Colossal Magnetoresistance in the Transition-Metal Zintl Compound $Eu_{14}MnSb_{11}$

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Magnetoresistance measurements have been carried out on single-crystal sample of the transition-metal Zintl compound $Eu_{14}MnSb_{11}$. $Eu_{14}MnSb_{11}$ is the first compound of the $Ca_{14}AlSb_{11}$ structure type in which magnetoresistive effects have been measured. Colossal magnetoresistance (CMR) at 92 K and 5 T with $\Delta\rho/\rho(0) = -36\%$ and at 5 K and 5 T with $\Delta\rho/\rho(0) = -42\%$ were observed. CMR is observed at the ferromagnetic−paramagnetic phase transition (92 K). A large negative magnetoresistance is observed below the second magnetic transition (15 K) and is attributed to a field-induced antiferromagnetic−ferromagnetic ordering of the Eu^{2+} lattice. The MR is highly anisotropic with respect to the crystallographic axes. A sign change in the curvatures of ρ(H) curves below and above 92 K has been observed, indicating that two different mechanisms are responsible for the magnetic scattering of the carriers in two separate temperature regions.

Introduction

There has been a great deal of interest in negative colossal magnetoresistance (CMR) in materials. Magnetoresistive (MR) materials might find potential application in magnetic devices such as read-heads.[1] Whereas all metals have a finite magnetoresistance, the majority show a very small increase (positive MR of less than a few percent) in electrical resistance upon application of a magnetic field. Metallic multilayers have recently been found to give rise to large, referred to as giant, magnetoresistive effects (10−50%).[2] The giant magnetoresistive (GMR) effect in magnetic layered materials is generally believed to be a result of spin-dependent scattering.[3] Besides layered materials, GMR has been observed in doped magnetic semiconductors RE_xSi_{1-x} (RE = Gd, Tb)[4] and in intermetallic compounds.[5−7] Some of the largest MR effects are associated with metamagnetic transitions in intermetallic antiferromagnets containing uranium.[5,6] Colossal magnetoresistance has been reported in the rare-earth manganates, $Ln_{1-x}A_xMnO_3$ (Ln = rare earth, A = divalent cation such as Ca, Sr, Ba, Pb).[8−10] Double exchange has been proposed as the mechanism which magnetically couples the heterovalent Mn pairs (Mn^{3+}/Mn^{4+}) in these perovskite compounds and leads to the CMR effects.[11−13] The term colossal was originally used to described the order of magnitude of the magnetoresistance effect.[14] However, more recently, the term has been used to distinguish these materials from the more well-developed GMR multilayers.[2] The phenomenon of CMR is now associated with critical ferromagnetic fluctuations and does not saturate until high fields (>6 T).[15,16] With this definition, compounds such as $Eu_{0.95}Gd_{0.05}Se$[17] can be considered the first CMR materials. CMR has been observed in the pyrochlore $Tl_2Mn_2O_7$.[15] Structural analysis from neutron and single-crystal X-ray diffraction data[15] and X-ray absorption spectroscopy indicate that Mn is not mixed valent in this compound.[18,19] Recently, the existence of CMR effects in the Cr-based chalcogenide spinels that also do not possess heterovalency is reported.[16] Therefore, it has been suggested that the mechanism responsible is magnetic ordering driven by superexchange rather than double exchange in these compounds. We now report on the magnetoresistive properties of $Eu_{14}MnSb_{11}$, which belongs to a new class of compound, distinct from other classes of compounds showing CMR.

