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Colossal negative magnetoresistance in an antiferromagnet

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The magnetization and resistivity of single crystals of the Zintl compound $Eu_{14}MnBi_{11}$ are measured as functions of temperature and applied magnetic field. The magnetization data show an apparent antiferromagnetic transition at $T_N=32$ K even though the high-temperature susceptibility suggests that the exchange coupling is ferromagnetic in nature. The zero-field resistivity is approximately independent of temperature above 32 K. Below 32 K the resistivity increases slightly and peaks at about 20 K before decreasing as the temperature is decreased. This temperature dependence is fairly normal for an antiferromagnetic metal. On the other hand, in contrast to other antiferromagnets, the single-crystal magnetoresistance is large and negative at all temperatures below about $3T_N$. In addition, the dependence of the resistivity upon the magnetization is quite similar to the colossal-magnetoresistance materials. [S0163-1829(98)51214-3]

Several types of materials have recently been variously categorized as having either ''giant'' or ''colossal'' magnetoresistance (GMR or CMR).[1–8] The application of a magnetic field to these materials decreases the resistivity by at least a few percent and as much as several orders of magnitude. Conventional metals and ferromagnets typically exhibit changes in resistivity of less than a percent in a moderate (1 T) field so it is clear that CMR materials are quite unusual. The extreme field sensitivity of these CMR materials offers the potential for technological advances, for example, in magnetoresistive read heads in the magnetic recording industry.[9] The precise nature of both the insulating and the conducting states in the various sets of materials which show CMR is not settled but remains a matter of intense current investigation.[10–14] However, generically these materials contain localized spins and are nearly insulating so that disorder in the local spins is an important factor in localizing the charge carriers. The application of a magnetic field to any of these materials in the appropriate temperature range decreases the spin disorder and so decreases the resistivity. This leads to a magnetoresistance which is largest near a phase transition from a state of low magnetization to a state of high magnetization and is quite dependent on temperature in this region. Indeed, most of the CMR compounds order ferromagnetically and have a magnetoresistance which depends strongly on temperature.[1–6,8] This observation is in contrast to the GMR in layered thin films for which the magnetoresistance does not depend strongly on temperature.[15] In this paper we show that the compound $Eu_{14}MnBi_{11}$, which appears to order antiferromagnetically at 32 K,[16] has a negative magnetoresistance at all H and T. In contrast to the ferromagnetic CMR materials, the magnetoresistance in this compound is quite large (varies between 5 and 70% at $H=5$ T) over the entire range of temperatures below 100 K.

$Eu_{14}MnBi_{11}$ is a member of an isostructural group of stoichiometric compounds with the formula $A_{14}MPn_{11}$ where $Pn=$P, As, Sb, or Bi and A is either an alkaline earth (Ca, Sr, or Ba) (Refs. 17 and 18) or a divalent rare earth (Eu) (Refs. 16 and 19), M is either Mn or a nonmagnetic main group element (Al, Ga, or In) (Refs. 20–23). These compounds crystallize in the space group $I4_1/acd$ and have a tetragonal unit cell with eight formula units in the cell. The main group analogs of this structure belong to a class of compounds called Zintl compounds.[24] In Zintl phases electropositive ions donate electrons to the more electronegative components which usually form covalently bonded units or networks (large anions) but may also exist as simple closed shell anions. Because Zintl compounds are salts, main group Zintl phases are all expected to be insulators (possibly with small band gaps); in particular, the main group compounds isostructural to $Eu_{14}MnBi_{11}$ are all known to be semiconducting.[25,26] Since all these phases are isostructural, one might expect the Mn compounds to be semiconductors with local moments on the Mn. However, most of the compounds containing the transition metal Mn are conducting, have ferromagnetic exchange coupling, and display an intimate connection between the conductivity and the magnetism.[23] The conductivity is unexpected because the materials are salts made up of isolated cations and isolated anion complexes and conducting paths are not apparent. In addition, magnetic transition temperatures as high as 100 K are unexpected because the Mn^{3+} ions, which are tetrahedrally coordinated with four Pn's, are quite isolated from their neighboring Mn ions, about 1.1 nm interionic spacing for the Mn.

