

Ferromagnetic semiconducting behavior of $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ compounds

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The magnetic and electrical transport properties of ferromagnetic semiconductor $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ ($x=0.04, 0.08,$ and 0.14) compounds have been investigated. These compounds have ferromagnetic behavior with hysteresis loops showing a coercivity of 300–985 Oe at 5 K. The hysteresis loop is observed even at room temperature for $\text{Mn}_{0.86}\text{Cr}_{0.14}\text{Te}$. The substitution of Cr for Mn leads to a change from an antiferromagnetic state of MnTe to a ferromagnetic (or ferrimagnetic) state of $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$. Moreover, the incorporation of Cr into the host antiferromagnetic semiconductor MnTe lattice is confirmed by the structural characterization, which proves further that the ferromagnetic properties are not a result of the secondary phase. The typical feature of the thermally activated conduction processes for semiconductors has been verified by electrical property measurement.

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Ferromagnetic semiconductors are key materials for spin injection in electronic and optoelectronic semiconductor devices,¹ such as spin transistors, polarizing light-emitting diodes, and nonvolatile storage devices² that can be controlled by weak magnetic fields. Usually, ferromagnetic semiconductors are obtained by doping magnetic impurities into host non-magnetic semiconductors, such as Mn-Ge, Mn-Si, Cr-Ge, and Mn-CuO.^{3–6} Recently, room temperature ferromagnetism was reported in Mn-GaN, Cr-GaN, Co-TiO₂, and Co-ZnO.^{7–10} Although the ferromagnetism in those materials was attributed to the expected ferromagnetism of the diluted magnetic semiconductors (DMSs) on the basis of magnetization measurements and crystallographic studies, it is still doubtful whether the ferromagnetism observed comes from the DMSs or the magnetic precipitates.¹¹ To obtain a real ferromagnetic semiconductor, it is important to ensure that after the doping, the same/similar crystal structure still exists with certain solid solubility between magnetic impurity and host semiconductor. On the other hand, it is interesting to detect whether any other possibilities exist for realizing a ferromagnetic semiconductor: Could the element substitution for an antiferromagnetic semiconductor induce a change from antiferromagnetic to ferromagnetic (or ferrimagnetic) state while maintaining its semiconductor behavior?

MnTe, which manifests antiferromagnetic properties with its Néel temperature $T_N=310$ K,¹² and, CrTe, a ferromagnetic material with its Curie temperature $T_C=342$ K,¹³ crystallize in a stable state as NiAs-type structure with lattice constants $a=0.4143$ nm, $c=0.6711$ nm¹⁴ and $a=0.4008$ nm, $c=0.6252$ nm,¹³ respectively. MnTe is also a *p*-type semiconductor with a band gap of $E_g=0.74$ eV.¹⁵ Because of the same crystal structure and comparatively small difference in their lattice constants, in this work, we attempt to combine the ferromagnetic metal conductor CrTe with the antiferromagnetic semiconductor MnTe, in order to synthesize a ferromagnetic semiconductor material.

$\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ polycrystalline compounds with the nominal composition of $x=0.05, 0.1,$ and 0.15 were prepared by melting appropriate metals with purity higher than 99.9% in a magnetocontrolled arc furnace under a high purity argon at-

mosphere. An excess (5%) of Mn and Te over the stoichiometric amount was added to compensate for their mass loss during melting. After melting, the ingots were ground and pulverized into powders, which were pressed into pellets. The pellets were annealed for 72 h at 725 °C and then quenched. X-ray diffraction (XRD) studies were carried out at room temperature with Cu K_α radiation in a $D/\text{max-}\gamma\text{A}$ diffractometer with a graphite crystal monochromator. The distribution and constitution of the phases were analyzed by using a scanning electron microprobe (SEM). The final compositions of the matrix of $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ compounds are $x=0.04, 0.08,$ and 0.14 , which are lower than the nominal composition of $x=0.05, 0.1,$ and 0.15 , respectively. A superconducting quantum interference device (SQUID, Quantum Design) was employed to investigate the magnetic properties of the compounds. The temperature dependence of resistivity was recorded by a standard four-probe technique in the range of 350 K to 5 K at a constant current of 1 mA.

