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Magnetotransport properties and magnetocaloric effects of $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ compound*

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The magnetotransport properties and magnetocaloric effects of the compound $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ have been studied. With decreasing temperature, a spontaneous first-order magnetic phase transition from ferrimagnetic (FI) to antiferromagnetic (AF) state takes place at T_s=200K. A metamagnetic transition from the AF to FI state can be induced by an external field, accompanied by a giant magnetoresistance effect of 57%. The magnetic entropy changes are determined from the temperature and field dependence of the magnetization using the thermodynamic Maxwell relation. $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ exhibits a negative magnetocaloric effect, and the absolute values of $\Delta S_{\rm M}^{\rm max}$ $(T, \Delta H)$ are 4.4, 4.1, 3.6, 2.8 and 1.5 J/(kg·K) for magnetic field changes of 0–5T, 0–4T, 0–3T, 0–2T and 0–1T, respectively.

Keywords: magnetotransport properties, magnetocaloric effect, magnetic phase transition
PACC: 7530V, 7530S

1. Introduction

Since the discovery of giant magnetoresistance (GMR) [1,2] and colossal magnetoresistance (CMR),[3] the magnetoresistance (MR) effect has attracted much interest. GMR has been subsequently observed in many multilayer systems and in rare-earth intermetallic compounds such as FeRh,[4] $La_{2/3}Ca_{1/3}MnO_3$,[5] $Ce_3Fe_{29-x}T_x$,[6] $La_{0.9}Sb_{0.1}Mn_3$,[7] etc. Great efforts have been made to increase the GMR ratio which is usually low in compounds, to increase the temperature of the antiferromagnetic ordering and to lower the magnetic field for the onset of GMR. This is very important for exploring the GMR effect in new intermetallic systems.

Magnetic refrigeration is based on the magnetocaloric effect (MCE). This is an isothermal magnetic-entropy change, $\Delta S_{\rm M}(T, \Delta H)$, or an adiabatic temperature change, $\Delta T_{\rm ad}(T, \Delta H)$, of a magnetic material upon applying/removing a magnetic field. The efficiency of magnetic refrigeration depends on many variables, one of which is the magnitude of $\Delta S_{\rm M}(T, \Delta H)$ of the material. For realizing magnetic refrigeration, a large magnetic entropy change is very important. Generally, heavy rare-earth elements and their compounds are considered to be the best candidate materials for finding a large MCE due to their high magnetic moments. The highest MCE known so far, involving a second-order transition, is produced by the rare-earth metal Gd, which has been demonstrated to produce cooling between 270K and 310K.[8] Many other materials have been studied with respect to their MCEs, such as $Gd_5Si_2Ge_2$,[9] $MnFeP_{1-x}As_x$ [10] and the Heusler alloys Ni–Mn–Ga.[11] Most recently, large magnetic-entropy changes comparable to that in Gd have been observed in $La(Fe,Co)_{11.83}Al_{1.17}$,[12,13] $LaFe_{11.4}Si_{1.6}$ [14] and $LaFe_{11.5}Si_{1.5}H_{1.3}$ [15] compounds, which are 3d-transition metal rich systems. These results are of significant importance because these compounds are excellent candidates for the working materials in magnetic refrigeration and are a new class of materials to study on MCE and their applications.

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All of these results show that large MCEs are not restricted to materials with very large magnetic moments but that, in the vicinity of a phase transition, the MCE depends strongly on the type of the magnetic phase transition. This is also important for further improvement of the MCE in given materials and for exploring new materials with large MCEs.