The importance of the Mn to both the magnetism and the conductivity is illustrated in an examination of the gross properties of the series, of which the alkaline earth containing compounds have been studied in the greatest detail.[17,18] There is a metal-insulator (M-I) boundary between the $Pn=$As compounds (semiconductors with resistivity $\rho(T=300\,\mathrm{K})>$few thousand $\mu\Omega$ cm and negative $d\rho/dT$) and the $Pn=$Sb compounds [semimetals with $\rho(T=300\,\mathrm{K})$ of order 1000 $\mu\Omega$ cm, but $d\rho/dT$ still slightly negative].[18] The $Pn=$Bi compounds are the most conducting [$\rho(T=300\,\mathrm{K})$ of order 100 $\mu\Omega$ cm and $d\rho/dT$ positive][17,27] of all, but may

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still be considered to be near a M-I boundary. Near-neighbor Mn spins in the conducting compounds all have fairly strong ferromagnetic exchange coupling and order at temperatures between 10 and 100 K.[16,23] The Mn spins in the semiconducting As compounds have an exchange coupling which is quite weak (Curie-Weiss $\Theta < 0.5$ K); however, under hydrostatic pressure *even these* As compounds have Mn moments which are coupled ferromagnetically with $\theta > 10$ K.[28] The Curie temperatures of the alkaline earth series of compounds can be accounted for within the Ruderman-Kittel-Kasuya-Yosida (RKKY) (Refs. 29 and 30) model[18,23] but, given the unknown origin of the conductivity, one should probably not draw strong conclusions from such a fit. Recently, the $\mathrm{Eu_{14}Mn}Pn_{11}$ ($Pn = \mathrm{Sb}$, Bi) compounds have been prepared with an aim towards raising the magnetic ordering temperature in these compounds.[16] Eu is $+2(4f^7)$ in these compounds and affects the ordering temperature. However, the Mn-Mn exchange energy still controls the magnetic energy scale. For example, $\mathrm{Sr_{14}MnSb_{11}}$ has only Mn magnetic ions and a $T_c = 45$ K (Ref. 18) compared to $\mathrm{Eu_{14}MnSb_{11}}$ which is much more magnetically dense (the magnetic moment of $\mathrm{Eu_{14}MnSb_{11}}$ is 25 times the magnetic moment of $\mathrm{Sr_{14}MnSb_{11}}$) but has $T_c = 92$ K, only a factor of 2 higher.[16] We note that $\mathrm{Eu_{14}MnSb_{11}}$ is similar to the CMR materials with a peak magnetoresistance ratio of 36% at $T_C = 92$ K.[31] Here we present a summary of the magnetoresistance $\rho(H,T)$ and the magnetization $M(H,T)$ of a single crystal of a related compound $\mathrm{Eu_{14}MnBi_{11}}$.

The measurements of $\mathrm{Eu_{14}MnBi_{11}}$ were made on needle-shaped ($0.04\ \mathrm{mm} \times 0.04\ \mathrm{mm} \times 0.64\ \mathrm{mm}$) single crystals with the needle long axis coincident with the tetragonal c axis. These needles were grown from the elements by loading stoichiometric quantities of the elements into Ta tubes in a drybox. The tubes were welded shut and then sealed in quartz tubes under vacuum. The sample was then placed in a zone furnace in a temperature gradient of about 10 °C/cm at an average $T = 1000$ °C for several days. The sample was examined in a drybox and appropriate needles were removed for measurement. Unlike the alkaline-earth containing compounds, the Eu compounds are apparently not very air-sensitive (as determined by powder x-ray diffraction and magnetization measurements).