Figure 1 shows XRD patterns for $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ ($x=0, 0.04, 0.08,$ and 0.14 ; hereafter we denote our compounds using final compositions of the matrix) compounds, which reveal that all the samples display peaks characteristic for the NiAs-

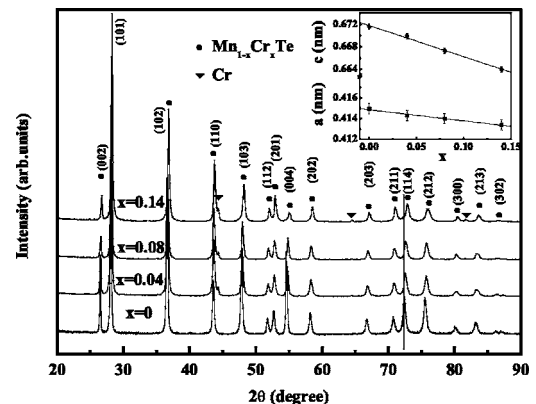


FIG. 1. XRD patterns and (the inset) Cr concentration dependence of lattice constants of $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ ($x=0, 0.04, 0.08,$ and 0.14) compounds.

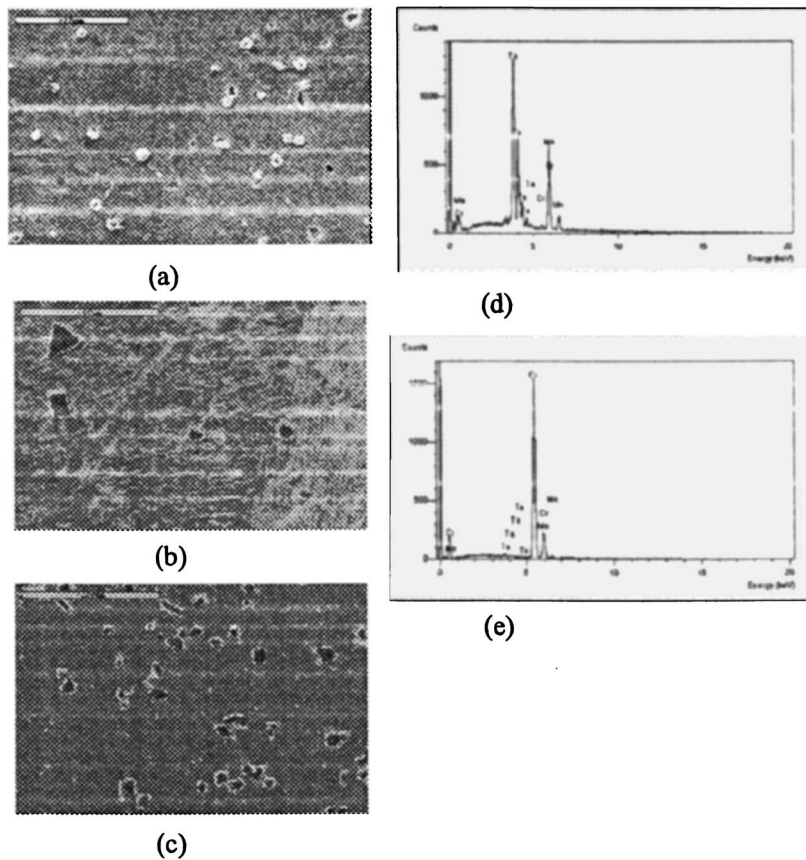


FIG. 2. SEM pictures of (a) $\text{Mn}_{0.96}\text{Cr}_{0.04}\text{Te}$, (b) $\text{Mn}_{0.92}\text{Cr}_{0.08}\text{Te}$, (c) $\text{Mn}_{0.86}\text{Cr}_{0.14}\text{Te}$, and EDS of (d) the primary and (e) the secondary phases.

type structure with a small amount of Cr as the impurity phase. With increasing Cr concentration, the positions of the XRD peaks of the main phase shift towards higher angles, indicating the decrease of the lattice parameters a and c (see the inset of Fig. 1 for the quantitative analysis of the lattice parameters with the error of $\pm 0.005 \text{ \AA}$ which follow the Vegard's law). The lattice contraction results from the Cr substitution for Mn in MnTe lattice, suggesting that $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ compounds form indeed. Figure 2 shows the SEM pictures of $\text{Mn}_{0.96}\text{Cr}_{0.04}\text{Te}$, $\text{Mn}_{0.92}\text{Cr}_{0.08}\text{Te}$, and $\text{Mn}_{0.86}\text{Cr}_{0.14}\text{Te}$ compounds, together with the energy dispersive x-ray spectroscopy (EDS) results of the primary and the secondary phases. It is illustrated further that the primary phase is $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ compound and the secondary phase is antiferromagnetic Cr, without existence of precipitates of other phases. No MnTe and CrTe phases are detected by either XRD or SEM (and EDS). Furthermore, the volume fraction of the secondary phase, antiferromagnetic Cr, estimated from the SEM pictures, is less than 3% for the three samples.

