Resistivity and magnetotransport in CrO_2 films

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The resistivity of films of the metallic magnet CrO_2 deposited onto ZrO_2 substrates has been measured in the temperature range $T=1.6$ to 410 K. Longitudinal and transverse magnetoresistances have also been measured between 0.55 and 380 K in magnetic fields up to 10 T. The resistivity has a decrease in slope as a function of temperature at the Curie point, $T_c=390$ K, and becomes linear in temperature below about 5 K. The magnetoresistances (MR) for both field orientations are negative and linear with field above about 200 K for fields up to 3 T, while they show a concave dependence on field below that temperature. Their magnitude decreases with decreasing temperature down to 200 K and then increases for temperatures down to 5 K. Below 5 K, the longitudinal MR values decrease and the transverse values stay about constant as T is lowered. Below 100 K, the resistance in a transverse field has a minimum at about 3 T. Chromium dioxide has been found theoretically to be a half-metallic ferromagnet. The low temperature transport measurements reported here are interpreted in terms of this model. [S0163-1829(98)05041-3]

INTRODUCTION

The metallic ferromagnet chromium dioxide has a Curie temperature T_c near 390 K. Its rutile crystal structure is the same as that of the insulator TiO_2, the antiferromagnet MnO_2, the good metal RuO_2, and VO_2 which shows a metal insulator transition. Recent band structure calculations by Schwarz[1] and others[2,3] imply that CrO_2 is a half metal; that is, the majority spin electrons have a metallic band structure while the minority ones have a semiconductorlike energy gap at the Fermi surface. Other applications for this material are suggested if this band structure is indeed correct. For example, if a half metal is used in a tunneling device such as was studied by Moodera *et al.*,[4] the device is expected to show very large magnetoresistance. Films of CrO_2 are made only by a chemical vapor deposition CVD technique, which means that it is difficult to make films directly in useful geometric shapes, CrO_2 being relatively difficult to etch. A method[5] of producing patterned films has been developed which may expand the possibilities for producing devices using this material.

Interest in the possible half-metallic nature of CrO_2 has led to several experimental and theoretical studies of this material. Good agreement between experiment and theory was found by Brändle *et al.*[6] in the diagonal optical conductivity and the reflectivity. Calculations of the off-diagonal magneto-optical conductivity by Uspenskii, Kulatov, and Halilov,[7] also agreed with experiment. Kämper, Schmitt, and Güntherodt[8] reported that the electrons observed in a photoemission experiment were nearly 100% polarized. Large magnetoresistance ascribed to intergrain tunneling in discontinuous films has been reported by Hwang and Cheong.[9] Vacuum tunneling measurements by Weisendanger *et al.*[10] also suggested nearly 100% polarization. These results are consistent with the band structure calculations, but the optical measurement techniques probed electrons 2 eV from the Fermi level. Thus the theoretical results are not yet firmly established. Recently Lewis, Allen, and Sasaki[2] pointed out that although the mean free path of electrons at 600 K is only a few angstroms, the resistivity continues to increase as the temperature rises. Also, the specific heat at low temperature[11] is considerably larger than the value predicted by band theory. Thus the nature of CrO_2 is not yet fully understood.

The absence of single-particle states at E_F for minority-spin electrons should affect the transport properties of a half metal. Although transport measurements give important information about the spin-dependent behavior of electrons near E_F in CrO_2, there have been only a few reports so far. Magnetoresistance data especially have been limited. The temperature and magnetic field dependences of the resistivity of CrO_2 films have now been measured and are reported here.

EXPERIMENTAL TECHNIQUE

The CrO_2 films were made on ZrO_2 substrates by a CVD method using a two-zone tube furnace as described by Ishibashi, Namikawa, and Satou.[12] The starting material was CrO_3, which was placed in the first zone at a temperature of 260 °C. Oxygen flowing at 0.5 l/sec was the carrier gas. The substrates were placed in the second zone at 400 °C. The deposition took several hours. X-ray diffraction measurements showed the films to have a highly textured rutile structure with the a axis normal to the substrate. The thickness of the film for which data are reported here was 0.80 μm as measured by atomic force microscopy.

