# Temperature dependence of the conductance and magnetoresistance of $CrO_2$ powder compacts

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$CrO_2$ cold-pressed powder compacts show different electronic transport property than the single crystals. We have analyzed the temperature dependence of the conductance and magnetoresistance (MR) of cold-pressed compacts of $CrO_2$ powders. Our results show that there exist two channels of the conductance $G$. One is the inter-granular spin-dependent tunneling conductance ($G_{SDT}$), which is found proportional to $\exp(-1/T^{1/2})$. The other is a spin-independent channel ($G_{SI}$) due to the higher-order inelastic hopping through the localized states due to imperfections in the barrier. $G_{SI}$ is found to follow the power law $T^{\gamma}$ and $\gamma$ is related to the number of localized states in the barrier. At low temperatures the conductance is determined essentially by the SDT channel. As the temperature increases, the hopping channel becomes dominant. This spin-independent inelastic hopping conductance is one of the main reasons for the rapid decrease of MR with increasing temperature.

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## I. INTRODUCTION

Chromium dioxide ($CrO_2$) has been predicted to be half-metallic by band-structure calculation.[1] Spin-polarized photoemission[2] and superconducting point-contact experiments[3] have shown that the $CrO_2$ has a high degree of spin polarization, close to 100%. The nearly perfect spin polarization of $CrO_2$ suggests that it would be ideal for applications in ferromagnetic tunneling junctions,[4] where a large magnetoresistance (MR) ratio is expected. Several recent publications have reported that $CrO_2$ polycrystalline films[5,6] and cold-pressed powder compacts[7,8] exhibit a MR ratio more than 35% at low temperatures ($<5$ K). The conduction mechanism of these $CrO_2$ structures is due to the intergranular tunneling that is affected by the so-called Coulomb blockade and shows a strong temperature dependence.[7,9,10]

Unlike the metallic transport of single-crystal $CrO_2$, the conductance $G$ of $CrO_2$ cold-pressed powder compacts and polycrystalline films significantly increases with increasing temperature. It is also found that the MR ratio decreases rapidly with increasing temperature. In general, MR becomes less than 5% when $T>100$ K and is almost zero at room temperature. What are the causes for the strong temperature dependence of $G$ and MR? Is it mainly determined by the nature of grain boundaries and grain sizes, or is it related to the intrinsic properties of $CrO_2$? Answers to these questions are important, and the analysis of the temperature dependence of the transport properties may help us better understand the physics involved and achieve a higher MR ratio at higher temperatures for practical purposes. There have been several suggestions made[7,8] in regard to the mechanism of MR reduction at high temperature in cold-pressed $CrO_2$ powder systems although detailed analysis is lacking so far.

The MR reduction at high temperature has been found and analyzed in a number of simple magnetic tunnel junctions not involving $CrO_2$ by Shang et al.,[11] and it is attributed to the existence of a spin-independent (SI) channel, which is a higher-order inelastic hopping conductance following the power law $T^{1.33}$. The power of 1.33 corresponds to the second-order hopping through two localized states in the tunnel barrier. A good fit of the theory with the experimental data is found in their study.

The higher-order inelastic hopping theory was proposed in 1988 by Glazman and Matveev,[12] who presented a microscopic theory on the inelastic hopping through two or more localized states ($N\geqslant 2$) involving electron-phonon interaction, in which a power-law dependence of temperature has been given. This theory has been applied and verified in analyzing the ''leak'' or SI conductance in tunneling structures.[11,13] In 1995, Xu, Ephron, and Beasley[13] analyzed the higher-order hopping through ''chains'' of $N$-localized states in their tunnel barriers and presented a confirmation to the hopping conductance $G^{hop}$, which is given as follows:

$$G_N^{hop}\propto T^{\gamma}, \tag{1}$$

where $\gamma$ is given by[12,13]

$$\gamma=N-[2/(N+1)]. \tag{2}$$

Notice the value of $\gamma$ is not continuous. In the case of the second-order hopping ($N=2$), $G_2^{hop}\propto T^{1.33}$. For the third-order hopping ($N=3$), $\gamma=2.5$, and for the fourth-order hopping, $\gamma=3.6$.

It is well known that the grain boundaries play the role of tunnel barriers in $CrO_2$ or $CrO_2+Cr_2O_3$ cold-pressed powder systems.[5–8] In this work, we analyze the temperature dependence of the conductance and the MR of cold-pressed powder compacts of $CrO_2$. It is found that the suppression of tunneling MR with increasing temperature in these systems is also caused by the inelastic hopping conductance, a spin-independent channel. At low temperature ($T<50$ K), the conductance $G$ of the cold-pressed $CrO_2$ samples is found to be proportional to $\exp(-1/T^{1/2})$, which is consistent with the theory of intergranular tunneling. At high temperature, a power-law $T^{\gamma}$ term dominates the conductance. Our results clearly show that there is an additional channel contributing to the conductance of the cold-pressed $CrO_2$ compacts, which is due to the inelastic hopping of electrons through the localized states in the grain-boundary barrier.

