Crystallographic and magnetic properties of Mn$_2$GeTe$_4$ and Fe$_2$GeTe$_4$ compounds

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Recibido el 30 de noviembre de 2006; aceptado el 8 de octubre de 2007

X-ray powder diffraction measurements, at room temperature, and magnetic susceptibility $\chi$ measurements, in the temperature range from 2 to 300 K, were made on polycrystalline samples of Mn$_2$GeTe$_4$ and Fe$_2$GeTe$_4$ compounds, which would be useful for spintronic device production. Magnetization measurements at various temperatures were carried out on these compounds. From the analysis of the x-ray diffraction lines, it was found that both Mn$_2$GeTe$_4$ and Fe$_2$GeTe$_4$ have an orthorhombic olivine structure-type (SG: Pnma No. 62, z=4). It was found that Mn$_2$GeTe$_4$ has a Néel temperature of 30 K and shows mainly antiferromagnetic behaviour with a weak superimposed ferromagnetic component which is attributed to spin canting. The resulting $1/\chi$ versus T curve for Fe$_2$GeTe$_4$ was found to have a form which is typical of a ferromagnetic material with a Curie temperature $T_C$ of 149.9 K.

Keywords: Magnetic semiconductors materials; magnetic susceptibility; antiferromagnetism; ferromagnetism.

Medidas de rayos-x, a temperatura ambiente, y de susceptibilidad magnética, en el rango entre 2 y 300 K, fueron hechas en muestras policristalinas de los compuestos Mn$_2$GeTe$_4$ y Fe$_2$GeTe$_4$, los cuales podrían ser útiles en la producción de dispositivos espintronicos. Medidas de magnetización a varias temperaturas fueron ejecutadas en esos compuestos. Del análisis de las líneas de difracción de rayos-x, se encontró que Mn$_2$GeTe$_4$ y Fe$_2$GeTe$_4$ tienen estructura ortorrombica del tipo Olivina (SG: Pnma No. 62, z=4). Se encontró que Mn2GeTe4 tiene una temperatura de Néel de 30 K, muestra un comportamiento principalmente antiferromagnético con una componente ferromagnética débil superpuesta la que es atribuida a spin canting. Se encontró que la curva resultante de $1/\chi$ versus T del Fe$_2$GeTe$_4$ tiene una forma típica de un material ferromagnético con una temperatura de Curie $T_C$ de 149.9 K.

Descriptores: Materiales semiconductores magnéticos; susceptibilidad magnética; antiferromagnetismo; ferromagnetismo.

PACS: 74.25.Ha; 75.40.-s; 75.50.Ee; 75.50.Pp

1. Introduction

Magnetic semiconducting materials (MSM) are of interest because of the manner in which the magnetic behavior associated with the concerned magnetic ion can modify and complement the semiconductor properties [1]. These MSM have received attention because of their potential application in optoelectronic and magnetic devices. The materials that have been mostly studied are the semimagnetic semiconductor alloys obtained from the tetrahedrally coordinated II-VI semiconductor compounds by replacing a fraction of the group II cations with manganese, giving alloys such as Cd$_{1-x}$Mn$_x$Te [1]. These studies have been extended to the investigation of the tetrahedrally coordinated I-III-VI$_2$, II-III$_2$VI$_4$ and I$_2$-II-IV-VI$_4$ compounds and alloys [2][3][4]. It has been found that most of these materials are antiferromagnetic showing spin glass behavior, bound magnetic polarons, large magneto-optical effects, etc. Recently, there has been a considerable interest in ferromagnetic semiconductor materials, with a Curie temperature near room temperature. The interest in these materials is due to their potential application in spintronic devices, because of the controlling degree of freedom from the spin and the charge and/or the alloy [5]. Another group of compounds which would show a similar tetrahedrally bounded form, as well as a ferromagnetic spin configuration, are the defect II$_2$-IV-VI$_4$ compounds with II=Mn, Fe and/or Co. These materials can be regarded as being derived from the II-VI binaries, in which the cation has been substituted by two types of cations and an array of vacancies is introduced. The crystal structure of various II$_2$-IV-VI$_4$ compounds has been investigated by several workers, and it has been indicated that three structure types exist: a distorted spinel structure [6], a olivine-type structure (Mg$_2$SiO$_4$, space group Pnma), and a structure type with the orthorhombic space group Cmmm reported for Mn$_3$SnS$_4$ [7]. The magnetic properties of these materials have not as yet been reported.

