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Proportional relation between magnetoresistance and entropy suppression due to magnetic field in metallic ferromagnets

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A temperature-independent proportional relation was discovered between magnetoresistance and magnetoentropy in metallic ferromagnets, $La_{0.6}Sr_{0.4}CoO_3$, $SrRuO_3$, and $CoPt_3$ up to 90 kOe above, at, and just below Curie temperature. This concludes that the magnetoresistance due to suppression of spin-disorder scattering is well scaled by the magnetic entropy rather than the magnetization. In contrast, no proportional relation was observed in $La_{0.825}Sr_{0.175}MnO_3$, which is understood by the characteristic magnetoresistance originating from Jahn-Teller effect and electronic phase separation.

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Magnetoresistance effects, a change in electric resistivity by applying a magnetic field, are generally classified into orbit and spin contributions. The orbit contribution is based on a change in electron orbit under electric and magnetic fields due to Lorentz force.[1] This is an useful physical quantity because it reflects the shape of Fermi surface.[2] The spin contribution is also useful, because this reflects the property of electron scattering due to spin fluctuation or spin disorder in magnetic metal.[3] It is well known that the spin contribution is correlated with magnetization.[3,4] However, there is inconsistency between theory and experiment on the relation between spin contribution and magnetization as described below.

The following relation is well known for metallic ferromagnets:

$$\frac{\rho_{\mathrm{sd}}(T,H)-\rho_{\mathrm{sd}}(T,0)}{\rho_{\mathrm{sd}}(T,0)}=-A\left\{\frac{M(T,H)}{M_{\mathrm{sat}}}\right\}^2, \qquad (1)$$

where $\rho_{\mathrm{sd}}(T,H)$ and $M(T,H)$ are resistivity due to spin-disorder scattering and magnetization, respectively, at a temperature T and under a magnetic field H and M_{sat} is a saturation magnetization at 0 K.[4–6] The theoretical investigations based on several models, s-d exchange model,[5] double-exchange model,[6] and so on[7] explain this proportional relation and predict the temperature-independent proportional constant A. Experimentally, Eq. (1) is, however, found only above but not near the Curie temperature T_{C}. The temperature-dependent nonlinearity has been observed in $\{\rho(T,H)-\rho(T,0)\}/\rho(T,0)$ versus $\{M(T,H)/M_{\mathrm{sat}}\}^2$ curve just above T_{C},[9–13] which makes the analysis based on Eq. (1) ambiguous. This inconsistency just above T_{C} between theory and experiment is naturally understandable, because these theories are based on a mean-field approximation and thus does not include a contribution from short-range spin order,[5,6] which is easily found from the fact that Eq. (1) is expressed by only a long-range order parameter M. As pointed out by Fisher and Langer,[8] short-range spin correlations play an important role on the resistivity around T_{C}. It is, of course, difficult to estimate the short-range order or correlation experimentally, but a magnetic entropy is expected to be a candidate for a measurable quantity reflecting both long-range and short-range spin orders. In fact, Rawat *et al.* have reported a similar dependence between magnetocaloric and magnetoresistance effects in TmCu and TmAg.[14]

In the present study, a relation between magnetoresistance and magnetoentropy (defined as a change in entropy by applying a magnetic field) is studied. A simple proportional relation,

$$\rho(T,H)-\rho(T,0)=K\{S(T,H)-S(T,0)\} \qquad (2)$$

is found in metallic ferromagnets, $La_{0.6}Sr_{0.4}CoO_3$, $SrRuO_3$, and $CoPt_3$, where $S(T,H)$ is an entropy at T and under H. The important results are that the relation of Eq. (2) is observed up to 90 kOe above, at, and just below T_{C} and that the proportional constant, K, is independent of temperature. This indicates that the magnetoresistance is well scaled by the magnetoentropy rather than the magnetization. Contrary to these materials, such a proportional relation is not observed in $La_{0.825}Sr_{0.175}MnO_3$.

The electromagnetic properties of materials used for the present study are summarized as follows. $La_{0.6}Sr_{0.4}CoO_3$ exhibits a long-range ferromagnetic ordering at $T_{\mathrm{C}}\approx 245$ K.[15] The electrical conductivity is metallic above and below T_{C}.[10] It has been proposed that $La_{1-x}Sr_xCoO_3$ is a double-exchange ferromagnet with $t_{2g}^5\sigma^{*1-x}$ configuration (localized t_{2g} and itinerant σ^* electrons).[16] $SrRuO_3$ also shows a ferromagnetic phase transition at $T_{\mathrm{C}}\approx 160$ K (Ref. 17) and a metallic conductivity above and below T_{C}.[18] $SrRuO_3$ has been believed to be an itinerant ferromagnet with π^{*4} configuration.[19] T_{C} of $CoPt_3$ is about 290 K when Pt and Co atoms are ordered in Cu_3Au type and increases with increasing the disordering.[20] The ferromagnetic phase transition at $T_{\mathrm{C}}\approx 283$ K in $La_{0.825}Sr_{0.175}MnO_3$ is simultaneously accompanied by a metal-insulator transition.[9] The corresponding colossal magnetoresistance has been understood by Jahn-Teller distortion[21] and electronic phase separation[22] rather than suppression of spin-disorder scattering.

