Comparison of negative magnetoresistance mechanisms in manganese perovskites and chromium spinels

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A transition of the field dependence of the electrical resistivity from a square law ($\sim H^2$) above T_c to a linear function ($\sim H$) below T_c is observed in the degenerate ferromagnetic semiconductor $HgCr_2Se_4(n)$. Together with the large negative magnetoresistance, these magnetoelectric effects correspond to effects observed in the perovskite-type oxides $La_{1-x}Ca_xMnO_\delta$. Inasmuch as the undoped semiconductor $HgCr_2Se_4$ is a ferromagnet with approximately the same critical temperature as the doped semiconductor and in view of the total lack of data on the Jahn–Teller effect in this compound, we infer that our results cast doubt on existing hypotheses (polaron and binary exchange) regarding the origin of the giant magnetoresistance in $La_{1-x}Ca_xMnO_\delta$. Impurity sd scattering is discussed as a possible magnetoresistance mechanism for both compounds. © *1999 American Institute of Physics.* [S1063-7834(99)01710-4]

A detailed analysis of the magnetoresistance of thin films of the perovskite oxide $La_{1-x}Ca_xMnO_\delta$ shows that the temperature and field dependences of the electrical resistivity are dictated entirely by the magnetization at temperatures both above and below T_c (Ref. 1). According to the interpretation of current carriers as small-radius polarons, $\rho(M) \approx \rho(0)(1-\gamma M^2)$ (Refs. 2–4). O'Donnell et al.[1] have observed an abrupt transition in the low-field ($H \to 0$) dependence of the resistivity from a square law ($\sim H^2$) above T_c to a linear function ($\sim H$) below T_c. According to polaron concepts, the low-field dependence of the electrical resistivity should exhibit a negative curvature at all temperatures, both above T_c and below T_c (Refs. 2–4). However, the experimental curves have a positive curvature below T_c (Ref. 1). Moreover, Eckstein *et al.*[5] have observed a dependence of the resistivity on the direction of magnetization in samples of the same compositions. A similar anisotropy of the magnetoresistance observed much earlier in transition metals has been well understood in terms of sd scattering.[6] These are all new problems for the theory of electrical conductivity in the oxides of transition metals.

The objective of the present study is to compare the experimental magnetoresistance curves of the ferromagnetic semiconductor $HgCr_2Se_4(n)$ at temperatures above and below the magnetic phase transition temperature T_c with the analogous curves for $La_{1-x}Ca_xMnO_\delta$. Like the latter, the degenerate magnetic semiconductor $HgCr_2Se_4(n)$ has a high negative magnetoresistance ($\Delta\rho/\rho \approx 100\%$) with a peak in the vicinity of T_c. According to band calculations,[7] the bottom of the conduction band in this compound has a $4s$-$3d$ nature. We have previously[8] proposed a $4s$-$3d$ mechanism for the impurity scattering of carriers in nonstoichiometric magnetic semiconductors, whereby the temperature and field dependences of the resistivity are governed by the corresponding dependences of the magnetization: $\rho = \rho(M(T,H))$. The results of calculations based on this scattering mechanism[9] for $HgCr_2Se_4(n)$ are quite consistent both with the actual existence of a large negative magnetoresistance and with its temperature dependence for this nonstoichiometric compound. It is reasonable therefore to assume, on the basis of the same sd-scattering mechanism, that the magnetoresistance of this compound could have the above-stated distinctive characteristics.

To identify the scattering mechanism responsible for the giant negative magnetoresistance, we have noted the low-field electrical resistivity curves, analogous to those in Ref. 1, for $HgCr_2Se_4(n)$ both above and below T_c. As in Ref. 1, we have observed a transition from square-law behavior of the magnetoresistance above T_c to linear behavior below T_c. Moreover, in the latter case we have also observed a separate magnetoresistance peak superimposed on the linear field curve, attesting indirectly to a dependence of the resistivity on the direction of the magnetic field. We emphasize that the object in question is a compound that differs altogether from $La_{1-x}Ca_xMnO_\delta$, the only common ground being phase

separation into conducting and nonconducting phases[10] and the same scattering mechanism.