The compound Mn_2Sb with a tetragonal Cu_2Sb structure is ordered ferrimagnetically below 550K. The ferrimagnetic (FI) structure is formed by the antiparallel arrangement of the Mn_1 and Mn_2 sublattices corresponding to the two different crystallographic positions of the Mn atoms with magnetic moments $2.1\mu_B$ and $3.9\mu_B$, respectively.[16,17] According to neutron diffraction measurements the magnetic structure can be regarded as the stacking of triple layers Mn_2–$2Mn_1$–Mn_2 with antiparallel magnetic moments on Mn_1 and Mn_2 sites in both the FI and antiferromagnetic (AF) states. The substitutions of a number of elements (Cr, Cu, Zn, Co and V) for Mn, as well as of As and Ge for Sb, result in magnetic phase transitions of first order from FI to AF states as the temperature decreases.[18,19] It has been reported that the Ga substitution has some interesting effects on magnetic structures and magnetic properties in some compounds, such as $Sm_2Fe_{14}Ga_3C_x$,[20] $Sm_2Fe_{17-x}Ga_x$ [21] and melt-spun $Sm_2Fe_{15-x}Cu_xGa_2C$ ribbons.[22] Most recently, antiferro–ferromagnetic transition has been observed in $YMn_6Sn_{6-x}Ga_x$ [23] compounds due to the replacement of part of Sn by Ga. Corresponding to the metamagnetic transition, a GMR of 32% under a magnetic field of 5T is observed at 5K in the $YMn_6Sn_{6-x}Ga_x$ sample with x=0.2. So it is worth studying the effects of Ga substitution on the magnetic structures, magnetic and electric properties of Mn_2Sb-based compounds. In particular, the well-known Kittel exchange inversion model has been applied to explain the nature of the phase transitions in Mn_2Sb-based compounds.[24] In this theory the exchange interaction depending on the interatomic distance changes its sign when the lattice parameter reaches a critical value. The chemical element, substituting the atoms in the starting matrix, is considered to be of no importance. However, some experimental results obtained for the Mn_2Sb-based compounds cannot be explained in terms of this model, e.g. the dependence of the critical temperature of the phase transition not only on the variations in lattice parameters but also on the types of substitutional atom or the large change in the electrical resistivity at the AF–FI transition.[25] To our knowledge, there is no report on the effects of Ga substitution on the Mn_2Sb-based compounds, which may be helpful to obtain additional information on the magnetic phase transitions in Mn_2Sb-based compounds. So in this paper we report on the magnetic properties, magnetotransport properties and magnetocaloric effects of the $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ compound.

2. Experiments

The sample of $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ was prepared by arc melting the constituent metals with a purity higher than 99.9% in an argon atmosphere. In order to obtain homogeneous alloys, the sample was melted three to four times. An excess (5%) of Mn over the stoichiometric amount was added to compensate for the mass loss during melting. The sample was sealed in an evacuated quartz tube and annealed at 700°C for 7 days. X-ray diffraction of the powder sample was carried out using Cu Kα radiation, and a main Mn_2Sb phase with a small amount of MnSb phase (less than 5%) was observed, which is typical of both the Mn_2Sb compound itself and its solid solution. The magnetization of the sample was measured in fields up to 5T using a superconducting quantum interference device (SQUID) magnetometer. Magnetotransport properties were measured using a standard four-probe dc method.

3. Results and discussion

Figure 1 shows the temperature dependence of the magnetization measured in a field of 0.01T for $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ in the temperature range from 5 to 350K. It is clear that a first-order magnetic phase transition from FI to AF state takes place below T_S=200K, which is close to the value for $Mn_{1.95}Cr_{0.05}Sb$ reported in Ref.[26]. At T_S, the magnetization exhibits a large temperature-induced jump, indicating that the exchange interactions between the magnetic moments change drastically. Figure 2 shows the field dependence of magnetization at different temperatures. In the temperature ranges of 160–190K and 210–240K, the temperature interval is 5K. In the range 190–210K, the temperature interval is 2K. It can be seen that application of a magnetic field induces a metamagnetic transition near T_s. The critical field of the metamagnetic transition observed decreases with increasing temperature and vanishes around 210K,

