areas. Transition metal dichalcogenides (TMDCs) are one such material family that exhibits these properties, including tunability in bandgap depending on material composition and effective magnetic fields via the spin–orbit interaction, the latter being mediated by the heavy 5$d$ transition metal ion. Bandgap energies are further modified as a material transitions from 3D bulk behaviour to 2D layered properties [4].

Parallel to developments in electronic and optical tunability, magnetic properties can also be incorporated into the TMDC platform by appropriate intercalation of magnetic ions within the van der Waals gap of the host lattice [5]. With respect to the tunability of magnetic properties in this system, appropriate selection of host lattice and intercalant species can span the range from antiferromagnetic ordering to Ising or XY ferromagnetism, as well as providing for wide adjustment of Curie or Neel temperatures. As such, the range of tunability in both electronic and magnetic properties provide for a rich environment on which to study magnetic domain structure, interactions between emergent electronic states (CDW or superconductivity) and magnetism, as well as the dynamics of both electronic and magnetic states.
While there have been several studies of the ultrafast electronic [6], structural [7–9] and optical properties [10] of unintercalated TMDCs, here we make the first measurement of the magnetization dynamics in the intercalated compounds. We study two closely related compounds, Fe_{0.25}TaS_2 and Mn_{0.25}TaS_2, materials that share a common structure but differ in their intrinsic magnetic properties. The former is the primary TMDC showing Ising-like ferromagnetic behavior, while the latter is a prototypical XY ferromagnet. The two systems are further distinguished by the fully quenched orbital moment on Mn, while Fe exhibits a sizeable orbital contribution. The measurements detailed below include ultrafast magneto-optics for measuring the dynamics of the magnetization, as well as time resolved transient reflectivity, where we identify the excitation of Raman active coherent lattice vibrations.

2. Materials and methods

The materials under investigation are bulk 3d ion intercalated TMDCs with chemical formula (M)_xTaS_2 (M = Fe and Mn). Their three dimensional structure is shown in figure 1(a). Specific intercalant concentrations (x = 1/4, 1/3) result in long-range crystallization (figure 1(b)) of ions residing between the layers, which can be visualized [11–14] using a range of techniques such as LEED, STM, and TEM. For these concentrations, as one progresses through the series of transition metal intercalants (Cr, Mn, Fe, Co, Ni) and dichalcogenide hosts (TaS_2, TaSe_2, NbSe_2, etc), the magnetic properties can be varied while maintaining the same local crystallographic environment for the magnetic ion. Meanwhile, the low density of intercalated ions ensures that the material properties (band structure, optical response, etc) are dictated by the host lattice.

Of the two samples under investigation, Fe_{0.25}TaS_2 exhibits c-axis magnetization, a transition temperature of T_C = 160 K, saturated magnetic moment of m_sat \approx 4 \mu_B/ion, and coercivity in excess of several Tesla at low temperatures [13, 15]. As reported previously [14, 16], in Fe_{0.25}TaS_2 a large orbital moment resides on the intercalant species which can be measured using x-ray circular dichroism spectroscopy. Meanwhile, Mn_{0.25}TaS_2 is an in-plane ferromagnet with T_C = 120 K, saturated magnetic moment of m_sat \approx 5.5 \mu_B/ion and low coercivity. Orbital contributions for our samples were independently verified using transmission x-ray magnetic circular dichroism on thinned samples [14]. For both samples, the 2H polytype of TaS_2 supports intercalation, and is metallic throughout the entire temperature range of study.

Prior to optical measurements, sample quality was verified by magnetic property measurements to ensure that a narrow magnetic transition is visible at their respective Curie points. Further verification of intercalant concentration is performed by sectioning and transmission electron diffraction measurements [14] on samples from the same batch as those used in the optical measurements. These sectioned samples were also used for XMCD measurements in transmission and show transition temperatures in good agreement with those reported in literature.

Time-resolved magneto-optic Kerr effect (tr-MOKE) [17] and transient reflectivity measurements were performed using a two-color pump-probe scheme. The output of a 1 kHz amplified Ti:sapphire laser was split and a portion was frequency doubled to \lambda = 400 nm for probing the sample response, while the pump wavelength was kept at the laser fundamental 800 nm. Probing at higher photon energies suppresses potential spurious artifacts seen in tr-MOKE signals, while also optimizing the sensitivity to energetically buried 3d orbitals of the intercalant [18, 19]. The pump and probe impinged nearly collinearly onto the ab plane of the sample, which was held in an optical cryostat for scans across the respective magnetic transitions. Fe_{0.25}TaS_2 was magnetically biased in the polar MOKE configuration, while Mn_{0.25}TaS_2 was biased in the longitudinal MOKE configuration, in both cases \vec{k} \cdot \vec{M} are equivalent for an incidence angle of 45 degrees. Probe light reflected from the sample surface was polarization resolved using appropriate waveplates and a Wollaston prism to measure both Kerr rotation and ellipticity. The temporal resolution of our experiment is independently measured to be 200 fs full width half maximum, using a third order cross correlation. Experiments were performed at incident fluences not exceeding 0.7 mJ cm^{-2} to ensure sample recovery is complete between pulses and care is taken to ensure that the same portion of the sample is probed at all temperatures and across several days of experimentation. An additional set of data was acquired using a home built broadband nonlinear optical parametric amplifier (NOPA) [20]. Detection for this set of data was implemented using a synchronously gated spectrometer to collect transient reflectivity of the entire bandwidth simultaneously. Broadband transient reflectivity data was taken first and used to inform the subsequently acquired data at the probe wavelength of 400 nm, however, this method of acquisition had poorer signal to noise ratio.