In the present program of work, we are studying the properties of some II$_2$-IV-VI$_4$ materials with II=Mn, Fe: IV=Si, Ge, Sn and VI= Se, Te. The aim of the present paper is to show some results of the initial work on the crystallographic and magnetic properties of the Mn$_2$GeTe$_4$ and Fe$_2$GeTe$_4$ compounds.

2. Samples and measurements

The polycrystalline samples used were prepared by the usual melting and annealing technique. The appropriate amounts of the component elements were melted together, at 1150°C for three hours, and then cooled to 550°C. After annealing at
this temperature, the ingot was very slowly cooled to room temperature. From previous work, this treatment was found to give a very well ordered sample. X-ray powder diffraction pattern of each compound was recorded at 300 K to check the equilibrium conditions as well as the presence of secondary phases. Measurements of magnetic susceptibility \( \chi \) as a function of temperature \( T \) in the range 2 - 300 K were made with a fixed value of magnetic field \( B \) of 100 G, using a Quantum Design SQUID magnetometer. Measurements of magnetization \( M \) as a function of applied field \( B \) up to 5 T were made over the temperature range 2 - 300 K with the SQUID system up to 5 T.

3. Results analysis and discussions

3.1. X-ray results and analysis

The resulting x-ray powder diffraction patterns, obtained for each compound, were indexed with the computer program DICVOL91 [8] using an absolute error of 0.03° (2\( \theta \)) in the calculations. It was found that the best solution produced by the program for \( \text{Mn}_2\text{GeTe}_4 \) as well as for the \( \text{Fe}_2\text{GeTe}_4 \) showed an orthorhombic structure with lattice parameter values of \( a=13.600(1) \) Å, \( b=10.745(1) \) Å and \( c=7.775(1) \) Å for \( \text{Mn}_2\text{GeTe}_4 \) and \( a=13.520(2) \) Å, \( b=10.699 \) Å, \( c=7.757(1) \) Å for \( \text{Fe}_2\text{GeTe}_4 \). It is to be mentioned that for the \( \text{Mn}_2\text{GeTe}_4 \) no traces of secondary phases were observed in the x-ray diffraction pattern. However, in the case of the \( \text{Fe}_2\text{GeTe}_4 \) compound, the x-ray pattern also contained additional weak diffraction lines which could be explained as due to the presence of \( \text{FeTe}_2 \) (PDF 14-419). In fact, the x-ray powder diffraction pattern obtained for each \( \text{Fe}_2\text{IV-Te}_4 \) sample prepared in this program showed traces of this \( \text{FeTe}_2 \) secondary phase; moreover, these traces were also observed in the \( \text{I}_2\text{-Fe-IV-VI}_4 \) compounds [9].

3.2. Magnetic results and analysis

The obtained magnetic susceptibility \( \chi \) vs temperature \( T \) curve for the \( \text{Mn}_2\text{GeTe}_4 \) is shown in Fig. 1 for 2K\( < T < 300 \)K, and the corresponding inverse of susceptibility \( 1/\chi \) vs \( T \) curve is illustrated in Fig. 2. It is seen from Fig. 1 that in this range of \( T \) one transition occurs, at about 30 K. It is seen in Fig. 2 that this curve is not a straight line, as in the ferromagnetic and antiferromagnetic cases. This curve has a form which is similar to that of a ferrimagnetic material. From the Néel theory of ferrimagnetism, the variation of the magnetic susceptibility \( \chi \) with temperature \( T \) in the range \( T > T_N \) is given by the relation [10]

\[
C/\chi = T - \theta_a - (T_N - \theta_a)(T - T_N)/T
\]  

(1)

where \( \theta_a \) is the asymptotic Curie-Weiss temperature, \( T_N \) is the Néel temperature, \( \theta \) is a parameter that depends upon the magnetic ion concentration, exchange interaction, etc., and \( C \) is the Curie constant given by

\[
C = N_A g^2 \mu_B^2 J(J+1)/3K_B W
\]  

(2)

where \( N_A \) is the Avogadro number, \( \mu_B \) the Bohr magneton and \( W \) the molecular weight.