which is a little higher than that of $Mn_{1.95}Cr_{0.05}Sb$.[26] Though the Kittel theory yields, in general, a satisfactory mechanism of the AF–FI transition, the recently available experimental data, including this work, suggest that the nature of the AF–FI transition in Mn_2Sb-based compounds should be associated with the itinerant magnetism of the d-electrons and the peculiarity of the electronic structure. According to band calculations of Mn_2Sb, the 3d-electrons of Mn have an itinerant character and the Fermi level lies between two peak structures on the curve of the density of electronic states (DOS).[27,28] Thus the AF–FI transition in $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ can be explained as being due to the doping element, which results in the change of d-electron concentration and hence a large decrease of the DOS near the Fermi level. In accordance with this, the AF–FI transition must be accompanied by an abrupt increase of electrical resistance.

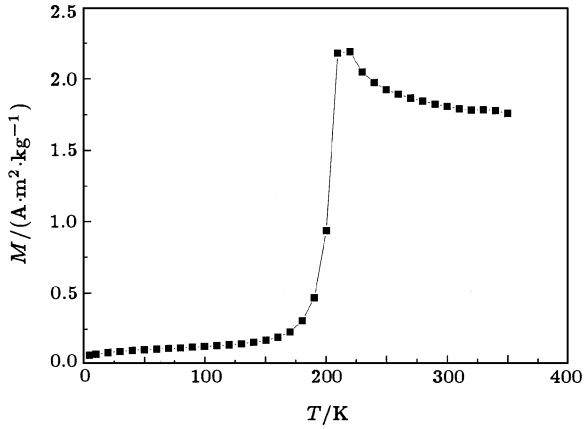


Fig.1. Temperature dependence of the magnetization at 0.01T for $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$.

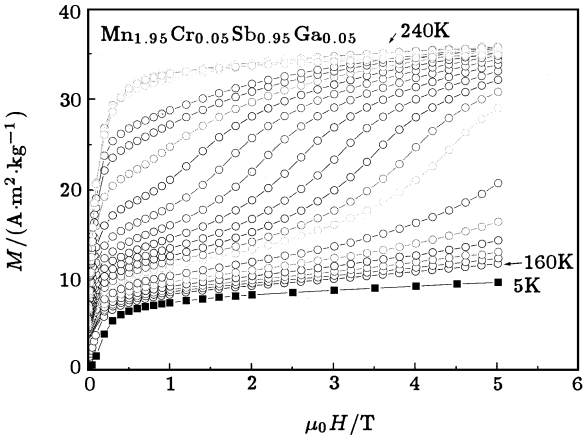


Fig.2. Field dependence of the magnetization for $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ at various temperatures.

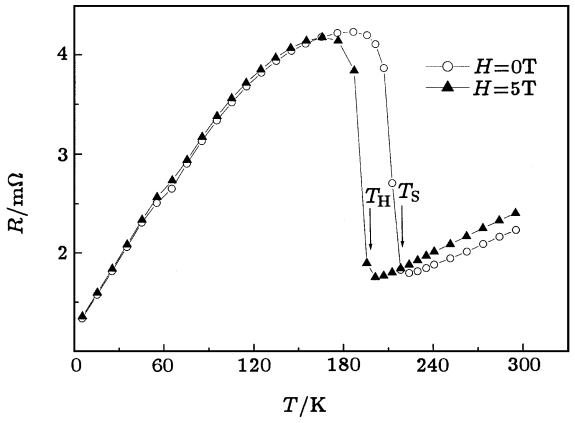


Fig.3. Temperature dependence of the resistance for $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ measured in zero field and an applied field of 5T.

