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Room temperature ferromagnetism in diluted magnetic semiconductor $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nanoparticles synthesized by chemical method

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Nanoparticles of diluted magnetic semiconductor $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ with various Cr concentrations were synthesized by a chemical method, and their magnetic properties were investigated. The synthesized nanoparticles show ferromagnetism, and the saturation magnetization increased with increasing Cr concentration in the range from $x=0.002$ to $x=0.02$. The $\text{Zn}_{0.98}\text{Cr}_{0.02}\text{Te}$ nanoparticles showed ferromagnetism above room temperature, where the Curie temperature T_C was estimated to be about 520 K. This is much higher than the reported value of T_C in the $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ thin films. © 2008 American Institute of Physics. [DOI: 10.1063/1.2931705]

Diluted magnetic semiconductors (DMSs), in which electron spin, in addition to electron charge, plays a significant role through the interaction of s and p electrons with d electrons in a semiconductor, are expected to be a key material for a research field: spintronics.¹ The room temperature (RT) ferromagnetism is indispensable for the device application of DMSs. The RT ferromagnetism was observed in some DMSs, e.g., $\text{TiO}_2\text{:Co}$ (Ref. 2) and ZnO:Co .³ However, the magnetic origin of DMSs has been insufficiently understood based on conflicting viewpoints, i.e., ferromagnetism is attributed to the intrinsic nature of DMSs and is an extrinsic contribution from magnetic precipitates.

The Cr based II-VI-type DMS has attracted attention since the RT ferromagnetism of $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ has been theoretically predicted.⁴ Recently, the ferromagnetic behavior was observed at 300 K in $\text{Zn}_{0.8}\text{Cr}_{0.2}\text{Te}$ thin film, prepared by molecular beam epitaxy (MBE), where the intrinsic nature of ferromagnetism was verified based on the magnetic and magneto-optical properties.^{5,6} In addition, $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ is also applicable for magneto-optical devices because the large magneto-optical effect is expected without application of magnetic field even at RT.⁷

The preparation of $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ is difficult using conventional method at thermal equilibrium state because ZnTe and CrTe hardly form their solid solution. Thus, the low-temperature MBE method has been exclusively used in previous works. In a chemical method, on the other hand, the synthesis of $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nanoparticles can proceed in a non-equilibrium process. Thus, the substitution of Cr with Zn, enough to show ferromagnetism at RT, may be easily realized. So far, the substitution of Mn and Co with Zn in ZnO nanoparticles has been performed using chemical methods.^{8,9} However, the preparation of $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nanoparticles, showing ferromagnetic behavior above a RT, has not been reported. The purpose of this work is to synthesize the $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nanoparticles showing the RT ferromagnetism

and to characterize the temperature and Cr concentration dependencies of magnetization.

$\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nanoparticles were synthesized by the hot soap method¹⁰ by which the size-controlled and good crystalline nanoparticles can be obtained. Diethylzinc [$\text{Zn}(\text{CH}_2\text{CH}_3)_2$], chromium acetate ($[\text{Cr}(\text{CH}_3\text{COO})_2]_2$), and trioctylphosphine telluride ($[\text{CH}_3(\text{CH}_2)_7]_3\text{PTe}$) were used as reaction precursors. Trioctylphosphine oxide ($[\text{CH}_3(\text{CH}_2)_7]_3\text{PO}$) and trioctylphosphine ($[\text{CH}_3(\text{CH}_2)_7]_3\text{P}$) were used as the reaction solvent and surfactants. In this method, the $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nuclei are generated after the thermal decomposition of reaction precursors, and the particles grow by collision of nuclei with each other. The reaction temperature was 320 °C, and the synthesis time was 50 min. After cooling the reaction solution to 80 °C, the nanoparticles were obtained as a precipitate by centrifuging the mixture of ethanol and the reaction solution. All the synthesis procedures were performed in the globe box (DB-ZL-TH from Miwa Mfg. Co., Ltd.) which was filled with pure Ar gas with water and O_2 less than 0.1 ppm. The crystal structure and lattice constant of the synthesized nanoparticles were studied by x-ray diffraction (XRD). A transmission electron microscope (TEM) was used for the observation of shape and determination of particle size. Furthermore, an electron probe microanalyzer and inductively coupled plasma atomic emission spectroscopy (ICP-AES) were used for the evaluation of composition, and a commercial superconducting quantum interference device magnetometer was used for magnetic measurements.

The TEM image in Fig. 1 shows the spherical-shaped nanoparticles of $\text{Zn}_{0.98}\text{Cr}_{0.02}\text{Te}$. The Gaussian distribution of the diameters, with an average value of 14.7 nm, was evaluated based on the TEM image, which is characteristic in nanoparticles synthesized by the hot soap method. All the diameters of nanoparticles of $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ and ZnTe, synthesized in the present work, were ~ 15 nm.