3. tr-MOKE

In figures 2(a) and (b) the time-resolved ellipticity results for both samples are shown for a range of temperatures.
approaching their respective phase transitions. All data are normalized and vertically offset for ease of viewing, while time-zero has been shifted by one picosecond for logarithmic display of the time axis. Data for transient Kerr rotation was also acquired, and in the low fluence regime shows good correspondence with ellipticity, although at poorer signal to noise ratios. The ellipticity data displayed are well fitted (solid lines) by a three exponential function that includes two demagnetization time constants and one recovery time constant. The first time constant accounts for the ultrafast jump witnessed at time zero, while the second measures the dynamics in the tens of picosecond range that slows as the sample temperature is increased. Finally the last time constant accounts for recovery. The fitted parameters are a result from a convolution with the instrumental resolution. As shown, all three effects reduce as the temperature is increased and disappear as the Curie temperature is reached. The amplitude of total demagnetization (figures 2(c) and (d)) exhibits a maximum just below the Curie temperature, which is a common feature in many material families [21].

From the fitted tr-MOKE response, we extract the amplitude and time constants of the various demagnetization effects. For both samples the initial decay in magnetization measures 300 fs ± 200 fs. This time constant is unchanged for all temperatures below \(T_C\), however the amplitude rapidly reduces as the temperature is increased, which is plotted in figure 3(a). The second demagnetization time constant is plotted in figure 3(b), and exhibits a slowing down effect as \(T_C\) is approached. Such effects have been attributed to critical phenomena near the magnetic phase transition, and termed critical slowing down. The relative and absolute amplitude of this component peaks just below \(T_C\), as is evident from the combination of figures 2(a), (c) and 3(a). Notably, both samples behave very similarly in their phenomenology, with the unexpected result that both exhibit the same demagnetization time constants.

4. Transient optical response

We now turn to measurements of transient reflectivity to elucidate the electronic and structural dynamics. Initial measurements were performed over a broad spectral bandwidth to monitor the evolution of hot carriers generated by the 800 nm pulse pulse. Data for Fe\(_{0.25}\)TaS\(_2\) with 650 nm probe wavelength is shown in figure 4(a), taken at 80 K. The transient reflectivity is marked by a sharp spike at time zero and a subsequent plateau, a feature common to many complex materials. The spike at time zero is seen to reduce steadily as the photon energy shifts to higher values, and is completely suppressed when the response is probed at 400 nm, here probed using a single channel detector rather than the spectrometer. The trend in amplitude for the time zero effect and the plateau is shown in figure 4(b). Notably, as the photon energy shifts towards higher energy, the response from excited carriers is reduced sharply, while the plateau region reduces.
to a lesser extent. When pumped at low fluences, probing at 725 nm has a peak $\frac{\Delta R}{R_0} = 0.25$, reducing to 0.07 at 575 nm, and −0.02 at 400 nm. The two dynamical regimes observed at lower photon energies are associated with non-equilibrium carrier distributions (or hot carriers) and a subsequent excited state characterized by a hot lattice. The persistence of this latter state exceeds the measurement time of our traces (1 ns), while the system fully recovers in the 1 ms between pulses.

The sample response probed at 400 nm shows a negative $\frac{\Delta R}{R}$, while the cross over regime from positive to negative response is at higher photon energies than the NOPA output but below the second harmonic of the laser. Importantly, in comparing the temporal evolution of the transient reflectivity and MOKE signals, we see that one of the time constants, namely the sub picosecond effect, exists for both measurement channels, while the slow demagnetization that occurs over tens of picoseconds does not have a corresponding timescale in the transient reflectivity.

Since probing with high energy photons (400 nm, 3 eV) suppresses the signal associated with hot or non-equilibrium carriers, we extend these measurements further. In figure 5 we show the representative scans for both samples at 80 K. A sharp onset of $\frac{\Delta R}{R}$ is superposed with structural vibrations for both samples. The extracted frequencies of the oscillations are $\pm f_{3.84 \pm 0.03}$ THz for Fe0.25TaS2 and $\pm f_{3.61 \pm 0.03}$ THz for Mn0.25TaS2. The oscillation amplitudes remain unchanged for all temperatures above and below $T_C$, while the frequency shifts down by less than 5% as the temperature is increased to room temperature.

Vibrational mode identification is accomplished by considering the irreducible representation of the point group $D_{6h}$, the symmetry classification for bulk TMDCs as well as that of the intercalant-ordered systems such as Fe0.25TaS2 [13]. In comparing with literature values, we can identify the vibrational motion to be that of the Raman active, basal plane $E_{2g}$ mode [22], which has been shown to have a strong enhancement.
around $x = 0.25$ intercalant concentration [23]. More generally, one expects a large number of vibrational modes to be present (both Raman and IR active) however in time resolved studies vibrational modes are excited impulsively, and thus many of high frequency modes are inaccessible due to our time resolution. This is the case for both $E_{2g}$ and $A_{1g}$ which are most often seen in layered materials.