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$Eu_{14}MnSb_{11}$ belongs to a family of compounds known as transition-metal Zintl compounds.[20−22] Zintl compounds are generally characterized as semiconductors whose structures can be understood as a combination of ionic and covalent bonding. In simple binary Zintl compounds made up of alkali or alkaline-earth metals and main-group elements, the electropositive element donates its electrons to the electronegative element, which forms the necessary number of bonds according to the $8 - N$ rule.[23] $Eu_{14}MnSb_{11}$ is isostructural to the Zintl compound $Ca_{14}AlSb_{11}$, which crystallizes in a tetragonal crystal system in the space group $I4_1/acd$.[24] Single-crystal X-ray diffraction and temperature-dependent magnetic data show no deviations from ideal stoichiometry.[20,22] A general formula unit, $A_{14}MPn_{11}$ (A = divalent cation, M = metal, Pn = pnictogen) consists of 14 A^{2+} cations, 4 Pn^{3-} anions, a MPn_4^{9-} tetrahedron, and a Pn_3^{7-} linear anion. The structure is characterized by alternating tetrahedra and linear Pn_3^{7-} anions. Theoretical calculations are in agreement with the Zintl interpretation of the structure.[25] A significant number of both main-group and transition-metal compounds of this structure type have been prepared to date.[20−22,24,26−33] The transition-metal compounds with M = Mn show unusual magnetic and electronic properties.[21,22,26,29,30,34] In these compounds high temperature magnetic susceptibility supports the hypothesis that the metal is formally Mn^{III}, a d^4 ion. The $A_{14}MnPn_{11}$ (A = Ca, Sr, Ba, Eu) compounds are unusual in that although the Mn atoms are approximately 10 Å apart, all the Sb and Bi compounds show long-range magnetic order. In addition, all of the compounds measured to date show a large decrease in resistivity at the magnetic transition. The highest transition temperature has been observed for $Ca_{14}MnSb_{11}$ which shows ferromagnetic ordering at 65 K.[29] Because of the large distances between Mn atoms and the absence of any covalent bonds between them, the magnetic coupling has been attributed to a Ruderman−Kittel−Kasuya-Yosida (RKKY) interaction[35,36] between the localized moments via conduction electrons.[29] The As analogues do not show any long-range magnetic order, but application of hydrostatic pressure leads to magnetic coupling and a low-temperature ferromagnetic state.[29,37] With an aim toward raising the transition temperature, the $Eu_{14}MnSb_{11}$ compound was prepared.[20] A ferromagnetic transition at 92 K is observed in the magnetization measurements along with a well-defined decrease in resisitivity at the transition temperature.[22] These two measurements provide incentive for measuring magnetoresistance (MR) in this compound.

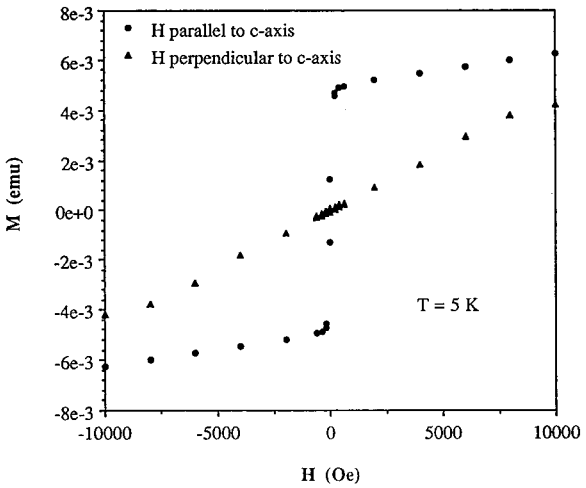

Figure 1. Hysteresis loop of $Eu_{14}MnSb_{11}$ single crystal measured parallel and perpendicular to the *c*-axis.

Experimental Section

Single crystals of $Eu_{14}MnSb_{11}$ were prepared from heating stoichiometric amounts of the elements, sealed in Ta tubes in a temperature gradient for 10 days. Synthesis and characterization have been described in detail elsewhere.[22] Magnetization and transport measurements were conducted in a commercial SQUID magnetometer[38] in magnetic fields up to 5 T and over a temperature range of 5−300 K. All samples, both single-crystal and bulk, provide reproducible T_c and magnetic data, consistent with a stoichiometric phase. Magnetoresistance measurements were made on a needle shaped single crystal with dimensions of $0.06 \times 0.06 \times 1$ mm^3 using a standard four-probe method with an applied current of 1 mA along the *c*-axis.

Results and Discussion

Figure 1 shows the hysteresis loops of $Eu_{14}MnSb_{11}$ single crystal with the magnetic field parallel and perpendicular to the *c*-axis. The large difference in magnetization between the crystal alignment is attributed to magnetocrystalline anisotropy. This effect is caused by the spin−orbit coupling leading to magnetic moments with preferred orientations in certain crystallographic directions and is important for certain magnetic applications.[39] There is large magnetocrystalline anisotropy and the *c*-axis is the easy axis. Figure 2 shows the temperature dependence of the magnetization, measured in an applied field of 1000 Oe, of polycrystalline $Eu_{14}MnSb_{11}$ and the temperature dependence of the resistivity of a $Eu_{14}MnSb_{11}$ single crystal with the *c*-axis parallel to both the applied magnetic field and the current.