Polycrystalline $La_{0.6}Sr_{0.4}CoO_3$ and $SrRuO_3$ were prepared by a solid-state reaction method. Polycrystalline $CoPt_3$ was prepared as follows. Fine particles of Pt-Co alloy and Co_3O_4 obtained by dissolving Co and Pt metals into aqua regia and then decomposed were reacted at 1773 K for 24 h in H_2 flow. The samples pressed into a pellet was sintered at 1773 K and then cooled from 1073 to 673 K at a rate of 2.5 Kh^{-1} in order to proceed the ordering of Pt and Co atoms.[20] A

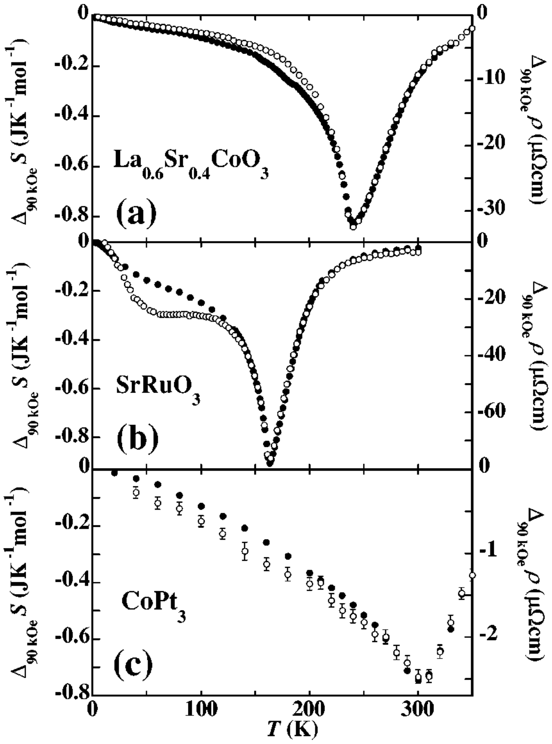

FIG. 1. Temperature dependences of $\Delta_{90\ \mathrm{kOe}}S$ (solid circles) and $\Delta_{90\ \mathrm{kOe}}\rho$ (open circles): (a) $La_{0.6}Sr_{0.4}CoO_3$, (b) $SrRuO_3$, and (c) $CoPt_3$ polycrystals. Error bars are less than the mark size except for $CoPt_3$.

$La_{0.825}Sr_{0.175}MnO_3$ single crystal was grown by a floating-zone method[9] and confirmed by a Laue back reflection method. Powder x-ray diffraction with Cu$K\alpha$ radiation using MAC Science MXP 18-HF detected no impurity phase in all samples and confirmed nearly ordered $CoPt_3$. Heat capacities were measured by a relaxation method using physical property measurement system (PPMS, quantum design). dc magnetizations were measured using a superconducting quantum interference device magnetometer (MPMS5S, quantum design; 0 Oe $<H\leqslant 50$ kOe) and PPMS (50 kOe $<H\leqslant 90$ kOe). Resistivities were measured by an ac four-probe method with a frequency of 47 Hz and an amplitude of 10 mA using PPMS. The magnetic field was applied parallel to the electrical current, because the orbit contribution is zero in this setup when Fermi surface is isotropic.[23]

In this paper, a difference in a physical quantity, $A(T,H)$, between under 0 Oe and H is denoted as $\Delta_H A(T) = A(T,H) - A(T,0)$. A magnetoentropy, $\Delta_H S(T)$, was calculated by the following equations:

$$\Delta_H S(T)=\Delta_H S(T_0)+\int_{T_0}^{T}\frac{\Delta_H C(T')}{T'}dT', \qquad (3)$$

or

$$\Delta_H S(T)=\int_0^H\left\{\frac{\partial M(T,H')}{\partial T}\right\}_{H'}dH', \qquad (4)$$

where $C(T,H)$ is a heat capacity at T and under H. Because the experimental error of $\Delta_H C$ is large in the temperature range far away T_C and under low field, the data under 90 kOe in the range $\sim 0.7\ T_C < T < \sim 1.2\ T_C$ shown in Figs. 1 (except for $CoPt_3$) and 4 were calculated by Eq. (3), and the other data were calculated by Eq. (4). In a ferromagnetic phase, a magnetoentropy estimated by Eq. (4) is incorrect because of irreversibility in M-H loop. However, the irreversibility of the present samples is not large and thus the deviation from the correct value is small at least under high fields. $\Delta_H S(T_0)$ in Eq. (3) was estimated from Eq. (4) at $T_0 = \sim 1.2\ T_C$.