Figure 3 shows the temperature dependence of the magnetization between 5 and 380 K of $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ ($x=0, 0.04, 0.08, \text{ and } 0.14$) compounds in a magnetic field of 50 Oe. For MnTe, a sudden rise is observed at 310 K, indicating an antiferromagnetic (AFM) order. The rise in M - T curve at low temperatures is due to a magnetoelastic coupling which strengthens intraplanar ferromagnetic interactions relative to interplanar antiferromagnetic interaction in the MnTe lattice.¹⁶ For $\text{Mn}_{0.96}\text{Cr}_{0.04}\text{Te}$, there are two transition temperatures, where the higher one ($T_C \sim 305 \text{ K}$) corresponds to the transition from paramagnetic to ferrimagnetic (FI) state,

and the lower one ($T_1 \sim 56 \text{ K}$) the transition from ferrimagnetic to ferromagnetic (FM) state. Similar results can be observed for $\text{Mn}_{0.92}\text{Cr}_{0.08}\text{Te}$. For $\text{Mn}_{0.86}\text{Cr}_{0.14}\text{Te}$, it is clearly demonstrated that the ferrimagnetic order persists over 380 K, the upper limit of our measurement. It is noticed that the magnetic moment of $\text{Mn}_{0.86}\text{Cr}_{0.14}\text{Te}$ is about 25 times that of MnTe. Thus few resemblances exist in M - T curves between MnTe and $\text{Mn}_{0.86}\text{Cr}_{0.14}\text{Te}$, since the values of the magnetic moments of the two compounds are not in same order. This fact excludes the possibility of the existence of a possible phase separation. Figure 4(a) shows the magnetization as a function of the external magnetic field at 5 K for $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ compounds. Clear magnetic hysteresis loops can be observed for $\text{Mn}_{0.96}\text{Cr}_{0.04}\text{Te}$, $\text{Mn}_{0.92}\text{Cr}_{0.08}\text{Te}$, and $\text{Mn}_{0.86}\text{Cr}_{0.14}\text{Te}$ with coercive fields of 300, 310, and 985 Oe, respectively, indicating the ferromagnetic behaviors of the materials. On the contrary, MnTe compound shows a linear M - H dependence with negligible coercive field. Figure 4(b) shows M - H curves at 5, 40, 285, and 295 K for $\text{Mn}_{0.86}\text{Cr}_{0.14}\text{Te}$. With increasing temperature, both the magnetization and the coercive field decrease. But the hysteresis loop still can be observed even at room temperature (see the inset for $x=0.14$). Considering any possible effects of magnetic clusters (or precipitates) on the magnetic properties observed above, we find from literatures that ferromagnetic compounds such as CrTe, Cr_2Te_3 , Cr_3Te_4 , and Cr_5Te_8 have their Curie temperatures of 342 K,¹³ 180 K,¹⁷ 330 K,¹⁸ and 220 K,¹⁹ which are all different with those of the present compounds. Note that Cr is an antiferromagnetic metal. Thus the magnetic properties observed in our MnTe-CrTe system appear to exclude possible cluster effects.

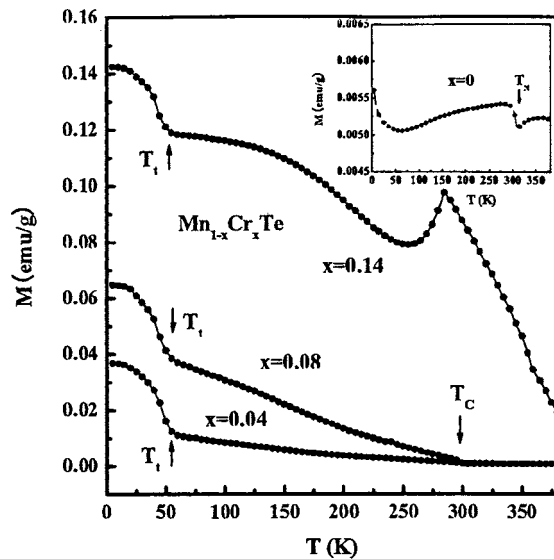


FIG. 3. Temperature dependence of the magnetization of $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ ($x=0, 0.04, 0.08$, and 0.14) compounds at a magnetic field of 50 Oe.

