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Anomalous Hall effect in thin films of $Pr_{0.5}Sr_{0.5}MnO_3$

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We report on the type and density of charge carriers obtained from Hall-effect measurements in the three different magnetic phases of $Pr_{0.5}Sr_{0.5}MnO_3$. The field dependence of the Hall resistivity has two contributions of opposite sign: one is related to skew scattering and dominates in low magnetic fields; the other one is due to the Lorentz-force contribution which prevails at higher fields. This second contribution corresponds to a temperature-independent carrier density in the order of 0.8 holes per chemical unit cell. The skew-scattering contribution is related to the susceptibility of the material and is maximum at the transition temperature from the ferro- to the antiferromagnetic state. [S0163-1829(97)51522-0]

I. INTRODUCTION

The rare-earth perovskites $R_{1-x}D_xMnO_3$ (R: rare earth, D: divalent dopant) are characterized by their intimate relationship between magnetic ordering and electrical conductivity, culminating in the giant negative magnetoresistance effect (GMR).[1,2] The conductivity in the paramagnetic state is thermally activated, while a metalliclike behavior, based on the double-exchange mechanism, is observed below the Curie temperature. The magnetic perovskite $Pr_{0.5}Sr_{0.5}MnO_3$ exhibits, apart from its para- to ferromagnetic transition at $T_C=260$ K, a second transition to the antiferromagnetic state at $T_N=160$ K.[3,4] In the antiferromagnetic regime the system is semiconducting, which was ascribed to an ordering transition of the charge carriers, provided by the 1 to 1 ratio of Mn^{3+} and Mn^{4+} ions.[4]

In the present paper we address the question of whether the carrier density determined by Hall measurements complies with the value expected from the chemical doping. Besides the influence of the temperature-dependent magnetic structure of $Pr_{0.5}Sr_{0.5}MnO_3$ on the mobility of the carriers, the strong decrease of longitudinal resistivity with increasing field at constant temperature might be caused by an increasing concentration of free carriers.[4] A difficult point in the evaluation of the Hall data, however, is the superposition of an extraordinary contribution to the usual Hall voltage, arising from the spin-orbit interaction of the moving carriers with the localized magnetic moments.[5] This ''skew-scattering effect'' scales with the magnetization of the sample and dominates the measured Hall voltage up to field values where the magnetization becomes saturated. The different types of magnetic ordering in $Pr_{0.5}Sr_{0.5}MnO_3$ will probably strongly influence the magnitude of this anomalous Hall contribution. It follows that the ordinary Hall effect is only accessible in fields above the saturation field of typically 1 T for all temperatures below T_C. These high fields are, however, sufficient to destroy also the antiferromagnetic spin structure found below T_N by generating ferromagnetic or canted spin configurations.

II. EXPERIMENTAL

Thin films of $Pr_{0.5}Sr_{0.5}MnO_3$ were prepared *in situ* by dc-magnetron sputtering from a composite target onto (1 0 0)-oriented $SrTiO_3$ substrates. The details of the preparation have been reported in Ref. 6. Epitaxial growth, phase purity, and composition were checked by x-ray diffraction and Rutherford backscattering. Superconducting quantum interference device (SQUID) magnetization measurements enabled the determination of the Curie point $T_C=263$ K and the Néel temperature $T_N=160$ K. The Hall measurements were performed on a 3000 Å thick unpatterned film stripe (10 mm$\times$2.8 mm), using evaporated and annealed gold contacts in a conventional four-point Hall configuration. The transverse resistance R_T was measured by an ac technique and the Hall resistance R_H was then calculated from the half difference of the two R_T measurements with the magnetic-field direction parallel and antiparallel with the film's normal axis. Typical values for R_T were 10 Ω in zero field while the actual Hall contribution was below 5×10^{-2} Ω. In order to minimize noise and instabilities we focused on measurements at constant temperature, performed according to the following scheme: After carefully stabilizing the temperature, the magnetic field was increased first to $+12$ T and then reversed to -12 T. The resistance R_T was measured while sweeping the field from -12 T to zero field within 6 h. Then the field was switched to $+12$ T and R_T was recorded during the sweep back to zero field, again within 6 h. The sweep rate is a compromise between the requirements of low noise level and sufficient long-term stability of the absolute sample temperature. The special sequence of field sweeps was chosen to eliminate artifacts caused by the small remanent magnetization of the superconducting field coil and by the magnetic hysteresis of the $Pr_{0.5}Sr_{0.5}MnO_3$ film itself. Although $Pr_{0.5}Sr_{0.5}MnO_3$ does not show any hysteresis at room temperature, we noticed a small coercive field in the range of 100 mT below 150 K.[6] This hysteresis is also observed in the field dependence of the resistivity. The measurements of R_T were therefore performed on equivalent branches of the (resistive) hysteresis loop. Finally, a difficulty arose from the resistive memory effect in $Pr_{0.5}Sr_{0.5}MnO_3$, appearing at 70 K and demonstrating a large amplitude at $T\rightarrow0$. These irreversible and time-dependent changes of resistivity did not allow Hall measurements at very low temperatures. We therefore restricted our studies to temperatures above 50 K.