 

TABLE I. Annealing effect of $CrO_2$ powder samples.

| Sample | Annealing temperature | Annealing time | Percentage of $Cr_2O_3$ | Resistivity | Δ |
|---|---|---|---|---|---|
| I | No annealing | 0 | <5% | 0.1 Ω cm | 6.2 K |
| II | 400 °C | 10 min | ~10% | 0.5 Ω cm | 6.5 K |
| III | 400 °C | 20 min | ~20% | 2 Ω cm | 30 K |
| IV | 400 °C | 60 min | ~35% | 14 Ω cm | 32 K |

## II. EXPERIMENTS

The $CrO_2$ samples in our experiments were prepared from commercial powders used for magnetic recording. The powders were characterized by x-ray diffraction and transmission electronic microscopy (TEM). The single-domain $CrO_2$ particles were rod shaped with an aspect ratio of about 9:1, and the average length was about 400 nm, which was determined from TEM micrographs. $CrO_2$ disks with a diameter of 9.5 mm and a thickness of about 1 mm were cold pressed using a hardened steel die under a pressure of $5\times10^8$ N/m$^2$. Four samples were made: sample I was the original $CrO_2$ containing no measurable $Cr_2O_3$ from routing x-ray diffraction; samples II, III, and IV were composites of $CrO_2$ and $Cr_2O_3$ of different ratios, which was induced by annealing $CrO_2$ in air at 400 °C for different times. Table I lists the annealing effects and the composition of the four samples, which were estimated from the x-ray diffraction (XRD) pattern. Figure 1 gives the XRD patterns of the original $CrO_2$ sample and an annealed sample, which shows that $Cr_2O_3$ is introduced by the annealing. The transport properties were measured using a Quantum Design physical properties measurement system (PPMS), and the magnetoresistance measurements were made in fields from −5 T to 5 T and over temperature range 5 K to 300 K. The resistivity of sample I is about 0.1 Ω cm at room temperature, and is about 0.5, 2, and 14 Ω cm for samples II, III, and IV, respectively. The resistivity increases significantly by heating due to the introduction of $Cr_2O_3$, a good insulator and antiferromagnet, which causes the dilution effect and the increase in barrier thickness.

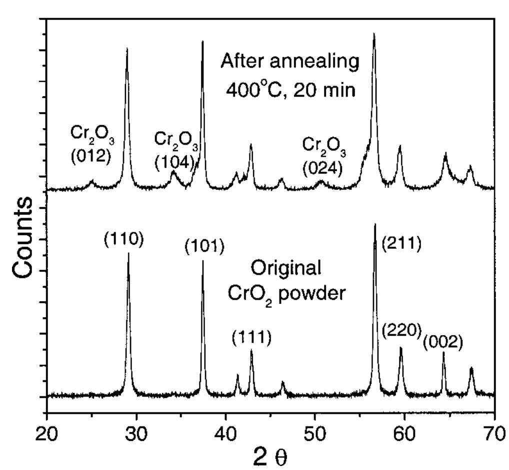


FIG. 1. Annealing effects as indicated by x-ray diffraction patterns.

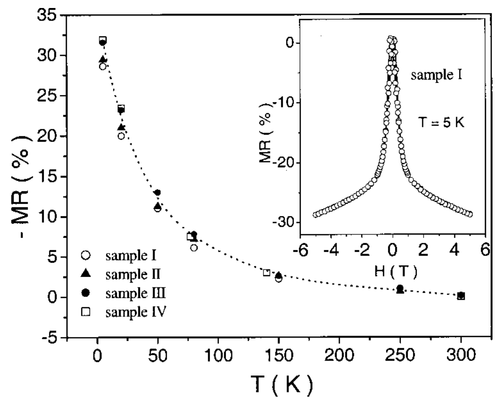


FIG. 2. The temperature dependence of the MR. The dotted line is the guide to the eye. Inset shows the MR at $T=5$ K for sample I.

## III. RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of MR for all four samples. The inset is the MR vs field plot at 5 K for sample I; other samples have similar MR behaviors. The MR ratio is defined as $(R_H-R_{H=0})/R_{H=0}$ and the large negative MR ratio at low temperatures is consistent with the intergranular spin-dependent tunneling (SDT) involving half-metallic grains. One can see that the MR ratios of samples III and IV are larger than that of samples I and II at 5 K, but the difference becomes negligible when the temperature is higher. The higher MR at low temperature of annealed samples III and IV is associated with the improved barrier layer due to the precipitation of $Cr_2O_3$ at the grain boundaries.