The resistivity was measured in the range between 1.6 and 410 K using a four-probe dc method. The longitudinal and transverse magnetoresistances were measured with a four-probe ac bridge in the temperature range 0.55 to 380 K and in magnetic fields up to 10 T. The current direction was parallel to the (100) crystallographic plane. Temperature was measured with a calibrated carbon glass thermometer and an ac thermocouple. All of the data were averaged by computer as they were collected to raise their precision. The magnetization of a film made under similar conditions was measured using a SQUID magnetometer in the temperature range 2 K

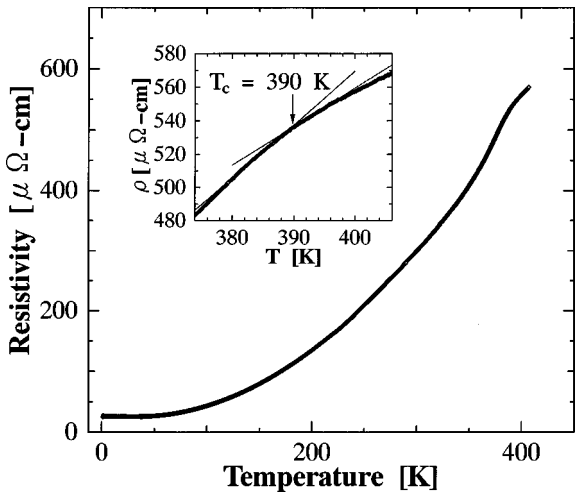

FIG. 1. Temperature dependence of the resistivity of a CrO_2 film. Inset: Change in slope of the resistivity near 390 K.

to 350 K with results similar to those observed by Brändle *et al.*[13]

RESULTS AND DISCUSSION

Resistivity

Figure 1 shows the temperature dependence of the resistivity of a CrO_2 film deposited onto ZrO_2. The resistivity increases with increasing temperature and has a bend at the Curie temperature of 390 K. The shape of the resistivity curve and the values of resistance observed are similar to the results of Rodbell, Lommel, and DeVries.[14] We found that the resistivity shows a T^2 dependence in a temperature range from about 130 K to about 240 K, as seen in Fig. 2, and also shows a change in slope at about 240 K. This change can be seen in the results by Rodbell, Lommel, and DeVries[14] as well. Similar behavior is seen in data for other putative half-metallic ferromagnets, NiMnSb,[15] PtMnSb,[15] and $La_{1-x}Sr_xMnO_3$ ($x=0.175$, 0.2).[16] The T^2 dependence ($T<200$ K) was also reported in the proposed half-metallic ferromagnets $La_{1-x}Sr_xMnO_3$ ($x=0.2$, 0.3, 0.4).[16] In CrO_2, the

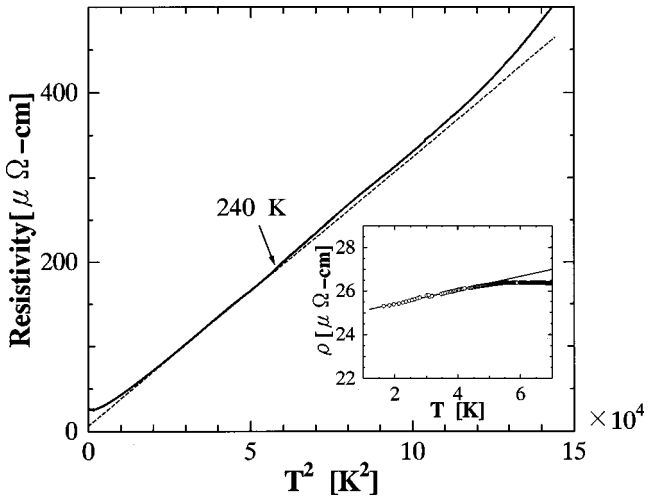

FIG. 2. Resistivity vs T^2. Note the change near 240 K. Inset: Low temperature resistivity showing the linear dependence.

value of the coefficient A of the T^2 dependence of the resistivity was 3.1×10^{-3} $\mu\Omega$ cm/K^2, which is very large compared to those of Ni, Co, and Fe ($1.3-1.6\times10^{-5}$ $\mu\Omega$ cm/K^2), contributed to by the magnon scattering process. If the T^2 dependence results from an electron-electron scattering process, the ratio A/γ^2, γ being the low-temperature specific heat parameter, is found to be constant and equal to about 0.9×10^{-6} $\mu\Omega$ cm(mole K/mJ)^2 in transition metals such as Pd, Pt, Fe, Co, and Ni. In CrO_2, the value of the ratio is large compared to this constant value, suggesting that the observed temperature dependence of the resistivity results from not only electron-electron scattering, but also some other mechanism. The other mechanism is probably an electron-phonon scattering process which produces a T^2 dependence. As Bloch-Gruneisen fits by Lewis, Allen, and Sasaki[2] actually show the T^2-like dependence in almost the same temperature range, it may be possible to explain this dependence by this means.