The open and solid circles in Figs. 1(a)–1(c) represent $\Delta_{90\ \mathrm{kOe}}\rho$ and $\Delta_{90\ \mathrm{kOe}}S$, respectively, for $La_{0.6}Sr_{0.4}CoO_3$, $SrRuO_3$, and $CoPt_3$. It is clear that the temperature dependences of $\Delta_{90\ \mathrm{kOe}}S$ and $\Delta_{90\ \mathrm{kOe}}\rho$ are similar to each other above, at, and just below T_C. Such a similarity was not observed below about 220, 120, and 200 K in $La_{0.6}Sr_{0.4}CoO_3$, $SrRuO_3$, and $CoPt_3$, respectively. Particularly, the magnetoresistance of $SrRuO_3$ showed an extraordinary shoulder around 60 K, which has been reported in an epitaxial $SrRuO_3$ thin film.[24]

The insets of Figs. 2(a)–2(c) show $\Delta_H\rho$–M^2 curves at a constant temperature for $La_{0.6}Sr_{0.4}CoO_3$, $SrRuO_3$, and $CoPt_3$, respectively. It is found that the curve is a downward convex one at least just above T_C and that $\Delta_H\rho$ is a many-valued function of M^2 ($\Delta_H\rho$ at any M^2 decreases as T_C is approached). On the other hand, $\Delta_H\rho$–$\Delta_H S$ plots at a constant temperature shown in Figs. 2(a)–2(c) exhibit an excellent linearity above, at, and just below T_C and even up to the high field of 90 kOe. Moreover, it is found that the proportional constant K is independent of temperature. This indicates that $\Delta_H\rho$ is a single-valued function of $\Delta_H S$. The proportional constants estimated by least-square fitting are 27, 82, and 3.5 $\mu\Omega\ \mathrm{cm\,J^{-1}\,K\,mol}$ for $La_{0.6}Sr_{0.4}CoO_3$, $SrRuO_3$, and $CoPt_3$, respectively. This proportional relation was also confirmed by the other plot of same data shown in Fig. 3. It is found that $\Delta_H\rho/\Delta_H S$ is constant and independent of temperature within the experimental error, though the data in the low-field region are scattered due to the large experimental error originating from the small magnitude of $\Delta_H\rho$ and $\Delta_H S$.

The magnetoresistance effects of $La_{0.6}Sr_{0.4}CoO_3$, $SrRuO_3$, and $CoPt_3$ are complex far below T_C (not shown). Steep decrease in resistivity was observed in the low-field region below about 50 and 200 K in $La_{0.6}Sr_{0.4}CoO_3$ and $CoPt_3$, respectively, possibly due to tunneling magnetoresistance across grain boundary[25] or domain-wall scattering.[26] In $SrRuO_3$, positive magnetoresistance was observed below about 10 K possibly due to the orbit contribution.[1] These behaviors far below T_C are discussed later again.

The proportional relation of Eq. (2) naturally suggests that,

$$\Delta_H\rho_{\mathrm{sd}}(T)=K\Delta_H S_{\mathrm{mag}}(T), \qquad (5)$$

where S_{mag} is a magnetic entropy. The reliability of Eq. (5) is supported by the following three facts, (i)–(iii). (i) Eq. (1) can be derived from Eq. (5) when the mean-field approximation is valid (far above T_C) and the magnetic field is relatively small. Namely, the relations of $\chi = C_{\mathrm{CW}}/(T-\theta)$, $M = \chi H$, and Eq. (5) result in $A = KM_{\mathrm{sat}}^2/2C_{\mathrm{CW}}\rho_{\mathrm{sd}}(T,0)$, where

