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Magnetic properties of the layered III-VI diluted magnetic semiconductor $Ga_{1-x}Fe_xTe$

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Magnetic properties of single crystalline $Ga_{1-x}Fe_xTe$ ($x = 0.05$) have been measured. GaTe and related layered III-VI semiconductors exhibit a rich collection of important properties for THz generation and detection. The magnetization versus field for an $x = 0.05$ sample deviates from the linear response seen previously in $Ga_{1-x}Mn_xSe$ and $Ga_{1-x}Mn_xS$ and reaches a maximum of 0.68 emu/g at 2 K in 7 T. The magnetization of $Ga_{1-x}Fe_xTe$ saturates rapidly even at room temperature where the magnetization reaches 50% of saturation in a field of only 0.2 T. In 0.1 T at temperatures between 50 and 400 K, the magnetization drops to a roughly constant 0.22 emu/g. In 0 T, the magnetization drops to zero with no hysteresis present. The data is consistent with Van-Vleck paramagnetism combined with a pronounced crystalline anisotropy, which is similar to that observed for $Ga_{1-x}Fe_xSe$. Neither the broad thermal hysteresis observed from 100-300 K in $In_{1-x}Mn_xSe$ nor the spin-glass behavior observed around 10.9 K in $Ga_{1-x}Mn_xS$ are observed in $Ga_{1-x}Fe_xTe$. Single crystal x-ray diffraction data yield a rhombohedral space group bearing hexagonal axes, namely R3c. The unit cell dimensions were a = 5.01 Å, b = 5.01 Å, and c = 17.02 Å, with $\alpha = 90°$, $\beta = 90°$, and $\gamma = 120°$ giving a unit cell volume of 369 Å^3. [http://dx.doi.org/10.1063/1.4945335]

I. INTRODUCTION

Gallium selenide (GaSe) has emerged as one of the best non-linear optical materials.[1–11] GaSe exhibits a rich collection of important properties for THz generation and detection applications including a large non-linear coefficient, high damage threshold, high-temperature operation, and a wide transparency range.[1–4] GaSe is highly efficient as a broadband tunable source up to 40 THz and as a sensor up to 100 THz.[4,5] In short, GaSe (and related doped and un-doped III-VI semiconductors such as GaTe) have emerged as valuable systems in the very active THz research field.[1–3,5,6,8–11] Work on GaTe and doped GaTe crystals includes the growth and characterization of these systems for broadband tunable THz sources and sensors.[5]

Doping with Te,[3,5] S, Cr,[2,6] Ag,[1] and Er[7] was found to strengthen GaSe. Doping with In was found to significantly enhance the physical properties and strengthen the crystals enough to allow optical surfaces to be cut and polished along additional directions. Unexpectedly, the In doping did not degrade the useful properties of GaSe but actually resulted in enhanced non-linear optical properties.[2,3,5,6,8–11] First-principles theoretical studies investigating the mechanical and electrical properties Te-based systems were also conducted.[3]

Unlike doping with In, the incorporation of a transition metal element raises intriguing possibilities for coupling the magnetic properties of the transition metal ion with the host III-VI semiconductor leading to optical or electrical transport effects. Specifically, the *sp-d* exchange coupling in related materials can sometimes have dramatic physical consequences such as giant Faraday rotation, bound magnetic polarons, or induced metal to insulator transitions.[12,13] Doping with the transition metal ion Cr in $Ga_{1-x}Cr_xSe$[2,6] has already been studied and shows improved mechanical properties while preserving the advantages of the host GaSe as a THz material.[2,6]

In this work we present magnetic and x-ray measurements on single-crystalline $Ga_{1-x}Fe_xTe$. This work complements work done on the other III-VI DMS systems investigated to date ($Ga_{1-x}Mn_xS$,[14–18] $In_{1-x}Mn_xS$,[19,20] $In_{1-x}Mn_xSe$,[21–23] $Ga_{1-x}Mn_xSe$,[24] and $Ga_{1-x}Fe_xSe$).[25]

II. EXPERIMENTAL DETAILS

A 0.0288 g single-crystalline $Ga_{1-x}Fe_xTe$ sample was taken from a boule grown using the vertical Bridgman method with a nominal concentration of $x = 0.05$. Magnetization measurements were performed using a Quantum Design MPMS XL7 superconducting quantum interference device (SQUID) magnetometer at temperatures between 1.8 and 400 K in fields up to 7 T. A pure GaTe crystal was measured to determine the value of the diamagnetic signal (-3.5×10^{-7} emu/g G) due to the semiconductor host GaTe, which was subtracted from the data.