Then it is the most interesting to understand how the magnetic behaviors of the $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ compounds change with increasing the Cr content, in consideration of the antiferromagnetic behavior of MnTe and the ferromagnetic one of CrTe. It is well established that in Mn-doped II-VI compounds, Mn ions neither introduce nor bind carriers except giving rise to the presence of localized spins,²⁰ which results in the paramagnetic, antiferromagnetic, or spin glass behavior of the material because of short-range superexchange interactions. In III-V compounds, Mn atoms when substituting trivalent metals supply both localized spins and holes, which can acquire ferromagnetic character by ferromagnetic interactions mediated by bands holes.^{21,22} Similar results can be observed in Cr-doped compounds such as Cr-Ge,⁵ Cr-GaN,⁸ and Cr-AlN.²³ So, the role of band carriers in promoting ferromagnetic ordering between localized spins is very important in ferromagnetic semiconductors. In the present

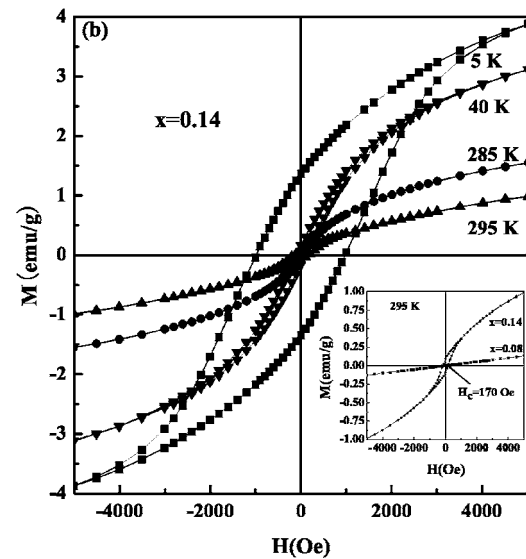
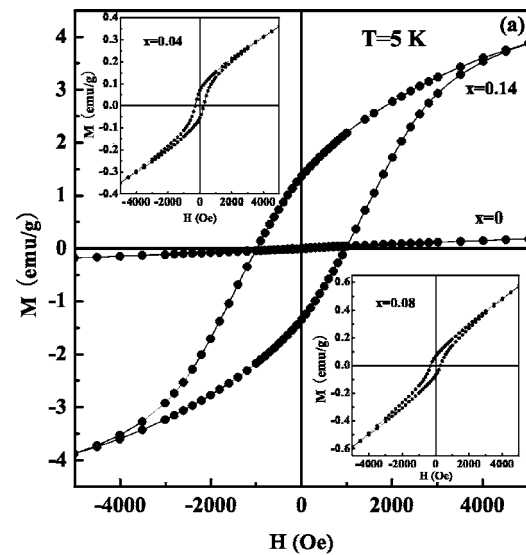


FIG. 4. (a) Magnetic field dependence of magnetization at 5 K for $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ ($x=0, 0.04, 0.08$, and 0.14) compounds. (b) $M-H$ curves at 5, 40, 285, and 295 K for $\text{Mn}_{0.86}\text{Cr}_{0.14}\text{Te}$. The inset in (b) shows $M-H$ curves at 295 K for $\text{Mn}_{0.92}\text{Cr}_{0.08}\text{Te}$ and $\text{Mn}_{0.86}\text{Cr}_{0.14}\text{Te}$.