The magnetization data were acquired with a quantum design superconducting quantum interference device (SQUID) magnetometer with a temperature range of $2\ \mathrm{K} < T < 350$ K and a magnetic field range of $-5\ \mathrm{T} < H < 5$ T. A single needle-shaped crystal was mounted at the center of a drinking straw with apiezon grease. Its axis was oriented either parallel to the applied magnetic field (H_{para}) or perpendicular (H_{perp}). The electrical resistivity measurements were performed in the same instrument in the same orientation of the crystal with the same ranges of temperature and field. Four leads were attached along the length of the crystal with silver paint for the resistivity measurements. Because of the geometry of the crystal, the current, I, is always applied along the c axis of the tetragonal cell but magnetic field may be applied either parallel or perpendicular to I. The magnetization and the resistivity data did not depend significantly on the orientation of the field (H_{para} or H_{perp}) except at fields $H < 0.1$ T when demagnetization effects may become important. In addition, the data do not have any history dependence (i.e., zero-field cooled data are the same as field cooled data).

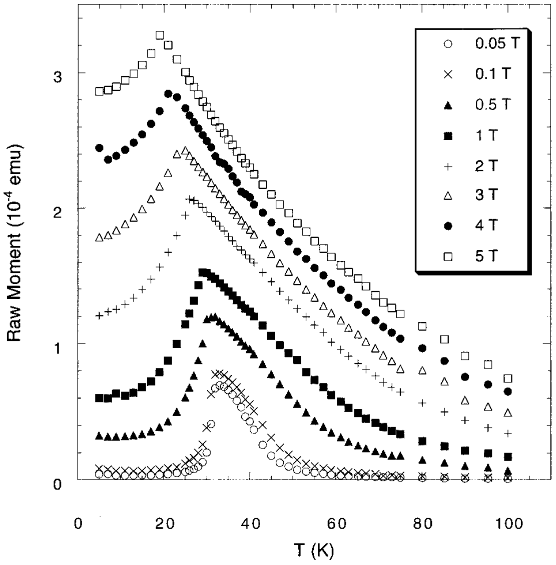

FIG. 1. Magnetization of single-crystal $\mathrm{Eu_{14}MnBi_{11}}$ as a function of temperature in eight magnetic fields applied parallel to the crystalline c axis.

The magnetization M at various magnetic fields is shown in Fig. 1 as a function of temperature for a single crystal parallel to the applied magnetic field. There is an apparent antiferromagnetic phase transition at a temperature T_N which decreases as H is increased. The low-field Néel temperature is $T_N = 32$ K and by $H = 5$ T, T_N has been reduced to about 20 K. A Curie-Weiss fit of the paramagnetic susceptibility of a sample of polycrystalline $\mathrm{Eu_{14}MnBi_{11}}$ provides a positive $\theta = 35$ K,[16] which, for a nearest-neighbor magnetic model suggests ferromagnetic exchange interactions. Presumably one or more of the magnetic sublattices have ferromagnetic intrasublattice coupling which is stronger than the antiferromagnetic intersublattice coupling. The Eu$\cdots$Eu coupling is expected to be antiferromagnetic and weak [$\mathrm{Eu_{14}InSb_{11}}$ orders at about 15 K (Ref. 16)]. A weak Eu-Eu coupling is also consistent with that seen in Eu-Bi binary phases.[32] Thus we attribute the relatively strong ferromagnetic coupling to the Mn-Mn exchange interactions.

This type of magnetic order and the proximity of this compound to a M-I transition have a significant effect on the magnetoresistance. Figure 2 shows the resistivity $\rho(T,H)$ as a function of temperature and magnetic field for some of the same fields as the data provided in Fig. 1. At zero field and high temperature, the resistivity is nearly independent of temperature as expected if spin disorder scattering were the dominant scattering mechanism. Below T_N the resistivity rises to a maximum upon cooling and then decreases upon further cooling. This is common behavior for the magnetic part of the resistivity in metallic magnets with periodic noncollinear spin structures such as observed in several of the rare earth elements.[33,34] The rise in the resistivity is the result of the change in the effective number of conduction electrons[35,36] due to the change in the Fermi surface caused by the new periodicity (the spin order periodicity) which appears on top of the crystalline periodicity for temperatures