Figure 3 shows the temperature dependence of the resistance for $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ measured in zero field (transition temperature T_{FI-AF}) and an applied field of 5T (transition temperature T_H). The resistance decreases first, then rises abruptly at a certain temperature reaching a maximum, and finally decreases with decreasing temperature. The transition temperature T_{FI-AF} is higher than T_H, due to the effect of the magnetic field. Figure 4 shows the temperature dependence of the MR ratio MR=$\Delta\rho/\rho$[=$(\rho_H - \rho_0)/\rho_0$] of $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ compound at a field of 5T. As expected, the magnetoresistance is small at low temperatures, because the AF structure is stable at 5T. When the temperature increases up to about 175K, the AF phase becomes unstable under the applied magnetic field and a metamagnetic transition occurs, which results in a rapid increase of $|\Delta\rho/\rho|$, reaching a maximum value of 57% at a temperature of T_m=200K (same as T_H). Above T_m, the values of $|\Delta\rho/\rho|$ decrease rapidly with increasing temperature. Figure 5 shows the magnetic field dependence of the MR ratio $\Delta\rho/\rho$ at 200K. It can be seen that $|\Delta\rho/\rho|$ is small at low fields, which is indicative of a stable AF state, then it increases drastically around a critical field H_m, associated with the metamagnetic transition to the FI state. As seen from Fig.2, the critical field at which the metamagnetic transition occurs coincides with H_m. A hysteresis curve is observed for the MR, which is characteristic of first-order transitions. As mentioned above, the mechanism for the GMR in $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ is probably due to the Ga substitution which results in the change in d-electron concentration, leading to the large decrease of DOS near the Fermi level. It has been reported that Mn_2Sb-based compounds exhibit a naturally magnetic

multilayer structure,[27] so another possible mechanism for the GMR in $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ is spin-dependent scattering which results in a reduction of relaxation time in the AF state. However, according to the mechanism of the AF–FI transition [29] and the abrupt increase of resistivities below the AF ordering temperature, the former mechanism should be dominant. It is noteworthy that a MR effect remains above 240K. This is probably due to the ordinary magnetoresistance (OMR) effect, which results from the conduction electron scattering by applied field.

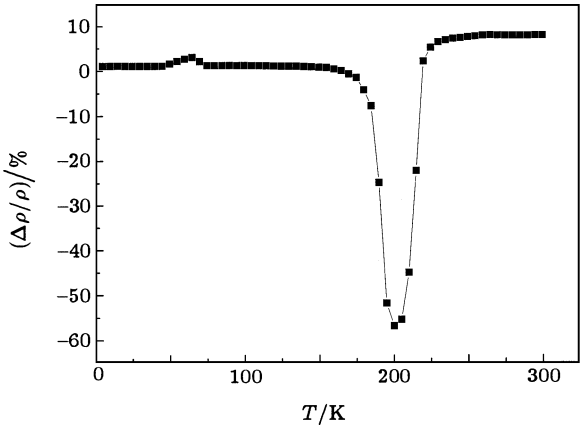


Fig.4. Temperature dependence of the MR ratio for $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ compound at a field of 5T.

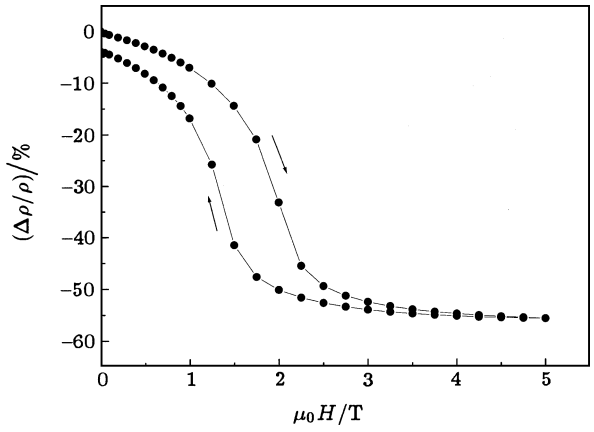


Fig.5. Magnetic field dependence of the MR ratio at 200K for $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$.