The mechanism of binary exchange affecting the magnetoresistance is ruled out: The undoped compound $HgCr_2Se_4$ is a ferromagnetic semiconductor with $T_c = 106$ K. As the doping level or the degree of nonstoichiometry is raised, the Curie temperature increases only slightly, whereas the carrier mobility at T_c increases by roughly two orders of magnitude.[11] Data on the Jahn–Teller effect are nonexistent. Consequently, the concepts of polaron-type carriers must also be excluded for this compound. Realistically, we can contemplate scattering by spin disorder and scattering by nonstoichiometry defects. However, the strong concentration dependence of the mobility at low temperatures[11] strongly supports the latter.

1. SAMPLES AND MEASUREMENT PROCEDURE

Single-crystal samples were prepared by the technology described in Ref. 12 and were subsequently additionally annealed in mercury vapor at a vapor pressure $P = 4.1$ atm and temperature $T = 350\,^\circ$C for sample 1 and at $P = 2.7$ atm and $T = 428\,^\circ$C for sample 2. This annealing procedure yields degenerate *n*-type $HgCr_2Se_4$ samples with a carrier density that depends only slightly on the temperature. For the resistivity measurements contacts were microwelded to the samples with the subsequent application of a mercury-indium amalgam. Thin silver wire of 6 μm diameter was used for the conducting leads. Four contacts were attached along a single line for the resistivity measurements and at the corners of a square for Hall measurements on the large face of the sample. A magnetic field up to 7 T was generated by a superconducting solenoid.

The Hall emf, which was obtained as the voltage difference on the potential contacts for opposite directions of the field, was found to be essentially constant in the temperature range 4.2–160 K, indicating a weak temperature dependence of the carrier density. Magnetic transport measurements were performed in the range of fields $H = 0 - 6$ T at two temperatures $T = 4.2$ K and 125 K for the first sample and at $T = 4.2$ K and 111 K for the second sample. The magnetic field was applied along the direction of the current. We have analyzed the initial segment of the magnetic field dependence of the resistivity ρ at $H < 0.6$ T. Figures 1a and 1b show the field dependence of the resistivity for the two investigated samples at temperatures $T = 125$ K for the first sample and $T = 111$ K for the second sample, both of which are above $T_c = 106$ K. Figures 2a and 2b show the field dependence of the resistivity at $T = 4.2$ K for the same samples.

2. EXPERIMENTAL RESULTS

In Figs. 1a and 1b, the field curves of the resistivity for the two samples exhibit a square-law behavior: $\rho(H)|_{H\to 0} \sim H^2$. In Figs. 2a and 2b, as the field is increased, the resistivity increases initially until it reaches a maximum, and then decreases monotonically in higher fields. The linear curves extracted from these data are shown in Figs. 2a and 2b, and the remaining peaks are shown in Figs. 2c and 2d. The most noticeable feature out of the entire set of experimental data is