5. Discussion

The magnetization dynamics observed in our samples closely align with previous measurements in other classes of complex materials. In a broad range of work, Ogasawara et al [21] demonstrated many of the same phenomenology for several perovskites and spinels, where a two step demagnetization was observed. Particularly, for many of these samples, critical slowing down was observed in the second demagnetization channel [24] closely resembling the dynamics we observe in our second timescale. In their work, the span over which the picosecond dynamics occurred was correlated to the magnetocrystalline anisotropy constant, demonstrating that the largest anisotropy constants yielded the fastest demagnetization times. On this basis, the observations suggest that these effects are related to an inherent coupling between spin and lattice mediated by the orbital angular momentum, a spin–lattice mechanism [25].

If we incorporate our results into their general classification, we would find the time constants extracted for Mn$_{0.25}$TaS$_2$ would reside perfectly within the range found for the other samples. While no anisotropy constants are available in the literature, we can estimate the value to be $K_1 < 10^6$ J m$^{-3}$, while the time constant measured ranges from 10 to 40 ps. Discrepancies arise however when we attempt to incorporate our second sample, Fe$_{0.25}$TaS$_2$. For this material, the magnetocrystalline anisotropy energy is known, precisely because it is so anomalously large at $E_{\text{MCA}} \approx 15$ meV [16] ($K_1 \approx 10^7$ J m$^{-3}$). As such, the second time constant which slows as $T_C$ is approached would be expected to reside in the sub-picosecond regime, which disagrees with our current measurement. It is unclear at present why the time constants for these two materials are so similar, and specifically why a spin–lattice mechanism that has been successful previously does not explain dynamics in Fe$_{0.25}$TaS$_2$.

Similar comparisons can be performed with materials such as Gadolinium and Terbium, the prototypical materials about which discussions of spin–lattice relaxation appear. As in our Fe$_{0.25}$TaS$_2$, Tb exhibits a large orbital moment while Gd has a quenched orbital moment similar to Mn$_{0.25}$TaS$_2$. The demagnetization results in these two materials fall within the expected range of spin–lattice effects, in that Tb shows a drastically faster effect [26]. To take this comparison further, two distinctions should be made with respect to our samples. First, while Fe$_{0.25}$TaS$_2$ does have a sizable orbital moment, the active orbitals are $3d$ and interact with the local environment much more strongly than the corresponding $4f$ orbitals of the lanthanides. Additionally, since they are involved in bonding, we can expect some level of itinerancy in their properties, making these materials a bridge between purely local moment systems ($4f$) and purely itinerant systems like $3d$ metals. All of these effects strongly impact that magnetization dynamics that are measured, and suggest for example, that the fast effect at time zero may be attributable to both magnetization dynamics of the host conduction band as well as dynamics on the intercalant ion. This latter effect may be direct in the sense spin–lattice in Fe$_{0.25}$TaS$_2$ or a higher order effect in that lattice vibrations induce a transient orbital moment and subsequent demagnetization on Mn$_{0.25}$TaS$_2$. On the other hand, the similarity in responses could be indicative of the level of itinerancy in both materials and the suppression of local moment properties. In fact the fast demagnetization channel might be attributable to Elliot–Yafet spin scattering which is present in both materials, and subsequently masks any additional channels associated with spin–lattice that might have been expected in Fe$_{0.25}$TaS$_2$.

Ultimately, an element selective probe such as time resolved XMCD will be needed to fully resolve the magnetization dynamics in these materials [27, 28]. In such measurements, spin and orbital contributions residing on the intercalated ion can be probed separately, as well as magnetic moments that reside on the host lattice. In line with these ideas, we have recently optimized a technique for manufacturing free-standing thin films of both Fe$_{0.25}$TaS$_2$ and Mn$_{0.25}$TaS$_2$ which have already been characterized using static XMCD spectroscopy [14]. Such a capability will allow us to measure femtosecond dynamics with elemental specificity. We expect that our sample fabrication technique can be applied for the entire family of intercalated TMDC, thus providing an avenue for assessing this broad class of materials using ultrafast x-ray and electron probes.

In summary, we have measured the ultrafast optical response and magnetization dynamics in two magnetic-ion-intercalated TMDCs. For the magnetization, we see two demagnetization effects that are distinct in time, namely a fast demagnetization measuring in the hundreds of femtosecond and a temperature dependent effect in the tens of picosecond regime. The latter effect is shown to slow as the sample temperature is raised towards $T_C$. Simultaneously, we measure the transient reflectivity and show the excitation of coherent lattice vibrations. Importantly, since the two samples share a common crystallographic environment, we attempt to isolate the effect of orbital angular moment active in one compound and absent in the other, while the experimental results suggest that the effect is more subtle than expected. We also discuss future x-ray measurements using our recently fabricated large area free standing thin films.

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