We adopt a model in which the metallic majority and semiconducting minority electrons act in parallel nearly independently to construct a simulation of the temperature dependence of the resistivity. For the semiconducting minority electrons, we use the well-known carrier density and drift mobility of an extrinsic semiconductor[17] at low temperature, while the electron-electron scattering process is used to describe the behavior of the metallic majority electrons because the experimental data show a T^2 dependence. The number of minority electrons excited into the conduction band from the valence band is very small below room temperature because of the size of the energy gap, expected to be about 1.2 eV. Therefore, we assume that electrons near the Fermi energy in the majority spin band are thermally excited into the minority conduction band, meaning that the Fermi level in the majority spin band plays the role of a donor level in an extrinsic semiconductor. The difference between the Fermi level and the edge of the minority-spin conduction band is taken to be the activation energy ΔE. As in itinerant ferromagnets, the exchange splitting is proportional to the magnetization and disappears above T_c, so we must take the temperature dependence of ΔE into consideration. We have estimated that the Fermi level of the majority spin band coincides with the minority conduction band edge at about 310 K using the band calculation by Lewis, Allen, and Sasaki.[2] Taking the above assumptions into consideration, we obtain the following formula for the resistivity:

$$\rho(T)=\frac{\alpha T^2\exp\left(\dfrac{\Delta E}{2k_BT}\right)}{\beta\exp\left(\dfrac{\Delta E}{2k_BT}\right)+\zeta T^{17/4}}+f(T), \tag{1}$$

with

$$\Delta E=\varphi+\psi\left(\frac{M(T)}{M(0)}\right),$$

$$f(T)=\begin{cases} aT^2 & (T\leqslant 240\ \text{K}) \\ bT^3 & (240\ \text{K}\leqslant T\leqslant 360\ \text{K}), \end{cases}$$

where k_B is the Boltzmann constant, $\rho(T)$ is the resistivity at T, and $M(T)$ and $M(0)$ are the magnetization at tempera-

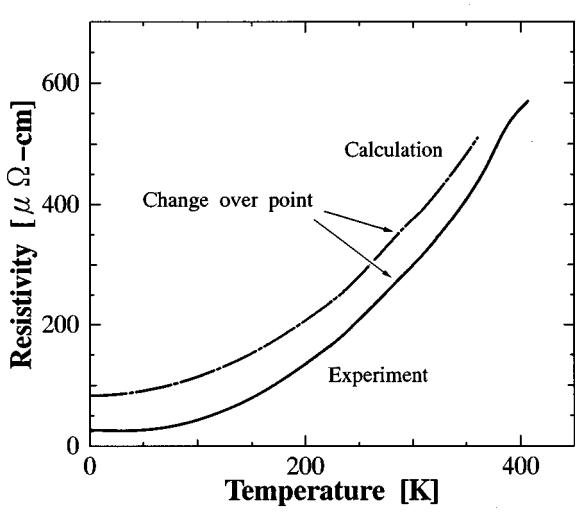

FIG. 3. Comparison between the measured resistivity and the simulation. The broken line shows the results of the simulation, shifted vertically, for parameter values fitting the measured CrO_2 results.