Structural analysis was performed on a small crystalline specimen taken from the same boule as the magnetization crystal. The crystalline fragment was mounted on a loop holder, suitable for single crystal x-ray analysis, using Paratone-N oil. It was then transferred to the goniostat where it was cooled to 100 K for characterization and data collection. The data were collected from a combination of phi and omega scans on a Bruker D8 Venture diffractometer equipped with an Iμ S Mo Kα source and a CMOS detector.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Magnetization versus temperature measurements taken on a single crystalline $Ga_{1-x}Fe_xTe$ sample with a magnetic field oriented perpendicular to the two-dimensional GaTe layers are shown in Figs. 1(a) and 1(b). The magnetization remains roughly constant and featureless for the entire

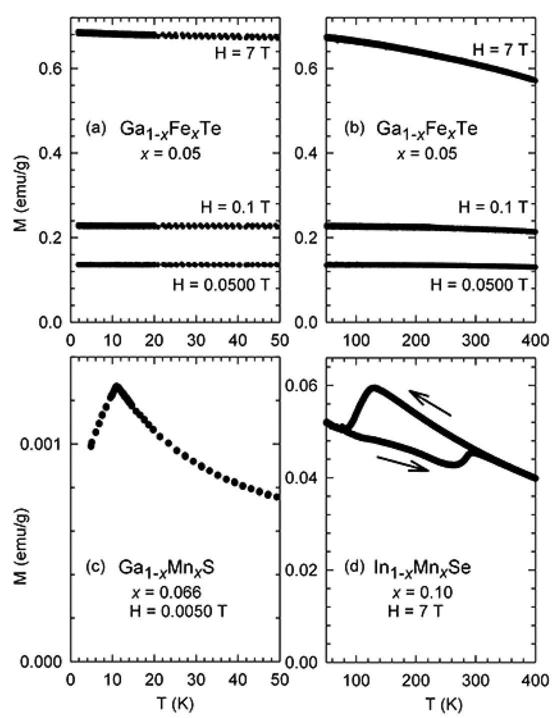

FIG. 1. The temperature-dependent magnetization of a $Ga_{1-x}Fe_xTe$ ($x = 0.05$) crystal sample in 0.0500, 0.1, and 7 T fields are shown in (a) and (b). The magnetization versus temperature for $Ga_{1-x}Mn_xS$ is shown in (c). The sharp cusp at 10.9 K indicates a transition to the spin-glass state. The magnetization versus temperature for $In_{1-x}Mn_xSe$ is shown in (d). A prominent thermal hysteresis is evident between 90 and 290 K.

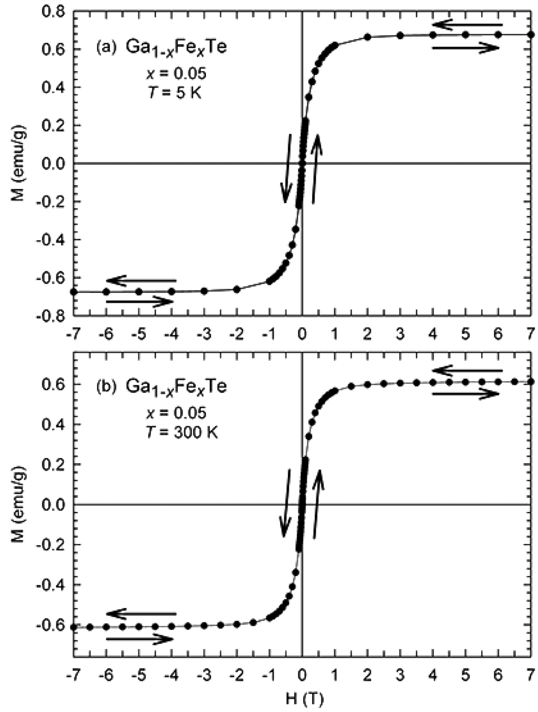

FIG. 2. Hysteresis trace taken at 5 and 300 K with the applied magnetic field oriented perpendicular to the two-dimensional $Ga_{1-x}Fe_xTe$ ($x = 0.05$) layers are shown in (a) and (b), respectively. Note the apparent absence of a coercive field. The data are shown as dots and the line is a guide to the eye. Arrows indicate the direction of changing magnetic field through a standard hysteresis loop.