$\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ system, the holes are introduced when Cr atoms ($3d^54s^1$) substitute Mn atoms ($3d^54s^2$). Similar to Mn-doped III-V compounds, one possible mechanism for the origin of ferromagnetism in the $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ compounds is the carrier-mediated spin-spin interaction.²⁰ Cr atoms substituting Mn atoms supply both localized spins and holes. With increasing Cr concentration, higher density of holes are introduced into the system and Cr-Cr ferromagnetic interactions mediated by band holes increase, which can be seen from the Cr concentration dependence of the magnetization shown in Fig. 3. Another possibility is the change of the magnetic structure from antiferromagnetic to canted spin structure (i.e., nonlinearly ferromagnetic or ferrimagnetic state) with the Cr substitution for Mn, because of different signs of Mn-Mn and Cr-Cr interactions in the NiAs-type structure,²⁴ which were observed also in $\text{Mn}_{1-x}\text{Cr}_x\text{Sb}$ system.^{25,26} The magnetization shown in Fig. 3 increases below T_c as the temperature de-

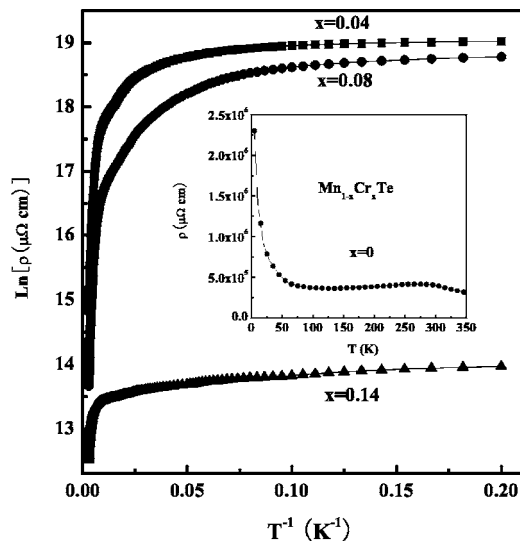


FIG. 5. Resistivity on a natural logarithmic scale as a function of $1/T$ for $\text{Mn}_{0.96}\text{Cr}_{0.04}\text{Te}$, $\text{Mn}_{0.92}\text{Cr}_{0.08}\text{Te}$, and $\text{Mn}_{0.86}\text{Cr}_{0.14}\text{Te}$ (the inset shows the temperature dependence of the resistivity of MnTe).

creases, which is the result of magnetic frustration introduced by the competition between AFM and FM interactions.²⁷

Temperature dependence of resistivity was measured for the present four compounds. For MnTe (see the inset of Fig.

5), the positive coefficient of the resistivity below the magnetic-ordering temperature $T_N \sim 310$ K is due to the spin disorder scattering with a large contribution from the influence of magnon drag.²⁸ For $\text{Mn}_{0.96}\text{Cr}_{0.04}\text{Te}$, $\text{Mn}_{0.92}\text{Cr}_{0.08}\text{Te}$, and $\text{Mn}_{0.86}\text{Cr}_{0.14}\text{Te}$, the resistivities increase dramatically with decreasing temperature, which decrease with increasing the Cr concentration. For $\text{Mn}_{0.92}\text{Cr}_{0.08}\text{Te}$, a positive magnetoresistance of about 30% can be observed at low temperatures in a field of 50 kOe, similar to observation in Cr-doped bulk Ge single crystal⁵ and Co-doped anatase thin film.⁹ As can be seen in Fig. 5, the natural logarithm of resistivities of the $\text{Mn}_{0.96}\text{Cr}_{0.04}\text{Te}$, $\text{Mn}_{0.92}\text{Cr}_{0.08}\text{Te}$, and $\text{Mn}_{0.86}\text{Cr}_{0.14}\text{Te}$ compounds are proportional to $1/T$, which can be fitted well with an Arrhenius plot, or $\rho = \rho_0 \exp(E_a/k_B T)$, the typical feature of the thermally activated conduction processes for semiconductors.⁴

In summary, the structural, magnetic, and electrical transport properties of the ferromagnetic semiconductor $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ compounds have been investigated. Structural analysis with XRD and SEM confirm the incorporation of Cr in the lattice of antiferromagnetic MnTe compound and the formation of the $\text{Mn}_{1-x}\text{Cr}_x\text{Te}$ compounds. Ferromagnetism is observed in $\text{Mn}_{0.96}\text{Cr}_{0.04}\text{Te}$, $\text{Mn}_{0.92}\text{Cr}_{0.08}\text{Te}$, and $\text{Mn}_{0.86}\text{Cr}_{0.14}\text{Te}$ compounds, and their semiconductor conduction behaviors are verified.

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