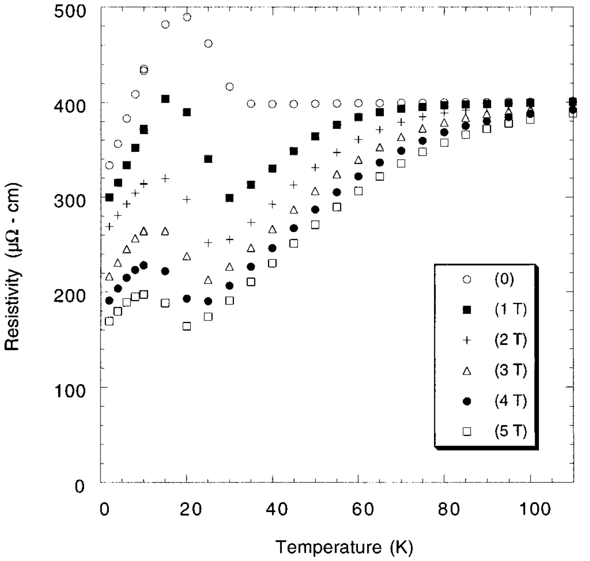

FIG. 2. Electrical resistivity of a single crystal of $Eu_{14}MnBi_{11}$ as a function of temperature and applied field.

below T_N. In the presence of an increasing magnetic field, the sharp kink at 32 K is slowly shifted down to 20 K for $H=5$ T. This matches the shift observed in the T_N for the $M(T,H)$ data. The point of greatest interest in Fig. 2, however, is the large negative magnetoresistance which appears upon cooling below temperatures of order $3T_N$. The magnetoresistance ratio, $\text{MR}=([\rho(H=0)-\rho(H)/\rho(H=0)]\times 100\%)$, is as large as 67% at 20 K and $H=5$ T. This large negative magnetoresistance is clearly not a critical-point effect. We suggest that the negative magnetoresistance is due to ferromagnetic spin fluctuations in this material, a conclusion which is consistent with the relatively strong ferromagnetic Mn-Mn exchange. Figure 2 can be compared to data on amorphous thin films of amorphous $R_{1-x}Si_x$ ($R=$Tb or Gd) (Ref. 7) where the magnetoresistance is also large over a wide range of T and there is no curie temperature.

The fact that $Eu_{14}MnBi_{11}$ has a large negative magnetoresistance over a wide range of T is quite unusual. Since the physics behind this effect may be of importance in designing materials that work at room temperature, it seems useful to discuss the effect in more detail. First, it is possible that the magnetic part of the resistivity can be explained by spin disorder scattering of the conduction electrons (generically s electrons) by the magnetic electrons (generically d electrons) via an s-d type exchange. If the magnetic scattering of the conduction electrons is much larger than that due to phonons then the zero-field resistivity should look like the $H=0$ data of Fig. 2. For a high-T resistivity of 400 $\mu\Omega$ cm, and assuming a spherical Fermi surface with $k_F=0.05\ \text{nm}^{-1}$,[18] we find that the conduction electron mean-free path is about 1 nm which is the distance between Mn-Mn nearest neighbors. If these Mn moments are the important scatterers then they scatter conduction electrons much more efficiently than in most d-electron systems where a mean-free path for magnetic scattering in the paramagnetic state is of order 20 or more near-neighbor distances.[37] The local s-d exchange also leads to an indirect d-d exchange via the conduction electrons which is known as the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange.[29] We have suggested this type of Mn-Mn exchange coupling previously[18] in discussing the alkaline-earth compounds in this series and a fit to the RKKY theory gave the estimate of k_F used above. The magnetoresistance in the paramagnetic state should,[38,39] to lowest order, be proportional to the square of the magnetization. In Fig. 3 the data from Figs. 1 and 2 are replotted as $[\rho(H=0)-\rho(H)]/\rho(H=0)$ as a function of M^2. One sees that the magnetoresistance is, in fact, proportional to M^2, for all T and H, as expected for small M^2. It may be that the magnetoresistance is unusually large in this material for the same reason that the high-temperature spin disorder resistivity is large; namely, strong s-d interactions. We are then led to conclude that the Mn d orbitals are strongly hybridized with the conduction electron wave functions. Alternatively, one might propose a picture, similar to the double exchange model, where some of the Mn d electrons are the conduction