tures T and 0 K, respectively. The values of φ and ψ in the activation energy were determined to be 0.90 and 0.55 eV, respectively, using experimental magnetization data. Above 240 K, the T^3 dependence is used as the base resistivity which corresponds to the electron-phonon term and other mechanisms because the resistivity shows a T^3 dependence in the range between about 305 and 360 K where the contribution from the first term in Eq. (1) is negligible. The fitting parameters were chosen so that the change-over point of the experimental results agrees with that of the simulation, yielding $\alpha = 4.0\times10^3$ $(\mu\Omega\,\mathrm{cm})^2\,\mathrm{K}^{1/4}$, $\beta = 1.0\times10^7$ $\mu\Omega$ cm $\mathrm{K}^{9/4}$, $\zeta = 4.0\times10^{-4}$ $\mu\Omega$ cm/K^2, $a = 2.7\times10^{-3}$ $\mu\Omega$ cm/K^2, and $b = 8.7\times10^{-6}$ $\mu\Omega$ cm/K^3. The dot-dash line of Fig. 3 shows the simulation results. The residual resistivity is simply added to the results of the simulation. The simulation of the temperature dependence of the resistivity agrees qualitatively with the observed data as seen from Fig. 3. The solid line is the measured temperature-dependent resistivity. The two curves are offset vertically for clarity. The model can also produce a bump in the resistivity as is observed[16] in $La_{1-x}Sr_xMnO_3$, for example, with a suitable choice of the parameters. The model not only reproduces qualitative features of the resistivity of half metallic ferromagnets, but also is in good agreement with the data over a wide temperature range below the Curie point. Moreover, the value of A/γ^2 is modified by using the value of ζ obtained from the present simulation and becomes very close to the value,[18] about 1.0×10^{-5} $\mu\Omega$ cm(mole K/mJ)^2, in the heavy fermion materials such as UBe_{13}, CeB_6, and UPt_3. Therefore, it is inferred that the large γ (7 mJ/K^2 mole CrO_2) probably reflects the mass enhancement by not only electron-phonon coupling but also the strong interactions between itinerant d-electrons like the strong correlations[19] between itinerant f-electrons in heavy fermion materials. The discrepancy between experimental results and the simulation below about 130 K is probably due to the change from a T^2 dependence to another dependence in the electron-phonon scattering as shown in Bloch-Grüneissen fits.

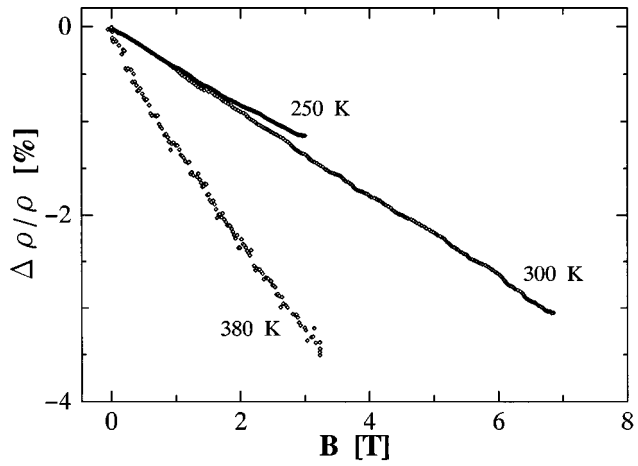

FIG. 4. Longitudinal magnetoresistance in higher temperature range for B up to 7 T.

At the lowest temperature, we found that the resistivity is proportional to the temperature between 1.6 and about 5 K as shown in the inset in Fig. 2. In normal ferromagnets such as Fe, Co, and Ni, the resistivity has a T^2 dependence at very low temperature. Theoretically, this dependence results from the spin flip scattering of the charge carriers by magnon excitations at temperatures low enough that electron-phonon scattering can be neglected. Since the low temperature resistivity of CrO_2 does not show this T^2 dependence, a lack of magnon scattering and/or spin fluctuations can be inferred, consistent with an absence of minority spin states at very low temperature in a half metallic conductor. Thus the data of Figs. 1 and 2 may represent intrinsic properties of a half metallic ferromagnet.

Longitudinal magnetoresistance

Figures 4 and 5 show longitudinal magnetoresistance (MR) data for various temperatures as a function of magnetic field. The MR in Fig. 4 are negative and nearly linear in field

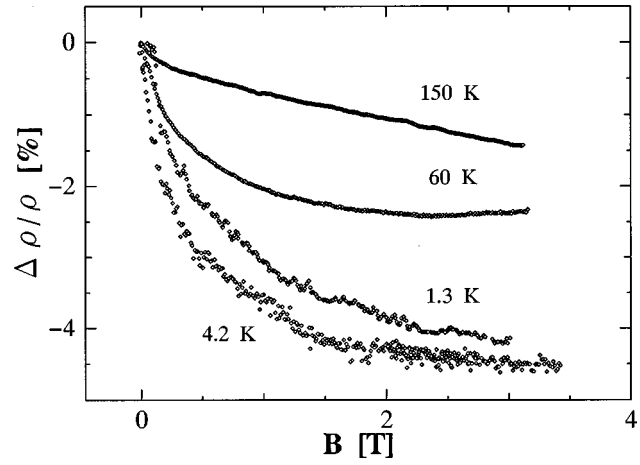

FIG. 5. Longitudinal magnetoresistance in lower temperature range for B up to 3.5 T.