The magnetocaloric effect can be characterized by the isothermal magnetic entropy change ΔS_M $(T, \Delta H)$ upon application of a magnetic field H. The value of ΔS_M $(T, \Delta H)$ can be determined using the Maxwell relation [30]

$$\Delta S_M(T, \Delta H) = S_M(T, 0) - S_M(T, H) = \int_0^H -\left(\frac{\partial M}{\partial T}\right) dH.$$

From the magnetization isotherms (see Fig.2), we have calculated the value of ΔS_M as a function of temperature and field changes. The results are presented in Fig.6. The value of ΔS_M is positive, which can be explained by the fact that the magnetic field decouples some of the anti-parallel aligned Mn_1 and Mn_2 moments, thus increasing the disorder of the total spin system and raising the magnetic entropy. The maximum of ΔS_M is shifted to lower temperatures as the magnetic field becomes larger, indicating that the magnetic field suppresses the antiparallel coupling. The absolute values of $\Delta S_M^{max}(T, \Delta H)$ are 4.4, 4.1, 3.6, 2.8 and 1.5 $J \cdot kg^{-1} \cdot K^{-1}$ for the magnetic field changes of 0–5T, 0–4T, 0–3T, 0-2T and 0-1T, respectively. These values are lower than those of $Mn_{1.95}Cr_{0.05}Sb$.[26] This is probably due to the doping of 4p electrons which results in the modification in the 3d band structure induced by 3d–4p hybridization. It is noteworthy that the peak of the magnetic-entropy change is round and broader than one would expect for a first-order transition. The reason for this is not clear and needs to be confirmed by further experiments and theoretical investigations.

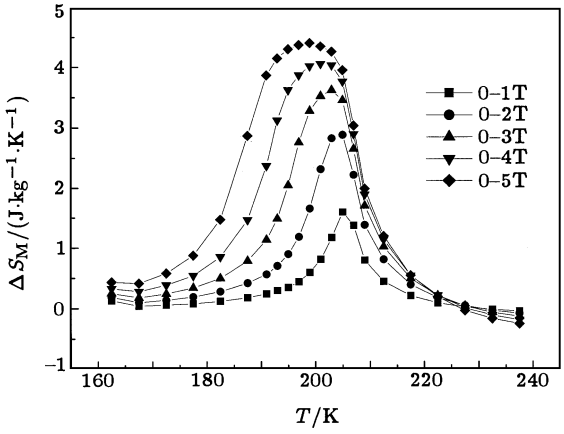


Fig.6. Magnetic-entropy changes of $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$ under field changes of 1T, 2T, 3T, 4T and 5T.

4. Summary

In summary, we have studied the magnetotransport properties and magnetocaloric effects of the compound $Mn_{1.95}Cr_{0.05}Sb_{0.95}Ga_{0.05}$. A first-order magnetic phase transition from FI to AF state takes place below T_S=200K, and application of a magnetic field induces a metamagnetic transition near T_S. These are explained by the change in the d-electron concentration due to substitution which results in a significant

change in DOS. The AF–FI transition is accompanied by a GMR effect, and the largest MR ratio is 57% at 200K in a magnetic field of 5T. The magnetocaloric effects are discussed in terms of the modification in the 3d band structure induced by 3d–4p hybridization. The absolute values of $\Delta S_{\mathrm{M}}^{\max}$ $(T, \Delta H)$ are 4.4, 4.1, 3.6, 2.8 and 1.5J·kg^{-1}·K^{-1} for magnetic field changes of 0–5T, 0–4T, 0–3T, 0–2T and 0–1T, respectively.