III. RESULTS AND DISCUSSION

Figure 1 shows the field dependence of the Hall resistivity $\rho_{xy}=dR_H$ (film thickness $d\approx$ 3000 Å) measured at different

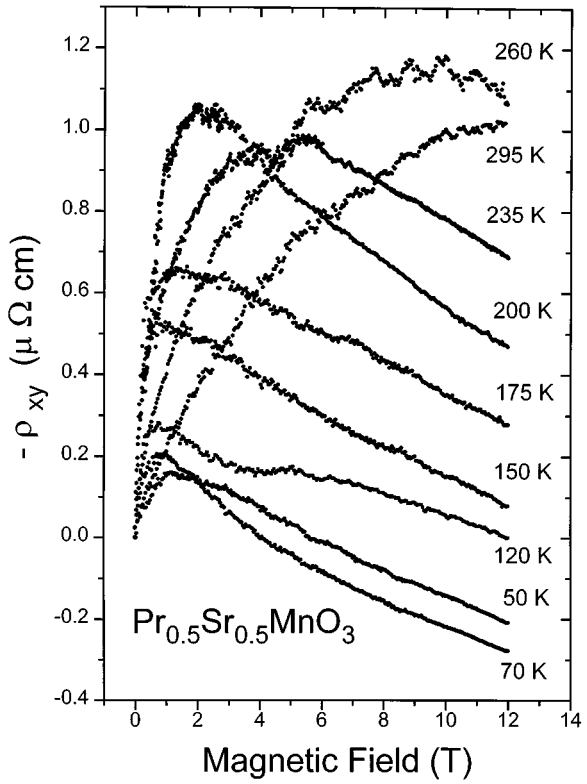

FIG. 1. Field dependence of the Hall resistivity ρ_{xy} for different temperatures between 50 and 295 K, covering the three magnetic regimes of $Pr_{0.5}Sr_{0.5}MnO_3$. The slope at high fields is almost temperature independent and results from the Lorentz force acting on hole-type carriers, while the anomalously steep increase at small fields emerges from magnetic scattering.

temperatures between 50 and 295 K. For clarity the curves measured at 100 and 280 K are omitted. All ρ_{xy} curves exhibit similar characteristics, which can be summarized as follows: (i) a steep increase at low fields, with the initial slope $d\rho_{xy}/dB$ depending on temperature; (ii) the presence of a maximum in ρ_{xy} with a particular temperature dependence of its value $\rho_{xy}^{max}(T)$ and of the respective magnetic field $B^{max}(T)$; (iii) a linear decrease at high fields with a slope practically independent of temperature. The maximum is much less pronounced at $T \geqslant 260$ K, because the field range was then apparently too small.

These experimental facts strongly resemble the features associated with the anomalous Hall effect in Co and CoNi alloys[7] as well as in the heavy-fermion system $CeCu_6$,[8] which have been partially explained by skew scattering. The enormous enhancement of ρ_{xy} at low fields is also observed in Fe,[7,9] where there is, however, no maximum, since the high-field and low-field slopes of $\rho_{xy}(B)$ have the same sign. In the following, our experimental data will be discussed in the framework of the model of Karplus and Luttinger,[5] which takes into account the ordinary Hall effect together with the spin-orbit contribution. The Hall resistivity is given by[5,10]

$$\rho_{xy}(B) = R_0 B + R_A(4\pi\mu_0)M(B), \qquad (1)$$

where $M(B)$ is the magnetization, R_0 the ordinary Hall constant given by the carrier density, and R_A the anomalous Hall coefficient, determined by the strength of the spin-orbit interaction between carriers and the localized magnetic moments. We note that this formalism was originally developed for metals, while $Pr_{0.5}Sr_{0.5}MnO_3$ exhibits semiconductorlike properties.[6] In small fields the absolute values of the longitudinal resistivity (8–20 mΩ cm in zero field) indicate that we are dealing with an anomalously low conductivity, which is quite close to the values typical for a Mott metal-insulator transition.