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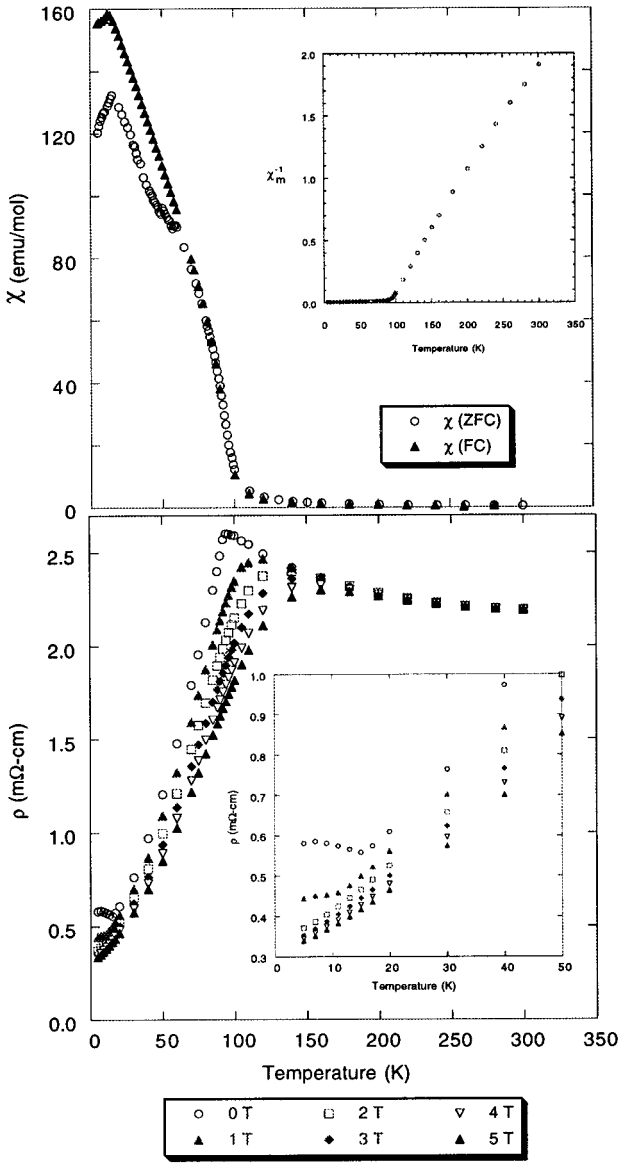

Figure 2. Top: temperature-dependent magnetization of polycrystalline $Eu_{14}MnSb_{11}$, where circles represent the zero-field cooled (ZFC) and triangles represent the field cooled (FC) data. Inset shows the inverse magnetic susceptibility. (Reproduced with permission from ref 22.) Bottom: magnetoresistance of $Eu_{14}MnSb_{11}$ single crystal with *c*-axis parallel to applied field; from top to bottom, the corresponding fields are 0, 1, 2, 3, 4, and 5 T. Inset shows low-temperature transition.

The magnetic susceptibility shows a rise at about 100 K as the sample is cooled, characteristic of ferromagnetic ordering. The high-temperature data (120−300 K) can be fit with a modified Curie−Weiss law ($\chi_0 + C/(T - \theta)$) to obtain $\mu_{eff} = 27.0(1)\ \mu_B$ and $\theta = 93.55(3)$ K (Figure 2, inset). The θ is in good agreement with the observed magnetic transition. The moment is slightly reduced compared with the expected moment for $14Eu^{2+} + Mn^{3+}$ ($\mu_{calc} = 30\ \mu_B$).[22] The reduction in moment suggests that there is some ferrimagnetic coupling of the spins at high temperatures. Below the magnetic transition there is a second transition at 15 K which is assigned to ordering of the Eu^{2+} lattice. Consistent with this interpretation, magnetic susceptibility measurements on $Eu_{14}InSb_{11}$ show only one magnetic transition at about 15 K.[22] The magnitude of the transition temperature is consistent with that observed in other Eu^{2+}-containing compounds.[40,41] The 15 K transition is reminescent of an antiferromagnetic ordering (zero field-cooled (ZFC)) which is suppressed upon application of field ((field-cooled (FC) data). The hysteresis loop on powder samples shows a saturation moment of 102(1) μ_B, in agreement with the assigned valencies.[22]