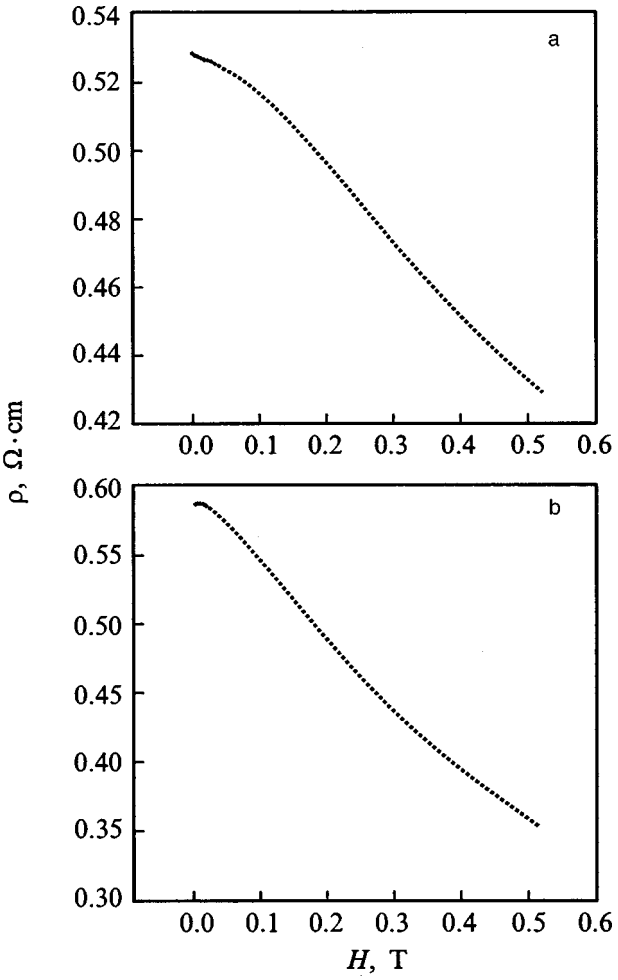

FIG. 1. Field dependence of the electrical resistivity at two temperatures: (a) $T = 125$ for the first sample; (b) $T = 111$ for the second sample.

the transition from a square-law dependence of the resistivity (Figs. 1a and 1b) above T_c to a linear dependence below T_c (Figs. 2a and 2b). The occurrence of the magnetoresistance peak superimposed on the linear curve at low fields can be attributed to the onset of a resistivity dependence on the angle between the directions of the magnetization and the current in the presence of magnetization rotation processes. The amplitude of the peak tends to zero as $T \to T_c$. Each of the two peaks has its own corresponding field at which the maximum is observed and its own particular amplitude of the maximum. Auxiliary measurements aimed at clarifying the dependence of the magnetoresistance on the angle between the applied field and the current have not been performed. However, existing data reveal a similarity to results obtained for epitaxial $La_{1-x}Ca_xMnO_\delta$ films.[5] We recall that magnetoresistance anisotropy has not been observed to date in bulk $La_{1-x}Ca_xMnO_\delta$ samples.

3. DISCUSSION OF RESULTS

Thus, having observed similar field dependences of the electrical resistivity in the radically different compounds $La_{1-x}Ca_xMnO_\delta$ and $HgCr_2Se_4(n)$, we conclude that, apart from the mechanism of binary exchange affecting the mag-