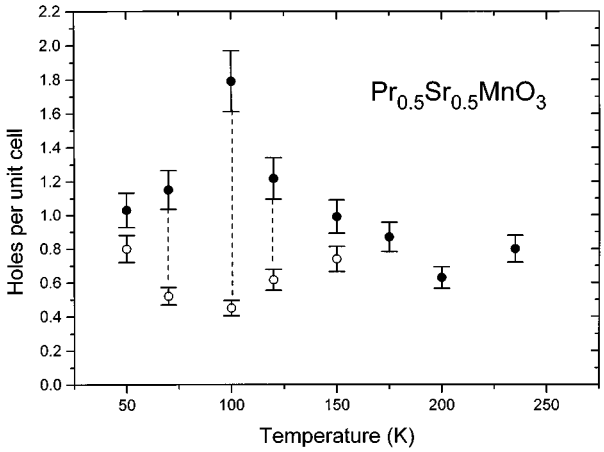

FIG. 2. Concentration of charge carriers, determined from the slope of the linear parts of the $\rho_{xy}(B)$ curves in Fig. 1. The average value corresponds to 0.82 holes per unit cell. A particular temperature dependence of the carrier concentration cannot be assumed. Below 150 K there is an apparent difference between the carrier densities in high fields (full circles) and in low fields (open circles).

A. The normal Hall effect

At high magnetic fields the sample magnetization becomes constant and the slope $d\rho_{xy}(B)/dB$ corresponds therefore to R_0 [Eq. (1)]. Using the data of Fig. 1 as R_0 values we calculated the carrier concentration within the one-band model, taking a unit-cell volume of 56.3 $Å^3$.[3] The resulting number of hole-type carriers per unit cell is shown in Fig. 2. The slopes are well-defined for temperatures between 175 and 235 K, but at lower temperatures we found two apparently different linear parts in the $\rho_{xy}(B)$ curves: the carrier densities determined from the high-field slopes (between 6 and 12 T) are represented in Fig. 2 by full dots, carrier densities determined at low fields (between 1 and 4 T) by open symbols. Since the transition between the two regimes seems to be gradual we suppose that there are also intermediate slope values, indicated by dashed lines. An explanation for this bending of the ρ_{xy} curves might be found in a substantial enhancement of carrier mobility through the increasing external field, which leads to the GMR effect of the longitudinal resistivity. A field-induced transition from a low-carrier to a high-carrier state in the sense that the external field supresses the charge ordering is improbable, because the calculated carrier densities are unphysically high (especially at 100 K).

Ignoring the less reliable data in Fig. 2 (at 70, 100, and 120 K) gives an average value of $\langle n \rangle = 0.82$ holes per unit cell with an uncertainty of 30%. This differs from the value of 0.5 holes that was suggested in Ref. 4. This might be

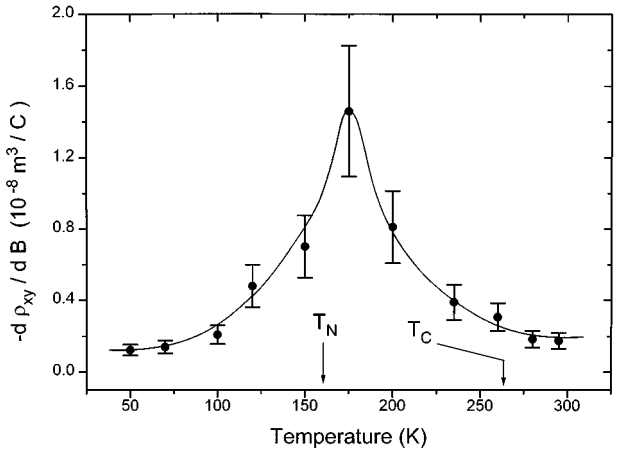

FIG. 3. Temperature dependence of the initial slope of $\rho_{xy}(B)$, reflecting the strength of the anomalous Hall contribution. The relationship with the magnetic susceptibility is evident from the small values for the paramagnet, a steep increase for the ferromagnet, and a breakdown upon entering the antiferromagnetic phase. The transition temperatures are indicated, the solid line is a guide to the eye.