temperature range from 1.8 to 400 K for measurements taken in both 0.1000 and 0.0500 T. In 7 T, the magnetization increases by only 20% as the temperature is decreased from 400 to 1.85 K. In contrast, the sharp cusp shown in Fig. 1(c) is due to the long-range collective interaction of spins resulting in the spin-glass[17,18] transition at 11.2 K in $Ga_{1-x}Mn_xS$. At higher temperatures, the broad thermal hysteresis[21–23] shown in Fig. 1(d) is likely due in part to a long-range collaborative spin-density-wave in $In_{1-x}Mn_xSe$. No evidence for comparable long-range interactions of spins is observed in $Ga_{1-x}Fe_xTe$ (Fig. 1(a)) for the entire temperature range. The long-range interaction of spins in $Ga_{1-x}Fe_xTe$ apparently does not play the same prominent role in $Ga_{1-x}Fe_xTe$ that the transition metal ions play in related III-VI DMS systems. Nonetheless, it is important to note that the magnetization in $Ga_{1-x}Fe_xTe$ remains high even as the temperature increases well above room temperature. This is reminiscent of Van-Vleck paramagnetism.

To explore the possibility of a ferromagnetic minority phase, magnetization hysteresis loops were taken on $Ga_{1-x}Fe_xTe$ at 5 and 300 K (Figs. 2(a) and 2(b)). The magnetization increases rapidly at low field, reaching over 50% of the 7 T value in a field of only 0.2 T and over 90% by 1 T at both 5 and 300 K. Since, there is no apparent coercive field on this scale, the region near zero field was examined further and is shown in Figs. 3(a) and 3(b). In this region the coercive field was measured to be less than 0.0005 T at 5 and 300 K as well as 1.8 and 10 K (not shown), which is within the experimental uncertainty of the instrument.

Having ruled out multi-domain ferromagnetic regions, single domain super-paramagnetic regions might account for the rapid rise observed in the magnetization at low fields that is clearly seen in Figs. 2(a) and 2(b). If this data is plotted together, the magnetization at 300 K should increase significantly slower than at 5 K. However, the magnetization at both 300 and 5 K rise nearly identically as can be seen in Fig. 4(a). This is true when the two-dimensional $Ga_{1-x}Fe_xTe$ layers are aligned perpendicular to the field (up and down triangles) or parallel to the field (circles and squares). This suggests that we have a good quality crystal with neither multi-domain ferromagnetic regions nor single domain super-paramagnetic clusters present in our sample.

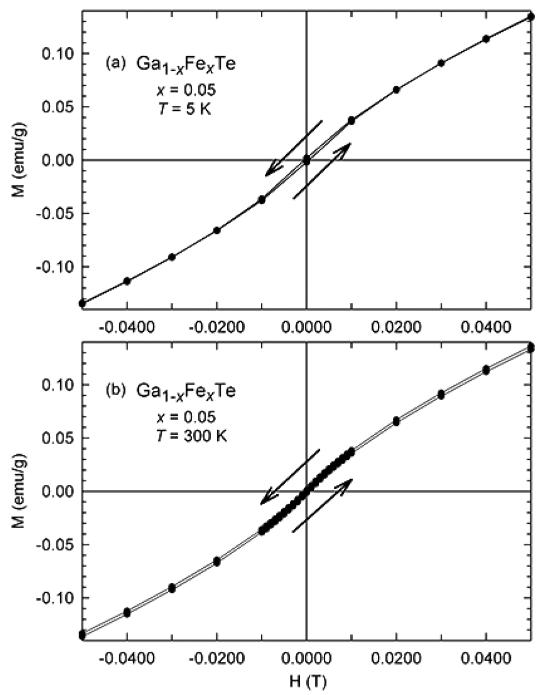

FIG. 3. Close-up views of the hysteresis loops taken at 5 and 300 K are shown in (a) and (b), respectively. The measured coercive field is less than 0.0005 T and 0.0003 T for the 5 and 300 K traces, respectively, which is within the uncertainty of the instrument.