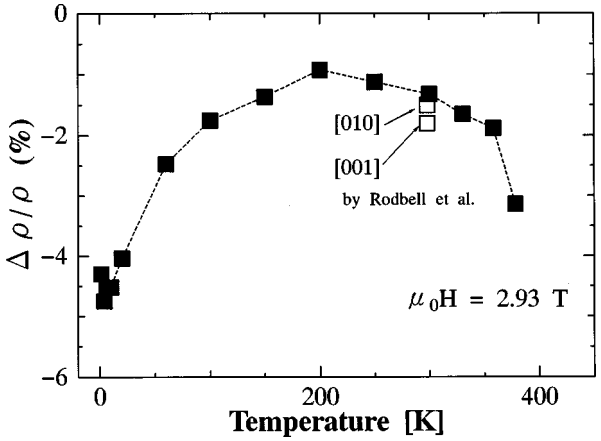

FIG. 6. Temperature dependence of longitudinal magnetoresistance for $B=2.93$ T.

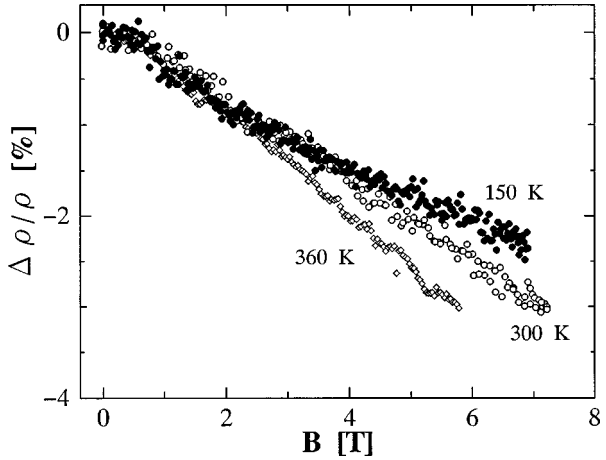

FIG. 8. Transverse magnetoresistance in the higher temperature range for B up to 7 T.

while those in Fig. 5 are concave, the nonlinear behavior occurring below a temperature of about 200 K. Figure 6 shows the temperature dependence of the longitudinal MR at a field of 2.93 T to compare with that measured by Rodbell, Lommel, and DeVries.[14] The agreement is good. As seen in the figure, the magnitude of the MR has a minimum for T near 200 K, the change due to the field being greater at both high and low temperatures. However, below about 5 K, the change in resistance again decreases as shown in Figs. 5 and 7. This temperature region is where the resistivity measurements implied a lack of magnon excitations and/or spin fluctuations. The decrease in the magnitude of the magnetoresistance is also consistent with a vanishing of spin-flip scattering processes. Similar behavior was also reported in the putative half metallic ferromagnets $La_{1-x}Sr_xMnO_3$ ($x=0.175$, 0.2).[16]

Transverse magnetoresistance

Figures 8 and 9 show the results of transverse magnetoresistance measurements for several temperatures as a function of applied magnetic flux density B. In these measurements, the magnetic field is oriented normal both to the current and to the plane of the film. Both figures show an increase in the magnitude of the slope of the MR at about 0.5–0.7 T. The CrO_2 film has an easy axis in the plane of the film. This low-field feature in the MR probably represents the effect of self-demagnetization induced by the rotation of the magnetization into the perpendicular direction, an effect that cannot be neglected in this geometry. Otherwise, the field and temperature dependence of the transverse MR is similar to that of the longitudinal MR for fields less than about 3 T; however, the low temperature results are almost independent of T in the transverse case. In the higher field range, the magnitude of the MR decreases as the field increases, possibly reflecting cyclotron orbital motion of the conduction electrons because of the B^2 dependence.