understood in the following way: Pr exhibits intrinsic mixed-valence properties as seen from the composition of the oxide Pr_6O_{11}, i.e., the average valence is $+3.67$. If we assume that the bonds in $Pr_{0.5}Sr_{0.5}MnO_3$ have mainly ionic character, we can balance the valencies of the individual ions only with a statistical ratio of 0.83 Mn^{3+} and 0.17 Mn^{4+} ions per chemical unit cell. The deficient conduction electron provided by Mn^{3+} compared to Mn^{4+} might be considered as a hole-type carrier. The numerical value of the ordinary Hall coefficient R_0 is 4.3×10^{-10} m^3/C. Comparing R_0 with the room-temperature value of zero-field resistivity (8 mΩ cm) gives a typical carrier mobility $\mu=5\times10^{-2}$ cm^2/V s. This is relatively low and the carriers seem therefore to interact strongly with the localized magnetic moments, giving in turn rise to the anomalous Hall contribution.

B. The anomalous Hall effect

The precise determination of the anomalous Hall contribution R_A in Eq. (1) requires knowledge of the field-dependent magnetization of the system. The $M(B)$ measurements of the $Pr_{0.5}Sr_{0.5}MnO_3$ film suffered, however, from the temperature-dependent diamagnetic background of the $SrTiO_3$ substrate and gave values that were too low. Moreover, these SQUID measurements were only possible in the in-plane geometry and not in the configuration with the field perpendicular to the film's surface. The two geometries should provide different results due to the demagnetization effects. Therefore we will focus the discussion at present to the small-field regime, where the magnetization $\mu_0 M$ in Eq. (1) can be calculated from the susceptibility as χB.

The slope $d\rho_{xy}/dB=R_0+R_A(4\pi\chi)$ for $B\rightarrow0$ reflects the product of the anomalous coefficient R_A with the susceptibility, while R_0 is a minor correction. Figure 3 shows the numerical values of these initial slopes from the curves in Fig. 1. They were determined by linear regression in the field interval between 0.15 and 1.0 T. In cases where a flattening of $\rho_{xy}(B)$ was already observed around 1 T (mainly for intermediate temperatures), we restricted the field interval to the upper limit of the linear initial part. Above the Curie point at 260 K, $d\rho_{xy}/dB$ is small due to the comparatively low susceptibility in the paramagnetic state and increases substantially in the ferromagnetic regime. This increase should be fully related to χ since the decrease of R_A with falling temperature is experimentally well established.[5] Upon entering the antiferromagnetic state at $T_N\approx160$ K the initial ρ_{xy} slope collapses to values similar for the paramagnet, which is caused by a decrease of susceptibility, probably corroborated by a decrease of R_A itself. The latter effect is indeed important because $\chi(T)$ has a nonzero value also for the antiferromagnetic regime.[6] In an ideal antiferromagnet one would actually expect the absence of the anomalous Hall effect. In order to estimate the coefficient R_A for the paramagnetic phase of $Pr_{0.5}Sr_{0.5}MnO_3$ quantitatively, one can approximate the susceptibility above T_C by the magnetization of independent ions in the low-field limit:[11]

$$d\rho_{xy}/dB=R_0+R_A(4\pi\mu_0)(Np^2\mu_B^2)/(3k_BT). \qquad (2)$$

N is the volume density of Mn ions, μ_B the Bohr magneton, and p the effective magneton number. With $p=4$ for Mn^{4+} and 5 for Mn^{3+}, $R_0=4.3\times10^{-10}$ m^3/C and $d\rho_{xy}/dB=-1.75\times10^{-9}$ m^3/C at 295 K, one ends up with R_A (295 K) $=-1.8\times10^{-8}$ m^3/C. The anomalous and the ordinary Hall coefficient are thus linked via $R_A(295\text{ K})=-42\times R_0$, with R_A being electronlike and R_0 being holelike. The absolute value of the proportionality factor is in the same range as in pure Fe (25.6) and NiCo alloys (up to 40),[7] each time determined at 280 K. The opposite signs of R_0 and R_A occur also in Co and CoNi alloys,[7] the heavy-fermion system $CeCu_6$,[8] and $La_{0.67}Ca_{0.33}MnO_3$.[12] It is worth noting that the sign of the anomalous contribution is not related in an evident way to the carrier type of the material.