References

[1] Baibich M N, Broto J M, Fert A, Nguyen van Dau F, Petroff F, Etienne P, Creuzet G, Frederich A and Chazeles J 1988 *Phys. Rev. Lett.* **61** 2472

[2] Binash G, Grünberg P, Saurenbach F and Zinn W 1989 *Phys. Rev.* B **39** 4828

[3] Kusters R M, Singleton J, Keen D A, Mcgreevy R and Hayes W 1993 *Phys. Rev. Lett.* **71** 2331

[4] Baranov N V, Markin P E, Zemlyanski S V, Michor H and Hilscher G 1996 *J. Magn. Magn. Mater* **157/158** 204

[5] Li R W, Sun J R, Li Q A, Wang Z H, Zhang J and Shen B G 2001 *J. Phys.: Condens. Matter* **13** 141

[6] Han X F, Sun Z G, Kato H, Oogane M, Shen B G, Yang F M and Coey J M D 2002 *J. Magn. Magn. Mater* **239** (1-3) 204

[7] Duan P, Tan G T, Dai S Y, Chen Z H, Zhou Y L and Lu H B 2003 *Acta Phys. Sin.* **52** 2061 (in Chinese)

[8] Zimm C, Sternberg A, Pecharsky V, Gschneidner Jr K, Osborne M and Anderson I 1998 *Adv. Cyrogen. Eng.* **43** 1759

[9] Pecharsky V K and Gschneidner Jr K A 1997 *Phys. Rev. Lett.* **78** 4494

[10] Tegus O, Brück E, Buschow and de Boer F R 2002 *Nature* **415** 150

[11] Hu F X, Shen B G and Sun J R 2000 *Appl. Phys. Lett.* **76** 3460

[12] Hu F X, Shen B G, Sun J R and Cheng Z H 2001 *Phys. Rev.* B **64** 012409

[13] Hu F X, Wang G J, Wang J, Sun Z G, Dong C, Chen H, Zhang X X, Sun J R, Cheng Z H and Shen B G 2002 *J. Appl. Phys.* **91** 7860

[14] Wang F, Chen Y F, Wang G J, Sun J R and Shen B G 2003 *Chin. Phys.* **12** 911

[15] Hu F X, Shen B G, Sun J R, Cheng Z H, Rao G H and Zhang X X 2001 *Appl. Phys. Lett.* **73** 3675

[16] Heaton L and Gingrich N S 1955 *Acta Crystallogr.* **8** 207

[17] Wilkinson M K, Gingrich N S and Shull C G 1957 *J. Phys. Chem. Solids* **2** 289

[18] Kanomata K and Ido H 1984 *J. Appl. Phys.* **55** 2039

[19] Beckman O *et al* 1991 *Handbook of Magnetic Materials* (ed K H J Buschow) vol 6 (Amsterdam: Elsevier) p181

[20] Shen B G, Kong L S, Wang F W and Cao L 1993 *Appl. Phys. Lett.* **63** 2288

[21] Shen B G, Wang F W, Kong L S and Cao L 1993 *J. Phys.: Condens. Matter* **5** L685

[22] Zhang S Y, Sun Z G, Zhang H W, Han B S, Shen B G, de Boer F R, Buschow K H J 1999 *J. Phys.* D: *Appl. Phys.* **32** 2990

[23] Zhang S Y, Zhao P, Cheng Z H, Li R W, Sun J R, Zhang H W and Shen B G 2001 *Phys. Rev.* B **64** 212404

[24] Kittel C 1960 *Phys. Rev.* **130** 335

[25] Bierstedt P E 1963 *Phys. Rev.* **132** 669

[26] Tegus O *et al* 2002 *Physica* B **319** 174

[27] Wijingaard J H, Haas C and de Groot R A 1992 *Phys. Rev.* B **45** 5395

[28] Motizuki K, Suzuki M and Shirai M 1993 *Japan. J. Appl. Phys.* **32** 221

[29] Wohlfarth E P 1963 *Phys. Lett.* **4** 83

[30] Hu F X, Shen B G, Pakhomov A B, Wong C Y, Zhang X X, Zhang S Y, Wang G J and Cheng Z H 2001 *IEEE Trans. Magn.* **37** 2328