Thus, using \( C, \theta_a, \theta \) and \( T_N \) as unknown parameters, a fit of the experimental curve in Fig. 1 to Eq. (1) was made for \( T \geq 115 \) K. It was found that a good fit could be obtained giving parameter values of \( C=0.0158 \) emuK/g, \( \theta_a=-375.0 \) K, \( \theta=83.9 \) K and \( T_N=117.5 \) K. The resulting fitted curve is shown in Fig. 1. It is observed that the value of \( C \) given above is 2.5 times higher that the theoretical value of \( C \) and the value of \( T_N \) is higher than the one (\( \sim 30\)K) given by the \( \chi(T) \) curve. When the theoretical value of \( C \), obtained from

\begin{figure}
\includegraphics[width=\textwidth]{figure1.png}
\caption{Variation of magnetic susceptibility \( \chi \) with \( T \) for the \( \text{Mn}_2\text{GeTe}_4 \) compound.}
\end{figure}

\begin{figure}
\includegraphics[width=\textwidth]{figure2.png}
\caption{Variation of \( 1/\chi \) with \( T \) for the \( \text{Mn}_2\text{GeTe}_4 \) compound. The line is the resulting fit of the experimental data to Eq. (1).}
\end{figure}
Eq. (2), is used with $\theta_a, \theta$ and $T_N$ treated as unknown parameters, no good fit to the $1/\chi$ versus $T$ curve was obtained. This result would indicate that below $T_N$, the $\text{Mn}_2\text{GeTe}_4$ is not ferrimagnetic and instead it consists of antiferromagnetically couple planes of spins with a weak superimposed ferromagnetic component which can be attributed to spin canting, and this mechanism can give a similar $1/\chi$ vs $T$ curve. This magnetic configuration has been observed by Bodenan et al in samples of olivine $\text{Mn}_2\text{SiSe}_4$ [11].

The obtained inverse of susceptibility $1/\chi$ vs $T$ curve for the $\text{Fe}_2\text{GeTe}_4$ compound is illustrated in Fig. 3. It can be seen from this figure that this curve has a form which is typical of a ferromagnetic material, with a Curie temperature $T_C$ of about 150 K, and no effects from the secondary $\text{FeTe}_2$ spin-glass antiferromagnetic ($\theta=-350$ K, $T_N=5$ K) phase [12] to this curve is observed in the temperature range investigated here. Figure 4 shows a typical magnetization $M$ as a function of applied field $B$ curve recorded at 20 K for this compound; in the inset of this identified figure are the initial magnetization curve, the remanent magnetization $M_r$ and the coercive field $B_C$. In the case of a ferromagnetic material, below $T_C$, the saturation magnetization $M_S$ is the important property. Figure 5 shows the resulting curve of the saturation magnetization $M_S$ against $T$. The magnetization just below $T_C$ is described by a power law [13],

$$M_S \sim (T_C - T)^\beta$$  \(3\)

where $\beta$ is the critical exponent, which is typically between 0.33 and 0.37. Thus, using values of $T_C$ in the temperature range between 148 K and 152 K with $\beta$ as an unknown parameter, a fit of the experimental curve in Fig. 5 to Eq. (3) was made for each value of $T_C$. It was found that the best fit could be obtained with $T_C=149.9$ K giving $\beta=0.367$. This value of $\beta$ is in good agreement with the typical values for the critical exponent $\beta$ quoted in the literature [13, 14].

4. Conclusions

The x-ray results showed that both $\text{Mn}_2\text{GeTe}_4$ and $\text{Fe}_2\text{GeTe}_4$ have orthorhombic olivine structure-type (SG: Pnma No. 62, $z=4$). In the case of the $\text{Mn}_2\text{GeTe}_4$, the $1/\chi$ vs $T$ curve did not show the usual linear form typical of ferromagnetic and/or antiferromagnetic cases. The experimental data could not be explained by using the Néel theory of ferrimagnetism. Thus, it is suggested that $\text{Mn}_2\text{GeTe}_4$ consists of antiferromagnetically couple planes of spins with a weak superimposed ferromagnetic component which can be attributed to spin canting, similar to the magnetic configuration reported earlier for the $\text{Mn}_2\text{SiSe}_4$ [11]. The main difference between ferrimagnetism and canted antiferromagnetism is that in the former,
magnetic ions need to be present on non equivalent crystallographic sites, while for the latter case, crystallographically equivalent sites are postulated. The resulting $1/\chi$ versus $T$ curve for Fe$_2$GeTe$_4$ was found to have a form which is typical of a ferromagnetic material. The saturation magnetization was very well fitted to a critical power law equation giving a Curie temperature $T_C$ of 149.9 K and a critical exponent $\beta = 0.367$. This value is in the range of the critical exponent values for ferromagnetic materials.

Acknowledgements

This work was supported by the CDCHT-ULA (Projects. No C-1436-06-05-AA, C-1437-06-05-Ed and C-1438-06-05-F) (Mérida-Venezuela).