In ferromagnets, it is known[20] that the magnetoresistance due to s-d interactions is negative, the magnitude decreases with temperature, and the MR has a linear dependence on magnetic field in the ferromagnetic phase. The magnitude should therefore be small at low temperatures because T_c is rather high. However, here the magnitude increases with decreasing temperature, becomes rather large, and the magnetic

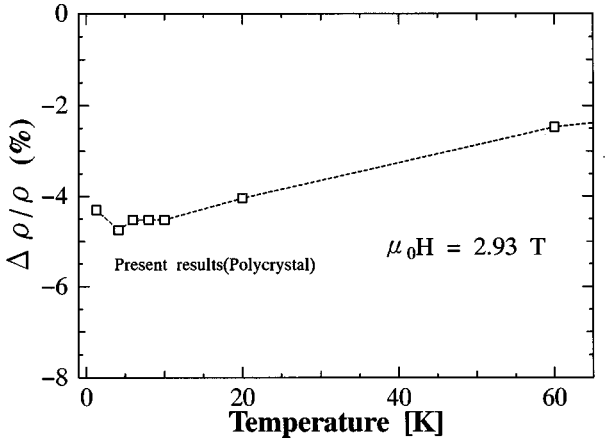

FIG. 7. Temperature dependence of the longitudinal magnetoresistance at low temperature and $B=2.93$ T.

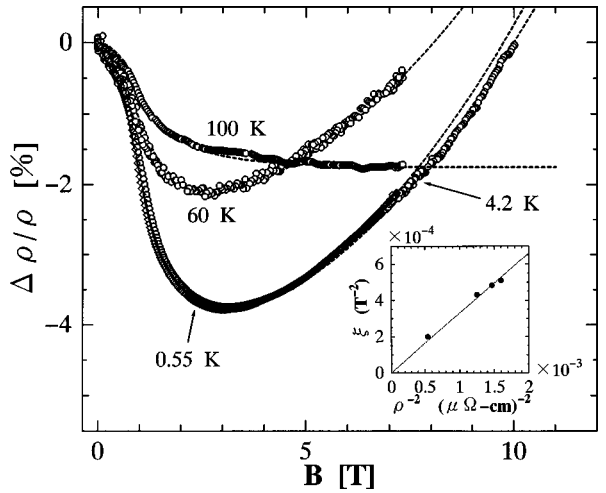

FIG. 9. Transverse magnetoresistance at lower temperatures for B up to 10 T. The dashed lines show the fits generated using Eq. (2). Inset: The coefficient of the cyclotron orbital motion term in Eq. (2) as a function of the inverse square of the resistivity.

field dependence becomes nonlinear below about 200 K, implying that other mechanisms should be used to explain the results.

According to Askerov, Kuliev, and Steinshreiber,[21] when the thickness of a degenerate film is of the order of the mean free path of the charge carriers, it is expected that the transverse MR shows a negative value. Since the thickness of the present film is 0.80 μm, this size effect is expected at low temperature where the mean free path is large. We found that the measured transverse MR at low temperature can be fitted by the following equation combining the effects of size and the cyclotron orbital motion:

$$\frac{\Delta\rho}{\rho(0)}=\frac{\rho(B)-\rho(0)}{\rho(0)}=-\frac{\eta B_e^2}{1+\lambda B_e^2}+\xi B_e^2, \qquad (2)$$

with

$$\eta=\lambda\left(\frac{3(1-P)}{8\delta}\right)^2, \quad B_e=B-N'B_d,$$

$$\lambda=\left(\frac{e\tau}{m^*}\right)^2, \quad \delta=\left(\frac{d}{l}\right),$$

where B_e is an effective magnetic flux density, N' is a coefficient determined by the self-demagnetizing factor and the relative susceptibility, ξ is a constant coefficient for each temperature, P is the fraction of electrons impinging on the surface of the film, e is the charge of the electron, τ is the relaxation time of the carriers, m^* is the effective mass, d is the thickness of the film, and l is the carrier mean free path. B_d is the applied magnetic flux density when B is less than the saturation value B_s, while it is B_s for $B>B_s$. The parameters η, λ, and ξ were evaluated by fitting Eq. (2) to the experimental data. In the fitting, 0.35 was the best value for N'.