The XRD pattern of $\text{Zn}_{0.98}\text{Cr}_{0.02}\text{Te}$ nanoparticles corresponds to the zinc blend structure with a lattice constant of 6.1003 Å, which is slightly larger than that of ZnTe nanopar-

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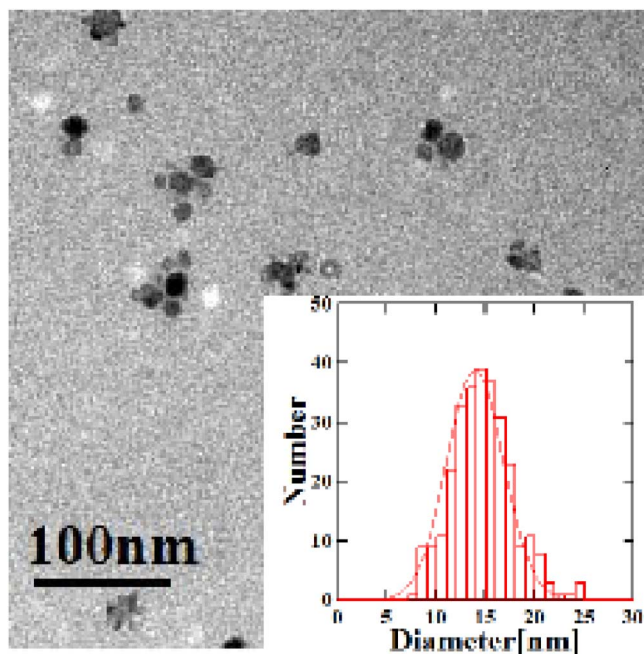


FIG. 1. (Color online) TEM image of $\text{Zn}_{0.98}\text{Cr}_{0.02}\text{Te}$ nanoparticles. Inset shows the Gaussian distribution of diameters.

ticles (6.0881 Å). The lattice constant of $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nanoparticles linearly increases with increasing Cr concentration up to $x=0.02$, above which it decreases, as shown in Fig. 2. Such a change in lattice constant was observed also in the $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ thin film.⁶ This indicates the substitution of Cr with Zn, i.e., the synthesis of $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nanoparticles, up to $x=0.02$.

The magnetic field dependent magnetization of $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nanoparticles with $0.002 < x < 0.1$ at 5 K shows the saturation behavior [Fig. 3(a)] together with the linearly increasing component χH . The ferromagnetic component M_{ferro} , which is obtained by subtracting χH from the total magnetization, linearly increases with increasing Cr concentration up to $x=0.02$, above which it rapidly decreases. This is similar to the Cr concentration dependent lattice constant in Fig. 2. We verify the positive linear correlation between the value of the saturation magnetization M_s and lattice parameter in Fig. 3(b). Provided that the lattice constant is proportional to the concentration of Cr, which is intrinsically substituted with Zn in the $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nanoparticles, this relation shows that the ferromagnetic magnetization is propor-

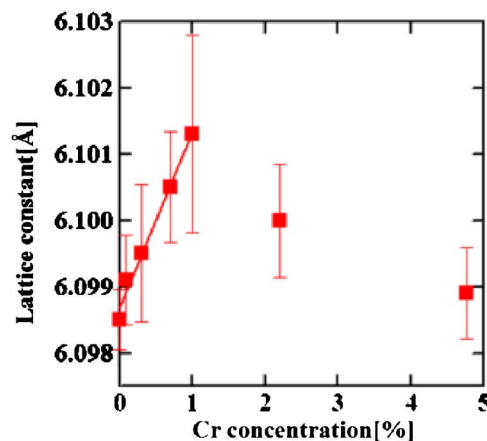


FIG. 2. (Color online) Cr concentration dependence of the lattice constant of $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nanoparticles with $0.002 < x < 0.1$.

tional to the Cr content. The peculiar behavior of the lattice constant and M_s , observed above $x > 0.02$, indicates that the difference between the nominal and intrinsic Cr concentrations becomes pronounced in the higher Cr concentration region. This can be explained in terms of the cluster formation of Cr atoms prior to the synthesis of the particle, which is rapidly accelerated when the Cr ion concentration increases up to a certain level in the reaction precursors. The cluster formation was also verified by the TEM observation.

The temperature dependent magnetizations of $\text{Zn}_{0.98}\text{Cr}_{0.02}\text{Te}$ nanoparticles are shown in Fig. 4, where the total magnetization ($=M_{\text{ferro}} + \chi H$) at 300 K is also shown. The hysteresis is observed even at 400 K, i.e., the ferromagnetism remains even at 400 K. This strongly indicates the intrinsic nature of ferromagnetic $\text{Zn}_{0.98}\text{Cr}_{0.02}\text{Te}$ because the CrTe compound, which can be segregated as a ferromagnetic by-product, has a Curie temperature T_C of 360 K.¹¹ The saturation magnetization M_s of $\text{Zn}_{0.98}\text{Cr}_{0.02}\text{Te}$ nanoparticles slightly decreases as temperature increases. The Curie temperature of $\text{Zn}_{0.98}\text{Cr}_{0.02}\text{Te}$, evaluated using a fitting by Brillouin function, is ~ 520 K, where the g factor of 2 and the spin quantum number S of 2 for Cr^{2+} were assumed. This evaluated value of T_C is much higher than that reported for the $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ thin films.⁴