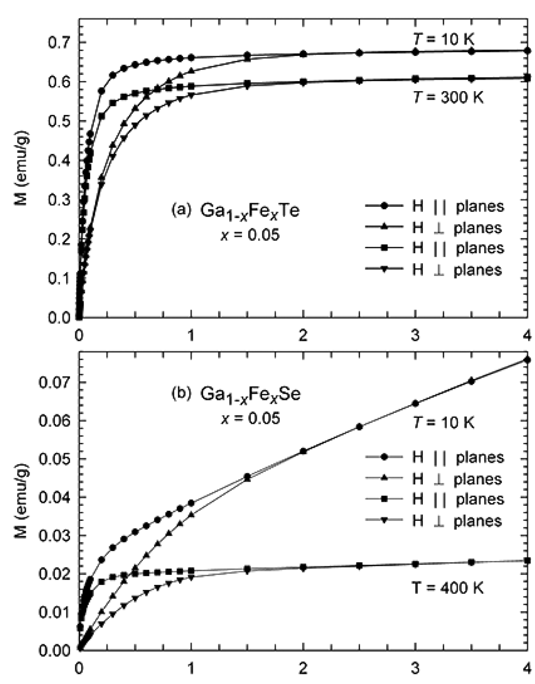

FIG. 4. Magnetization versus field data taken on a single crystalline $Ga_{1-x}Fe_xTe$ ($x = 0.05$) sample are shown in (a). Magnetization versus field data taken on a single crystalline $Ga_{1-x}Fe_xSe$ ($x = 0.05$) sample are shown in (b). Data taken with the field parallel to the planes at low and high temperature are shown by circles and squares, respectively. Data taken with the field perpendicular to the planes at low and high temperature are shown by the up and down triangles, respectively. A crystalline anisotropy is evident in fields between 0 and 2 T. The lines are a guide to the eye.

To further investigate the crystal quality of our sample, we collected single crystal x-ray diffraction data on a small fragment taken from the same boule as the magnetization crystal. An initial survey of the reciprocal space revealed a set of reflections with a monoclinic lattice, with unit cell dimensions a = 23.20 Å, b = 5.00 Å, and c = 6.36 Å, with α = 90°, β = 92.3°, and γ = 90°. These result in a unit cell volume of 737 $Å^3$. Our findings are in agreement with earlier work.[26,27] Upon analysis of a full data set, additional symmetry elements became apparent, resulting in a rhombohedral space group bearing hexagonal axes, namely R3c. The unit cell dimensions were a = 5.01 Å, b = 5.01 Å, and c = 17.02 Å, with α = 90°, β = 90°, and γ = 120°, and a unit cell volume of 369 $Å^3$. This is in agreement with a recent paper by Borisenko and coworkers,[28] where the authors found a hexagonal space group from single-crystal studies of pure GaTe.

A significant magnetocrystalline anisotropy is evident in the magnetization of our $Ga_{1-x}Fe_xTe$ (x = 0.05) crystal between 0 and 2 T at both 10 and 300 K. The easy axis is observed along a random direction parallel to the two-dimensional $Ga_{1-x}Fe_xTe$ layers. These layers have one-third of the Ga-Ga direct bonds aligned in the plane of the layers and two-thirds aligned perpendicular to the layers. The hard axis is along the direction perpendicular to the layers or along the direction with the majority of the direct Ga-Ga bonds.

Similar magnetocrystalline anisotropy was observed in $Ga_{1-x}Fe_xSe$ and is shown in Fig. 4(b).[25] Additionally, preliminary calculations were conducted for $Ga_{1-x}Fe_xSe$ using a model Hamiltonian including crystal-field, spin-orbit, spin-spin, and Zeeman terms. The model Hamiltonian used for $Ga_{1-x}Fe_xSe$ would be similar to a corresponding model Hamiltonian for $Ga_{1-x}Fe_xTe$. The $Ga_{1-x}Fe_xTe$ and $Ga_{1-x}Fe_xSe$ data as well as the theoretical calculations have the same easy and hard axis, where the hard axis is along the direction perpendicular to the layers and along the prominent direction of the direct Ga-Ga bonds. The easy axis in all cases is parallel to the two-dimensional layers. Although good qualitative agreement is made between theory and experiment, further work is needed to refine the parameter values (*e.g.* spin-orbit coupling constant, bond lengths, *etc.*) used in the theory before quantitative agreement is achieved.

IV. CONCLUSIONS

Magnetic properties of single crystalline $Ga_{1-x}Fe_xTe$ ($x = 0.05$) have been measured. The magnetization versus field for an $x = 0.05$ sample reaches a maximum of 0.68 emu/g at 2 K in 7 T. The magnetization of $Ga_{1-x}Fe_xTe$ saturates rapidly even at room temperature where the magnetization reaches 50% of saturation in a field of only 0.2 T. In 0.1 T at temperatures between 50 and 400 K, the magnetization drops to a roughly constant 0.22 emu/g. In 0 T, the magnetization drops to zero with no hysteresis present. The data is consistent with Van-Vleck paramagnetism combined with a pronounced crystalline anisotropy. Single crystal x-ray diffraction data yield a rhombohedral space group bearing hexagonal axes, namely R3c. The unit cell dimensions were a = 5.01 Å, b = 5.01 Å, and c = 17.02 Å, with α = 90°, β = 90°, and γ = 120° giving a unit cell volume of 369 $Å^3$. The *x*-ray data corroborates our observations from the magnetism studies and affirms that the crystal lattice of $Ga_{1-x}Fe_xSe$ is nearly the same as GaTe. As such we believe that Fe substitutes Ga in the lattice, as predicted by theory, and consistent with the magnetization studies presented.

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