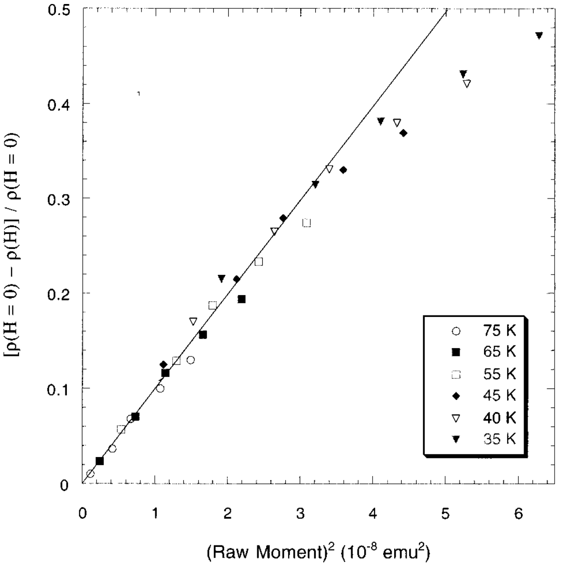

FIG. 3. Magnetoresistance $[\rho(H=0)-\rho(H,T)]/\rho(H=0)$ vs M^2 for several temperatures with T greater than T_N.

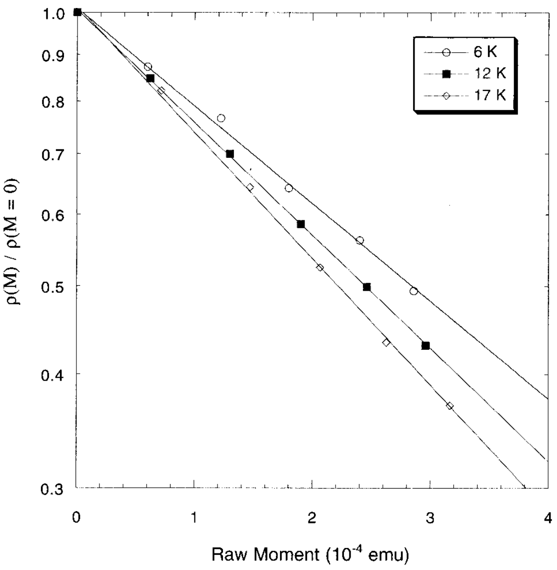

FIG. 4. Resistivity of single-crystal $Eu_{14}MnBi_{11}$ vs M for three temperatures with T less than T_N.

electrons and that a simple s-d interaction model with separate s and d electrons is not appropriate.

A major problem with the simple s-d exchange picture is seen in the magnetoresistance at low T. Theory predicts[40] that the magnetoresistance of this type of system is either (i) positive varying as $H^2(\approx M^2)$ if the magnetic field is applied along the easy axis, or (ii) negligible if the applied field is perpendicular to the easy axis. In contrast to these expectations, the magnetoresistance in the antiferromagnetic state of $Eu_{14}MnBi_{11}$ is not positive, does not vary as M^2, and is certainly not small. Shown in Fig. 4 is the resistivity, normalized by its $M=0$ value, as a function of M for three temperatures less than T_N. One sees that the resistivity is very simple in that it depends exponentially upon M with the form of the exponent being slightly dependent upon T. We note that some investigators[41] have found that the resistivity of the CMR compounds (La,Ca)MnO_3 in the ferromagnetically ordered state depends upon M as $\rho=\rho_m \exp(-M/M_0)$ where M_0 is a reference magnetization. The exponential dependence in the manganites may be explained[41] as the result of hopping of polarons whose hopping integral is dependent upon M. It is interesting that the resistivity in $Eu_{14}MnBi_{11}$ has a similar M dependence even though the magnetization in this material is the difference of the component sublattice magnetizations.

In summary, we have found that $Eu_{14}MnBi_{11}$ has a low-temperature ordered magnetic state, for $T<T_N$, without a spontaneous magnetization (it is probably an antiferromagnet). This low-T ordering occurs despite predominantly ferromagnetic Mn-Mn exchange. The result of this magnetic state is a negative magnetoresistance which is large for a wide range of temperatures, all $T<3T_N$.

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