The simulation results agree very well with the experimental ones as seen in Fig. 9. The inset shows that the coefficient of the B^2 term obtained from the fitting is proportional to ρ^{-2}, implying that this term results from cyclotron motion. Figure 10 shows the temperature dependences of η and λ. Both parameters increase with decreasing temperature in a reasonable way as seen from the above equation. The sudden increase of both parameters at $T<5$ K implies that the carrier mean free path and relaxation time suddenly become long. In this temperature region, the resistivity does not have a T^2 term caused by magnon scattering and/or electron-electron scattering related to spin fluctuations as mentioned above. Since spin fluctuations and/or magnon excitations are suppressed by the field, these parameters may include the suppression above 5 K, but the suppression may become small at lower temperature. Thus the resistivity and longitudinal and transverse magnetoresistances for temperatures below 5 K can be explained by the lack of spin-flip scattering as expected in a half metallic ferromagnet at low temperature.

It is easily understood that the temperature dependence of the MR in both orientations above about 200 K is due to the suppression of magnon excitations and/or spin fluctuations by the magnetic field. However, another mechanism is needed to explain the reenhancement of the magnitude of the longitudinal MR measured below about 200 K in the present films and in bulk samples of $La_{1-x}Sr_xMnO_3$ ($x=0.175$, 0.2).[16] Moreover, the temperature dependence of the resistivity is only qualitatively addressed by the simple model. Further study is needed.

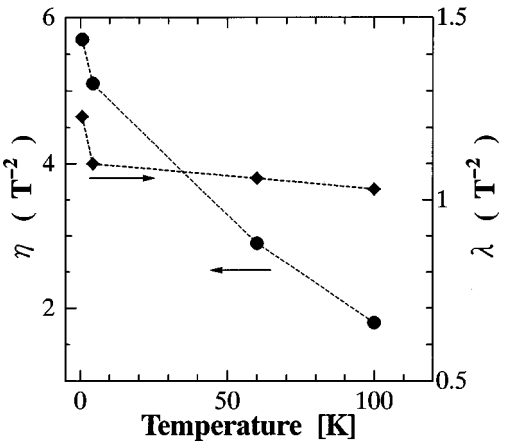

FIG. 10. Temperature dependences of the coefficients η and λ in Eq. (2) obtained by fitting to the measured transverse magnetoresistance in the lower temperature range.

SUMMARY

The temperature dependence of the resistivity of ferromagnetic CrO_2 films deposited onto ZrO_2 substrates shows metallic behavior with a change in slope at the Curie temperature, 390 K. Also, the resistivity is linear in temperature at low T, has a T^2 dependence in the range $130<T<240$ K, and shows a slight drop near 240 K, all of which can be explained by assuming that the conduction process involves a parallel combination of metallic majority-spin electrons and semiconducting minority-spin electrons and that the Fermi level plays the role of the donor level for the semiconducting minority-spin electrons. The ratio A/γ^2 of the coefficient of the T^2 term of the resistivity to the square of the specific heat parameter is very close to the value expected in heavy Fermion materials, suggesting that there is a strong correlation between itinerant d-electrons. The T^2 dependence was also reported in the presumed half metallic ferromagnets $La_{1-x}Sr_xMnO_3$ ($x=0.2$, 0.3, 0.4).[16] The lack of minority-spin states causes suppression of magnon scattering at low temperature. Similar behavior is seen in other candidates for half-metallicism, NiMnSb and PtMnSb.

The longitudinal and transverse magnetoresistances are negative and increase in magnitude linearly with field for temperatures above about 200 K, while having a concave shape as a function of field for lower temperatures. The magnitudes of both MR's have minima as functions of field for temperatures near 200 K. Similar behavior of the longitudinal MR was reported for $La_{1-x}Sr_xMnO_3$ ($x=0.175$, 0.2). At the lowest temperature, the magnitude of the longitudinal magnetoresistance decreases with decreasing temperature while the magnitude of the transverse magnetoresistance be-

comes temperature independent for a given field. The latter has a maximum at higher field for temperatures below about 200 K. This behavior can be reproduced by a simulation including size effect and the cyclotron orbital motion. This simulation implies that the carrier mean free path and the relaxation time suddenly increase at the lowest temperature. An explanation of this behavior is based on the limiting of spin-flip scattering processes by the field and by the presumed gap in the density of states of the minority-spin electrons.

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