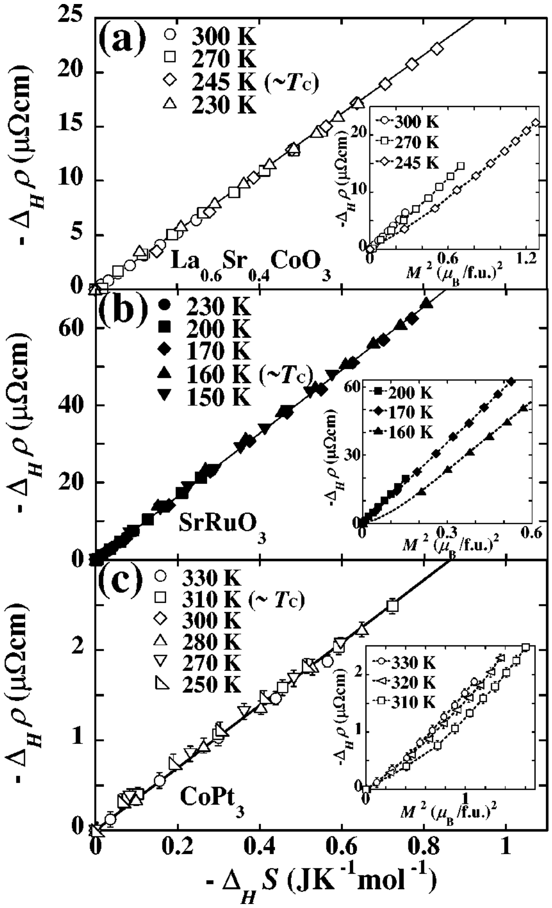

FIG. 2. $\Delta_H\rho$ vs $\Delta_H S$ plot in the range of 0 Oe $\leqslant H \leqslant$ 90 kOe at some temperatures: (a) $\mathrm{La_{0.6}Sr_{0.4}CoO_3}$, (b) $\mathrm{SrRuO_3}$, and (c) $\mathrm{CoPt_3}$ polycrystals. Solid lines represent results of fitting by Eq. (2). Insets show $\Delta_H\rho$ vs M^2 plot. Dotted lines in the insets are guides for the eyes. Error bars are less than the mark size except for $\mathrm{CoPt_3}$.

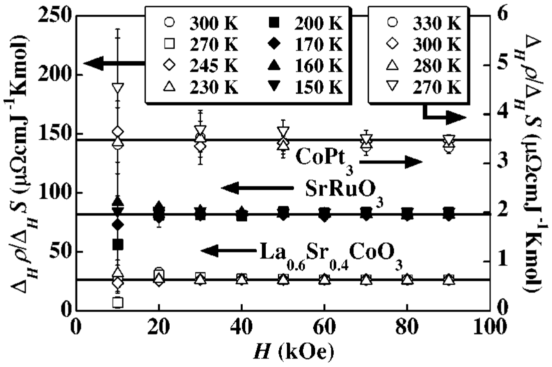

FIG. 3. Magnetic field dependence of $\Delta_H\rho/\Delta_H S$ for $\mathrm{La_{0.6}Sr_{0.4}CoO_3}$ (open symbols; left axis), $\mathrm{SrRuO_3}$ (solid symbols; left axis), and $\mathrm{CoPt_3}$ (open symbols; right axis). Horizontal lines represent that $\Delta_H\rho/\Delta_H S = 27$, 82, and 3.5 $\mu\Omega\,\mathrm{cm\,J^{-1}\,K\,mol}$, respectively.

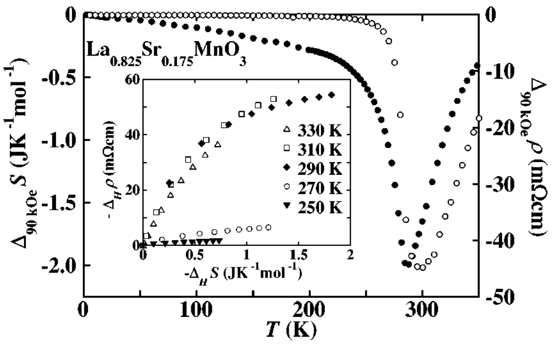

FIG. 4. Temperature dependences of $\Delta_{90\,\mathrm{kOe}}S$ (solid circles) and $\Delta_{90\,\mathrm{kOe}}\rho$ (open circles) for $\mathrm{La_{0.825}Sr_{0.175}MnO_3}$ single crystal. Inset shows $\Delta_H\rho$ vs $\Delta_H S$ plot in the range of 0 Oe$\leqslant H \leqslant$90 kOe.

