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Anomalous second ferromagnetic phase transition as a signature of spinodal decomposition in Fe-doped GeTe diluted magnetic semiconductor


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Structural and magnetic properties of diluted magnetic semiconductor Ge$_{1-x}$Fe$_x$Te thin films are investigated. The conventional structure analysis shows $c$-axis orientation with columnar growth of the films and no indication of Fe clusters or second phase. Magnetic measurements combined with theory models reveal that two ferromagnetic phase transitions occur. We consider that the second ferromagnetic phase transition in high Fe content thin film is from a ferromagnetic phase with long range exchange interaction to a superparamagnetic phase with dipole interaction between Fe clusters, which can be viewed as a signature of spinodal decomposition in Ge$_{1-x}$Fe$_x$Te material.

Spin manipulation has attracted much attention in last decades. It is mainly based on the diluted magnetic semiconductors (DMSs) which are synthesized by substituting magnetic or appropriate rare earth ions onto lattice sites of the host semiconductors. Extensive studies have been done to explore suitable DMSs for spintronic devices. But all the efforts face the question: whether the ferromagnetism in DMSs comes from inherent exchange interaction or magnetic clusters caused by spinodal decomposition? For example, the III-V DMS InMnAs has been applied to fabricate the spin injector. However, the Mn rich nano-clusters is observable. A promising II-VI DMS Co-ZnO has been found to have high Curie temperature ($T_C$). But whether the magnetic property is inherent or not is suspectable. Spinodal decomposition is known to cause the aggregation of magnetic ions in the host semiconductor but does not involve the precipitation of another phase and therefore is hard to detect experimentally. This makes the research of DMSs into a contradictory situation concerning the origin of ferromagnetism: no observation of clusters, but the concentration of magnetic ions or carriers is too low to mediate an efficient long range exchange interaction. Indeed, some groups reported they observed magnetic ion-rich nanocrystals by transmission electron microscopy (TEM), but the clusters were embedded artificially. There lacks a direct evidence to confirm the existence of magnetic clusters due to the spinodal decomposition in DMSs. In this letter, we report a second ferromagnetic phase transition which is caused by the coexistence of ferromagnetic GeFeTe phase and Fe clusters in Ge$_{1-x}$Fe$_x$Te films. It provides direct evidence that the spinodal decomposition exists in DMSs and influences the magnetic property.

Ge$_{1-x}$Fe$_x$Te films were deposited on Si (001) substrate by pulsed laser deposition. The structure of the films was analyzed by x-ray diffraction (XRD) and TEM. The magnetic measurement was performed using a superconducting quantum interference device (SQUID) magnetometer. The transport property was determined by Hall effect measurement.

Figure 1(a) shows the XRD patterns of Ge$_{1-x}$Fe$_x$Te films. Only (003), (006), and (009) peaks were observed in the films deposited on Si (001) substrate, indicating a preferred (001) oriented rhombohedral structure. As the content of Fe increases up to $x=0.38$, some secondary phase of FeTe can be observed. The lattice parameter $c$ of Fe doped GeTe films was found to increase slightly with an increase of Fe content as listed in Table I. Cross-sectional high-resolution TEM (HRTEM) and selected area electron diffraction (SAED) pattern of the films can provide convincing evidence of the spinodal decomposition process.
is previously reported that the material with magnetic anisotropy has an intrinsic long range ferromagnetic property. Next, we will demonstrate that the ferromagnetic behavior is dominated by magnetic anisotropy-related long range ferromagnetic exchange interaction.

It is known that the temperature dependent magnetization of a long range ferromagnetic system can be well depicted by a standard 3D spin wave model which obeys the law. We fitted the FC curve under 500 Oe magnetic field below than 2500 Oe, which can be seen in Figure 3. The measured data shows well temperature dependence, indicating a long range exchange interaction exists in Ge0.98Fe0.02Te film. A modified ZFC model was used to explain the relationship between ZFC measurement and coercive field. In ZFC treatment, the local anisotropic field \( \zeta(E) \), which can be reflected from \( H_c(T) \), resists the alignment of spin to the applied magnetic field. On the other hand, the applied magnetic field \( H_A \) and the total magnetization \( M_{FC} \) act to align the spin along the external field. Thus, a simple assumption can be made: \( M_{ZFC} \) is proportional to \( H_A \) and \( M_{FC} \), but it is inversely proportional to magnetic anisotropy or coercive field. We get the following equations:

\[
M_{ZFC}(T) \approx k H_A M_{FC}(T) / H_c(T), \quad k H_A \ll H_c, \quad (1)
\]

\[
M_{ZFC}(T) \approx M_{FC}(T), \quad k H_A \gg H_c, \quad (2)
\]