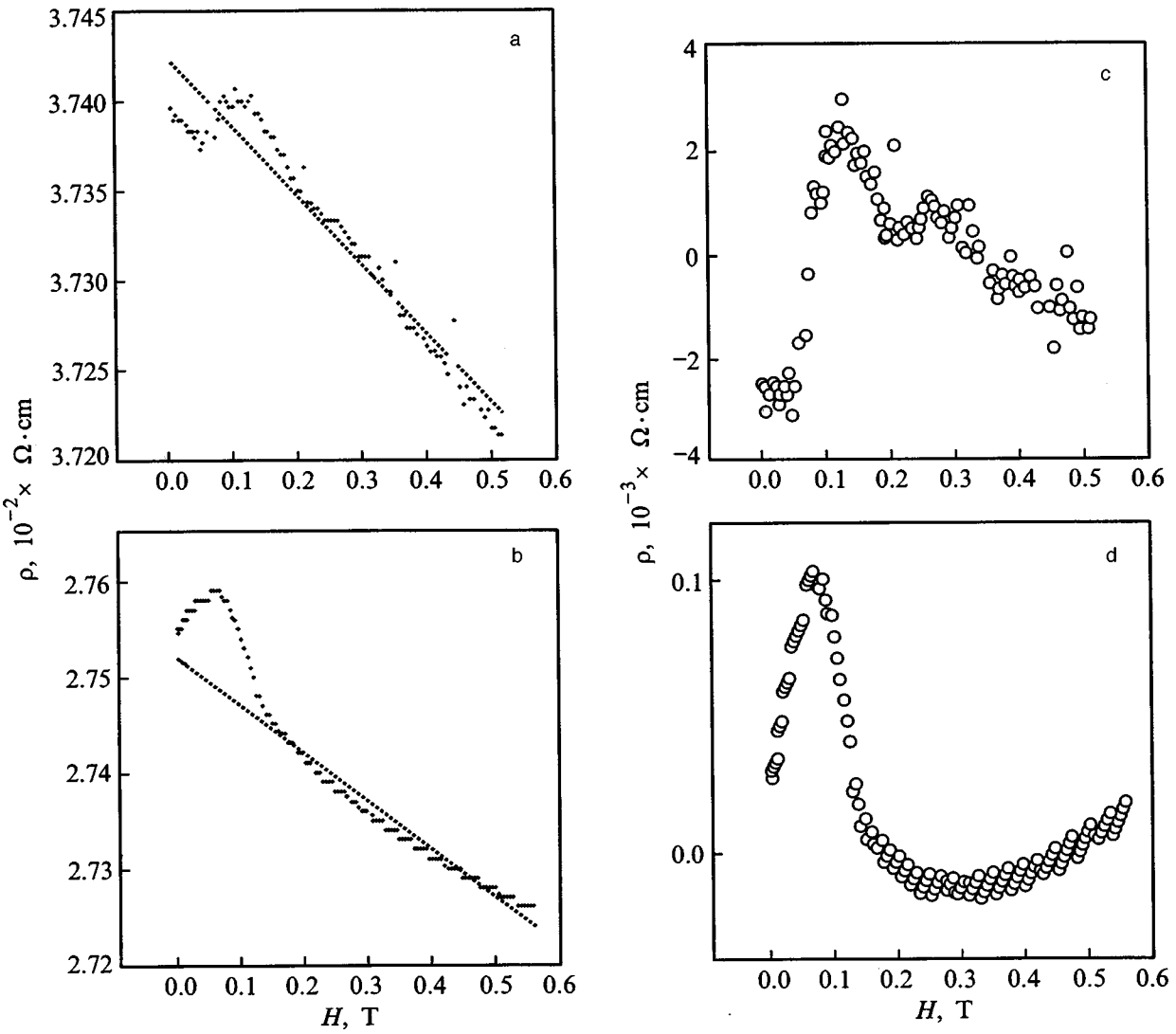

FIG. 2. Field dependence of the resistivity at a temperature $T=4.2$: (a) first sample; (b) second sample. Remaining positive magnetoresistance: (c) first sample; (d) second sample.

netoresistance and carriers of a polaron nature, an impurity mechanism of sd scattering may become the primary source for a large negative magnetoresistance.

The corresponding theory based exclusively on notions of an sd scattering mechanism also reproduces the required transition from a square-law temperature dependence of the resistivity above T_c to a linear dependence below T_c (Ref. 13). These theoretical notions are based on the results of calculating the band structure of a magnetic semiconductor taking into account the strong Coulomb correlation of carriers in the $3d$ states of chromium.[14] According to these calculations, the bands of $4s$ and $3d$ states behave altogether differently: Whereas the band of the more diffuse $4s$ states undergo strong spin splitting as a result of sd exchange when the temperature is lowered, the amplitude of the partial density of $3d$ states corresponding to the ${}^4A_2 \leftrightarrow {}^5E$ transition changes without any change in the energies of the states themselves. Shifts of the d band are possible only through Heisenberg exchange, but they are of the order of $T_c \approx 0.01$ K and are much smaller than for sd-exchange interaction. As a result, the fractions of $4s$ and $3d$ states and the effective hybridization parameter between them vary markedly in correspondence with the magnetization of the semiconductor. In addition, the distribution of carriers between the $4s$ and $3d$ scattering channels also changes, along with the relaxation rate in the latter channel. Calculations have shown[13] that a jump of the temperature dependence of the resistivity and a peak of the magnetoresistance ratio should be observed at $T \leqslant T_c$, the amplitude of the effect depending on the specific nature of carrier scattering in the $3d$ channel. The magnetoresistance anisotropy in this case emerges as a natural consequence of spin-orbit interaction, as found in the ferromagnetic transitions of metals.[6]

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