Finally, we note that the ICP-AES measurement showed a maximum Fe concentration of 23 ppm in the $\text{Zn}_{0.98}\text{Cr}_{0.02}\text{Te}$ nanoparticles, which may give the magnetic contribution of ~ 0.001 emu/g although this does not explain the observed

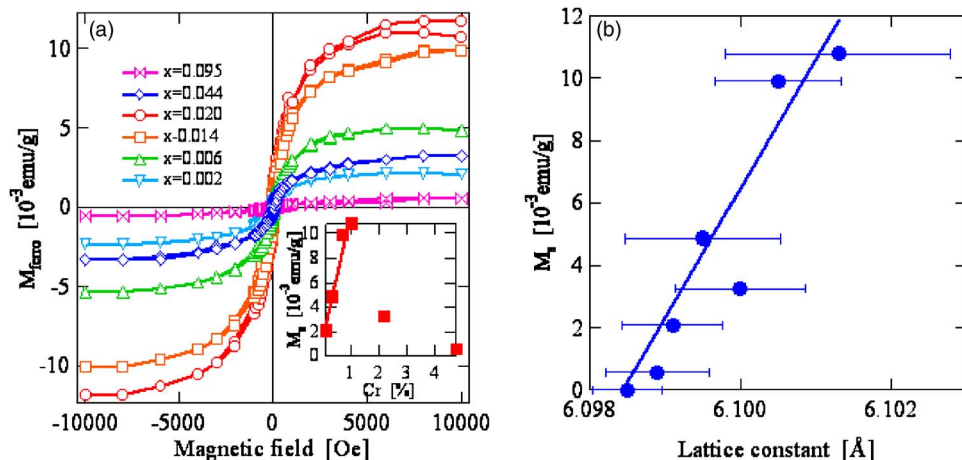


FIG. 3. (Color online) Magnetic field dependence of M_{ferro} of $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nanoparticles ($0.002 < x < 0.1$) at 5 K. Inset shows the Cr concentration dependence of M_s . M_s is plotted as a function of the lattice constant in (b).

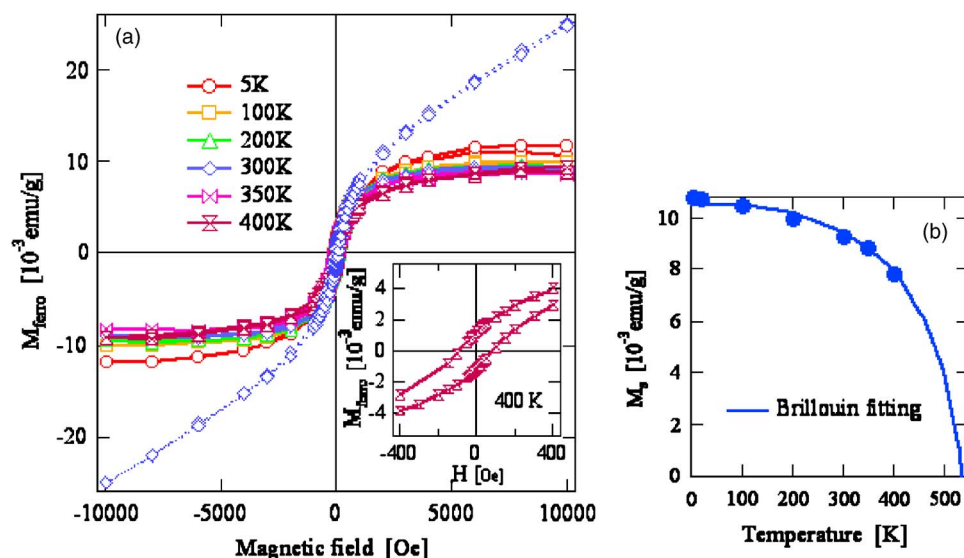


FIG. 4. (Color online) Magnetic field dependence of M_{ferro} of $\text{Zn}_{0.98}\text{Cr}_{0.02}\text{Te}$ nanoparticles. The total magnetization ($=M_{\text{ferro}} + \chi H$) at 300 K is also shown by the dotted curve. Inset shows the enlargement in low-field data at 400 K. (b) The temperature dependence of saturation magnetization M_s , fitted by a Brillouin function.

magnetization. Thus, we conclude that the origin of ferromagnetism of the $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nanoparticles is intrinsic in DMS.

In summary, the $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nanoparticles with the average diameter of ~ 15 nm, synthesized by the hot soap method, show ferromagnetism at $0.002 < x < 0.1$. The saturation magnetization increases as the intrinsic Cr content increases and the ferromagnetic behavior is observed even at 400 K in $\text{Zn}_{0.98}\text{Cr}_{0.02}\text{Te}$. All the data support the intrinsic origin of RT ferromagnetism in the $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ nanoparticles.

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