where \( k \) is a constant and \( H_A \) is a given applied magnetic field. When \( H_A \) is large, for example, 2500 Oe, the \( M_{ZFC}(T) \) will approximately equal to \( M_{FC}(T) \), which can be seen in Figure 3 that the ZFC curve is approximate to the FC curve. In principle, the external magnetic field is large enough to overcome the \( \zeta(E) \) and rotates the most spin in one direction. While \( H_A \) is small, there is a competition among \( H_A, \zeta(E) \), and thermal magnetic perturbation. We fitted the ZFC curve under the 500 Oe magnetic field. A clear cusp in the simulated curve (temperature above \( T_c \) of the ZFC curve equals to FC, not show in the figure) can be observed, which fits well with the ZFC data (Fig. 3). It gives a complex temperature dependence of \( H_c(T) \), not a simple \( H_c(T) \propto M_{ZFC}(T) \) \( \alpha^\nu \). The reproduction of ZFC measurement by the ZFC model gives further evidence that the ferromagnetism...
in Ge$_{0.98}$Fe$_{0.02}$Te film is dominated by intrinsic ferromagnetic exchange interaction.

Experimentally, we performed transport measurements to establish the relationship between carrier and ferromagnetism in Ge$_{1-x}$Fe$_x$Te films shown in Table I. Interestingly, when the maximum value of hole concentration of 1.21 x 10$^{21}$ cm$^{-3}$ at $x = 0.02$ is reached, both the average magnetic moment for Fe and the whole saturated magnetization get the maximum value, i.e., 4.4 $\mu_B$ and 14.9 emu/cm$^3$, respectively. While the hole concentrations in higher Fe content films are close with each other and the $M_s$ decreases with increasing Fe content. It shows a dependence of $M_s$ on both hole concentration and Fe content, which is most likely a Ruderman-Kittel-Kasuya-Yosida (RKKY) indirect interaction via carriers. Therefore, it is reasonable to speculate that the observed ferromagnetic phase in Ge$_{0.98}$Fe$_{0.02}$Te film is dominated by a long range ferromagnetic exchange interaction via itinerant hole.

Figure 4 shows the FC and ZFC curves of Ge$_{0.86}$Fe$_{0.14}$Te film. Regions I and II of the $M$-$T$ curves indicate a paramagnetic and ferromagnetic phase, which is consistent with Ge$_{0.98}$Fe$_{0.02}$Te film. The FC curve and cusp in ZFC curve under the 500 Oe magnetic field can be also depicted by the 3D spin wave and modified ZFC models. It means that region II in Figure 4 is also a ferromagnetic phase dominated by intrinsic ferromagnetic phase in Ge$_{0.98}$Fe$_{0.02}$Te film. The FC curve and cusp in ZFC curves indicate a paramagnetic and ferromagnetic phase, which is consistent with Ge$_{0.98}$Fe$_{0.02}$Te film.

The Curie-Weiss law fit it. As can be seen in the inset of Fig. 4, the FC curve under 500 Oe at temperature lower than 25 K is reproduced by $\chi = \chi_0 + c/(T - \theta)$, where $c = 2.997$ emuK/cm$^3$Oe is the Curie constant and $\theta = -4.067$ K is the Curie-Weiss temperature. The obedience of Curie-Weiss law and the apparent magnetization indicate a superparamagnetic phase for Ge$_{0.86}$Fe$_{0.14}$Te thin film at temperature lower than 25 K. It implies the existence of Fe cluster in Ge$_{1-x}$Fe$_x$Te system when the Fe content $x$ reaches up to 0.14 which can not be detected by XRD and TEM.

We believe that many of the observed DMSs may contain considerable magnetic clusters mixed with DMS phase, quite similar to our Ge$_{0.86}$Fe$_{0.14}$Te sample. In region II of Fig. 4, the magnetic anisotropy field $H_{an}$ dominates the magnetization among external magnetic field, thermal magnetic perturbation, and dipole field between Fe clusters. As the temperature decreases to the critical temperature of 25 K, the dipole field increases rapidly due to the decrease of thermal perturbation, resulting in the appearance of a ferromagnetic phase dominated by the superparamagnetic effect. Therefore, we conclude that the ferromagnetic phase transition in Ge$_{0.86}$Fe$_{0.14}$Te thin film is from ferromagnet with magnetic anisotropy to superparamagnetic phase at the critical transition temperature of 25 K. There is no second magnetic phase transition in Ge$_{0.98}$Fe$_{0.02}$Te film while the doped content increases to $x = 0.14$, a distinct ferromagnetic phase transition implying the existence of Fe clusters is observed, which could be considered as a signature of the spinodal decomposition in Fe doped GeTe DMSs.

In summary, we demonstrate that the anomalous ferromagnetic phase transition in Ge$_{1-x}$Fe$_x$Te films is due to the co-existence of DMS phase and Fe clusters. Since the clusters in DMSs are hard to detect with conventional crystallographic methods, we consider that the second ferromagnetic phase transition is a direct evidence for spinodal decomposition.

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