Finally, we will evaluate the temperature dependence of R_A, assuming that it does not vary with the external field at a given temperature. For ferromagnetic metals and alloys there is an indirect relationship between R_A and the temperature via the longitudinal resistivity: depending on the microscopic scattering mechanism one obtains $R_A(T)\propto\rho(T)^n$ with $n=1$ for pure skew scattering and 2 for side jumps.[13] In practice noninteger exponents are found, mostly between 1 and 2. For the GMR in perovskites things are less evident due to the strong field-induced resistivity decrease at constant temperature. To obtain nevertheless an estimate for the temperature dependence of the anomalous coefficient one can consider the local maxima of the ρ_{xy} curves in Fig. 1. Rewriting Eq. (1) allows the renormalization of ρ_{xy}^{max} with respect to the normal contribution by subtracting R_0B^{max}:

$$R_A(4\pi\mu_0)M(B^{max})=\rho_{xy}^{max}-R_0B^{max}. \qquad (3)$$

The quantity on the right-hand side of Eq. (3) is plotted in Fig. 4, with the error bars calculated from the maximum errors of ρ_{xy}^{max} and B^{max}. Furthermore, we assume that the magnetization is mainly saturated at B^{max}, i.e., $M(B^{max})\approx M_S$, with M_S being temperature independent. From this we conclude that the left-hand side of Eq. (3) is approximately proportional to R_A itself. The solid line in Fig.

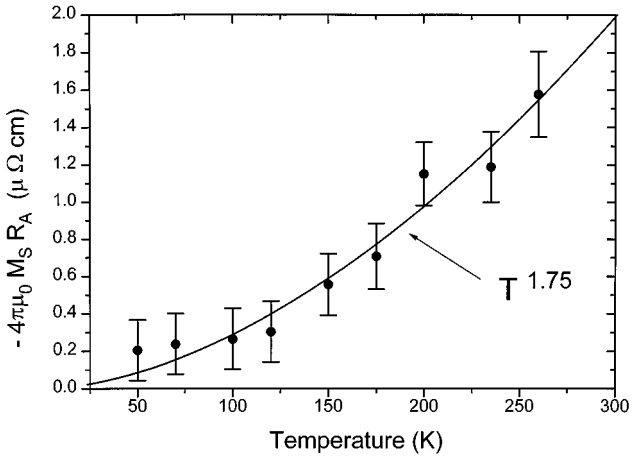

FIG. 4. Temperature dependence of the quantity $\rho_{xy}^{max}-R_0B^{max}$, being proportional to $R_A(T)$. The solid line is a fit curve $\propto T^{1.75}$.

4 is a fit of the power law T^{α} with $\alpha=1.75$ (uncertainty ± 0.20). This numerical value is similar to typical exponents n in the relation $R_A \propto \rho^n$ known for the magnetic metals.[13] In the case of $Pr_{0.5}Sr_{0.5}MnO_3$, however, there is no direct connection between the scaling $R_A \propto T^{\alpha}$ and the longitudinal resistivity ρ via $\rho \propto T$: $\rho(B^{max})$ increases gradually from 7 mΩ cm at 260 K to 10.5 mΩ cm at 50 K.[6]

In summary, we determined the carrier concentration of a thin $Pr_{0.5}Sr_{0.5}MnO_3$ film with 0.8 holes per unit cell and a typical zero-field mobility of 5×10^{-2} cm^2/V s. The carrier density does not depend on temperature nor on magnetic field for $T>150$ K, although the apparent field-induced increase of hole concentration found below 150 K requires further clarification. Besides that, we observed a strong anomalous Hall contribution, related to the product of the sample magnetization and the anomalous Hall coefficient. This ''skew-scattering'' contribution reflects the magnetic transitions of $Pr_{0.5}Sr_{0.5}MnO_3$ while the anomalous coefficient itself has an electron-type sign and a power-law dependence on temperature.

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