$C_{\rm CW}$ and θ are Curie-Weiss constant and parametric Curie temperature, respectively. In this case, A is independent of temperature, because $\rho_{\rm sd}(T,0)$ is a constant above $T_{\rm C}$ in the mean-field theory.[5,6] (ii) The deviation from Eq. (1) just above $T_{\rm C}$ (see the insets of Fig. 2) is explained by Eq. (5). In the critical region, $\chi = C'/(T-T_{\rm C})^{\gamma}$, where γ is the critical exponent. This and $M=\chi H$ relations result in $A = KM_{\rm sat}^2\gamma(T-T_{\rm C})^{\gamma-1}/2C'\rho_{\rm sd}(T,0)$. This explains the experimental result that the slope of $\Delta_H\rho - M^2$ curve at $M^2 = 0$ decreases as $T_{\rm C}$ is approached, because $\gamma > 1$. In addition, the downward convex $\Delta_H\rho - M^2$ curve is consistent with the upward convex M-H curve generally observed just above $T_{\rm C}$ and in the high-field region. (iii) Fisher-Langer relation (found only in the critical region),

$$\frac{\partial \rho_{\rm sd}}{\partial T} = kC_{\rm mag}, \tag{6}$$

can be derived from Eq. (5), where $C_{\rm mag}$ is a magnetic heat capacity and k is a constant.[7] Equation (5) is equivalent to the relation

$$\rho_{\rm sd}(T,H) = KS_{\rm mag}(T,H) + \rho_0 \tag{7}$$

at least in the measurement T and H ranges (relatively large entropy region), where ρ_0 is a constant. This results in

$$\frac{\partial \rho_{\rm sd}}{\partial T} = K\frac{C_{\rm mag}}{T} \approx \frac{K}{T_{\rm C}}C_{\rm mag} \tag{8}$$

in the vicinity of $T_{\rm C}$. It should be noted that Eq. (7) does not hold for the spin-wave scattering, because the corresponding resistivity and magnetic entropy are proportional to T^2 and $T^{3/2}$, respectively.[27] This implies that the magnetoresistance due to suppression of spin-wave excitation does not obey Eq. (2) or that Eq. (5) does not hold in the small entropy region.

The origin of metallic ferromagnetism has been believed to be different for $\mathrm{La_{0.6}Sr_{0.4}CoO_3}$,[16] $\mathrm{SrRuO_3}$,[19] and $\mathrm{CoPt_3}$.[28] In spite of this, the proportional relation between $\Delta_H\rho$ and $\Delta_H S$ was observed in these materials. It is difficult to consider that the proportional relation holds accidentally only for the three materials. It is thus natural to suggest that the proportional relation is universal for the magnetoresistance due to suppression of spin disorder. Of course, it is taken for granted that the resistivity due to spin-disorder scattering decreases with decreasing the magnetic entropy. However, the simple proportional relation is quite surprising, because the resistivity due to spin-disorder scattering is a complex functional of spin-correlation functions[8] that is not simply connected with a magnetic entropy.

As described below, the quantitative relation of Eq. (5) is found to be useful to detect a presence of other contributions to the magnetoresistance except for the suppression of spin disorder. Figure 4 and the inset show the temperature dependence of $\Delta_{90\ \mathrm{kOe}}\rho$ and $\Delta_{90\ \mathrm{kOe}}S$ and $\Delta_H\rho$–$\Delta_H S$ plot, respectively, for $La_{0.825}Sr_{0.175}MnO_3$. In this material, the proportional relation was not observed between $\Delta_H\rho$ and $\Delta_H S$ in the whole temperature region. (Similar results were also obtained for the polycrystalline samples.) This is easily understood, because the magnetoresistance of perovskite-type manganese oxides is well known to originate mainly from Jahn-Teller distortion[21] and electronic phase separation[22] rather than suppression of spin-disorder scattering. The deviation from Eq. (2) observed in $La_{0.6}Sr_{0.4}CoO_3$, $SrRuO_3$, and $CoPt_3$ far below T_C would be also explained by other contributions as mentioned before, namely, grain boundary, domain wall, spin wave, orbit contribution, and so on. Equations (7) or (8) predicts that $d\rho_{sd}/dT$ should be positive, because C_{mag} is always positive. However, negative $d\rho/dT$ has been observed above T_C in some metallic ferromagnets, such as Gd[29] and $Tl_2Mn_2O_7$,[11] which also implies a presence of other contributions.

The present study concludes that K in Eq. (5) is the most useful physical quantity reflecting the spin-disorder scattering. The theoretical derivation of Eq. (5) and systematic study on the material dependence of K will proceed to understand the transport and thermodynamic properties of metallic ferromagnets. However, using a single crystal is indispensable in order to estimate the intrinsic value of K, because the magnitude of resistivity is different between polycrystalline and single crystalline samples.[18]

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