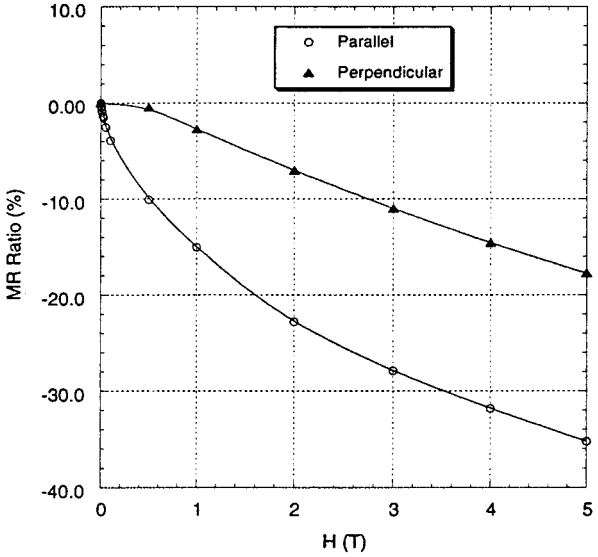

Figure 3. Magnetoresistance ratio (MR = $[(\rho(0) - \rho(H))/\rho(0)] \times 100\%$) versus field for single crystal of $Eu_{14}MnSb_{11}$ parallel and perpendicular to H at 92 K.

A large negative MR is observed below the ferromagnetic ordering temperature (Figure 2). Above the transition, the suppression of resistivity diminishes as temperature increases. The cusp in resistivity at the transition temperature broadens and shifts toward higher temperature as the field is increased. Figure 3 shows that a −36% suppression of resistivity is observed at 92 K when the field is increased from $H = 0$ to $H = 5$ T. The largest effect is observed when the *c*-axis of the crystal is oriented parallel to the magnetic field, consistent with magnetocrystalline anisotropy. Figure 4 shows the magnetoresistance ratio {MR = $[(\rho(0) - \rho(H))/\rho(0)] \times 100\%$} of a single crystal of $Eu_{14}MnSb_{11}$ oriented parallel and perpendicular to the applied magnetic field. The largest MR ratio is observed near the T_c for both orientation. However, for the *c* axis of the crystal oriented perpendicular to the field, positive and negative magnetoresistance is also observed below T_c. An onset of negative MR behavior at 15 K is also observed (Figure 2, bottom) where the transition temperature has been attributed to the antiferromagnetic ordering of the Eu spins. The suppression of resistivity at 5 K is −42%, from $H = 0$ to $H = 5$ T.

The temperature-dependent resisitivity shows semiconducting behavior above and metallic behavior below 95 K. The largest MR occurs near the transition temperature. The mechanism responsible for the magnetoresistive effects in $Eu_{14}MnSb_{11}$ must be related to this insulator-to-metal transition. However, the details of the mechanism are not understood. Semimetal behavior is observed for $H = 0$ and below 15 K. This is normal resistivity behavior coincident with antifer-

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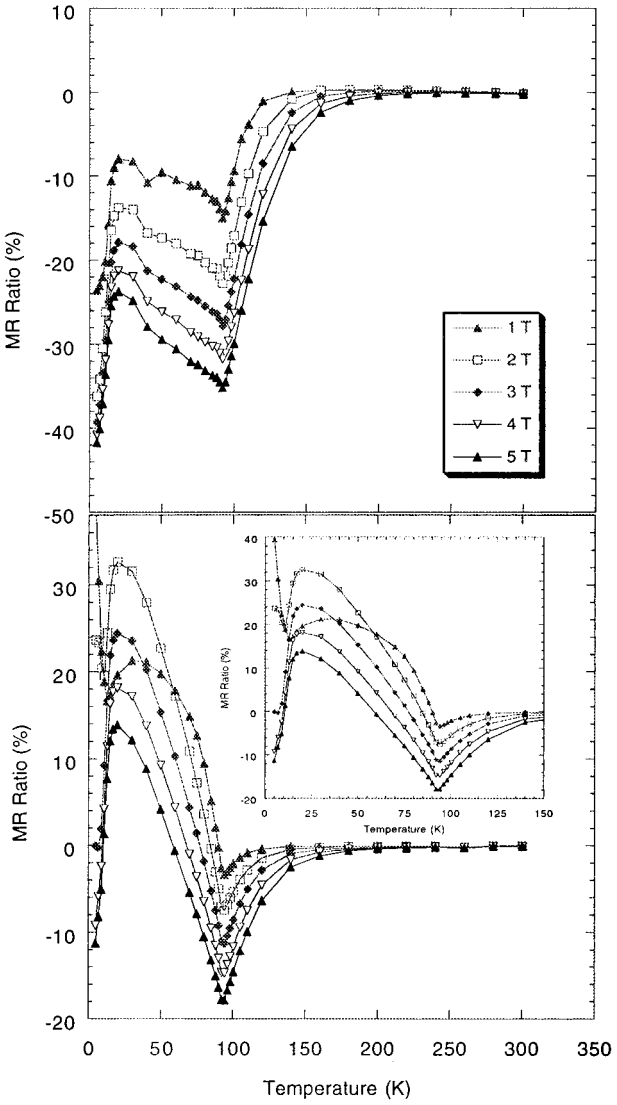

Figure 4. Magnetoresistance ratio versus field with the *c*-axis of the $Eu_{14}MnSb_{11}$ crystal oriented (top) parallel and (bottom) perpendicular to the applied field.

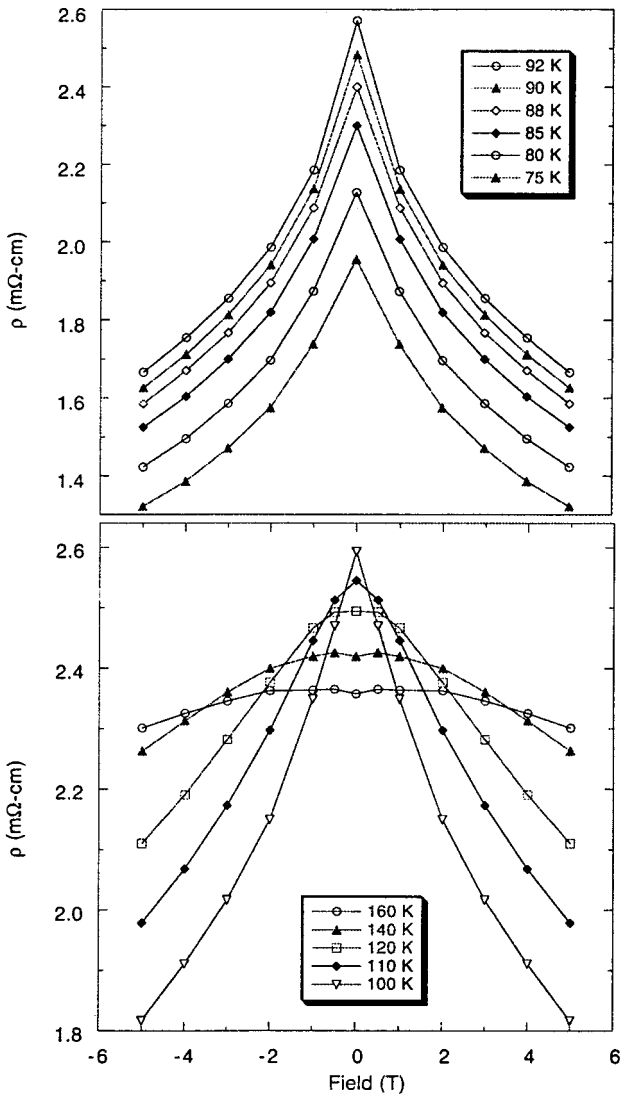

Figure 5. Top: field dependencies of the resistivity of $Eu_{14}MnSb_{11}$ crystal below 92 K. Bottom: field dependencies of the resistivity of $Eu_{14}MnSb_{11}$ crystal at temperatures above T_c.

romagnetic ordering. This effect disappears and the temperature dependence looks metallic with a magnetic field of 1 T or greater. The magnetoresistance below the 15 K transition is attributed to field induced ferromagnetic ordering of the Eu spins, thus reducing spin scatter and therefore resistivity.

Figure 5 shows the change in resistivity as a function of applied magnetic field at various temperatures. It is clear that below 120 K, the resistivity does not saturate at fields up to 5 T. A remarkable change in the curvature is observed. At T_c, the suppression is the greatest, and it is evident that above or below T_c, the negative MR effects are also observed. For temperatures less than 120 K, approaching T_c, the ρ(H) curves show a positive curvature. For temperatures greater than 120 K, the ρ(H) curves feature a negative curvature. This behavior is also observed in the $La_{0.65}(PbCa)_{0.35}MnO_3$ single crystals as well as the La−Ca−Sr−Mn−O ferromagnetic thin films.[14,42]

CMR has been observed in single crystals of $Eu_{14}MnSb_{11}$ with MR ratio up to −36% near the ferromagnetic transition at 92 K. The maximum MR is found near the magnetic transition, where the magnetization and the resistance are sensitive to the applied magnetic field. CMR effects have been observed in a variety of different compounds; however, $Eu_{14}MnSb_{11}$ does not appear to fit within any of the general classes outlined above. The origin of CMR at 92 K may be driven by superexchange through the Eu^{2+} spins with the conduction band being mainly the Mn d states. Zintl compounds are electronically situated on the border between semiconductor and intermetallics and one expects that all magnetic Zintl compounds will show CMR effects.

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