Figure 3 shows the temperature dependence of the conductance $G$ of these samples; all have been normalized to the conductance at $T=5$ K. One can see that the conductance increases with temperature and shows a significant slope change starting from about 50 K. In Fig. 4, $G$ is plotted in a logarithmic scale and the $x$ axis is $1/T^{1/2}$. From the $\ln G$ vs $1/T^{1/2}$ plot one sees that for $T<50$ K $\ln G$ is linear to $1/T^{1/2}$, which is typical of intergranular tunneling. The tunneling is usually treated as an elastic process and is a spin-dependent process. The intergranular tunneling conductance as a func-

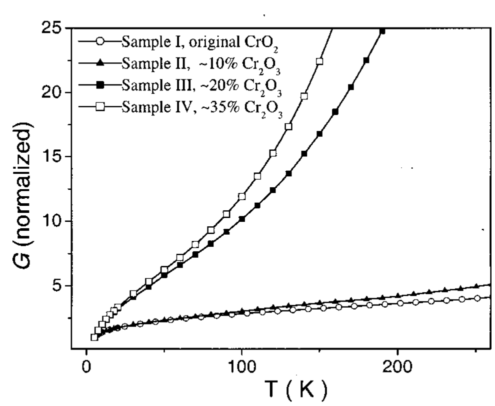


FIG. 3. The conductance $G$ as a function of temperature for all samples.

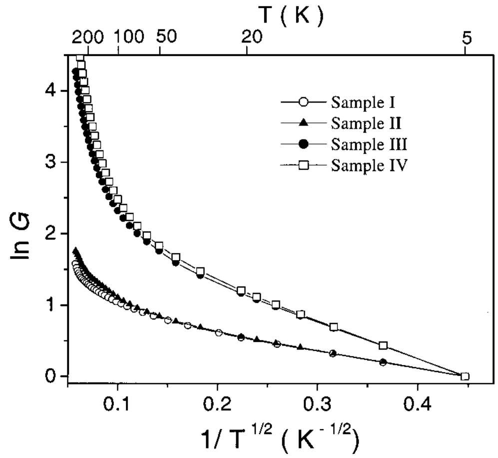


FIG. 4. Logarithmic conductance $\ln G$ as a function of $1/T^{1/2}$. A linear relationship exists at $T<50$ K. $\Delta \approx 6.2$ K, 6.5 K, 30 K, and 32 K for samples I, II, III, and IV, respectively, which is determined from the slope of the linear part of $\ln G$ vs $T^{1/2}$.

tion of temperature is given by[14–16]

$$G_{\mathrm{SDT}}=G_0(1+P^2m^2)\exp[-(\Delta/T)^{1/2}], \qquad (3)$$

where $P$ is the spin polarization, $m=M/Ms$ is the relative magnetization, $G_0$ is a constant, and $\Delta$ is proportional to the Coulomb charging energy $E_c$ and barrier thickness. At temperatures $T<50$ K, the linear relationship between $\ln G$ and $1/T^{1/2}$ shown in Fig. 4 implies that the intergranular tunneling is the major contribution to the conductance at low temperature. The $\Delta$ can be determined from the slopes of the linear part of Fig. 4. It is found that $\Delta=6.2$ K, 6.5 K, 30 K, and 32 K for samples I, II, III, and IV, respectively, as shown in Table I. The difference in the values of $\Delta$ corresponds to the difference in $Cr_2O_3$ barrier thickness and the Coulomb charge energy of the four samples.

It is found that the linear dependence of $\ln G$ on $1/T^{1/2}$ does not hold at high temperature. As seen in Fig. 4, when $T>50$ K, $\ln G$ starts to deviate from the linear behavior for all samples. This phenomenon suggests at high temperature $G_{\mathrm{SDT}}$ is not the major conduction mechanism and other mechanisms may become dominant. As mentioned before, the suppression of spin-dependent contribution to the conductance may result in a decrease of the MR at high temperature when a spin-independent channel (inelastic hopping conductance) becomes dominant with increasing temperature. As a matter of fact, a power-law temperature dependence of $G$, which is characteristic of the higher-order inelastic hopping, is observed over the high-temperature region ($T>50$ K), as seen in Fig. 3. Our analysis of the data shows that the conduction in the $CrO_2$ powder compacts contains mainly two channels: the tunneling channel with an exponential $1/T^{1/2}$ dependence and the hopping channel that follows a power law, and the total conductance is the combination of the two:

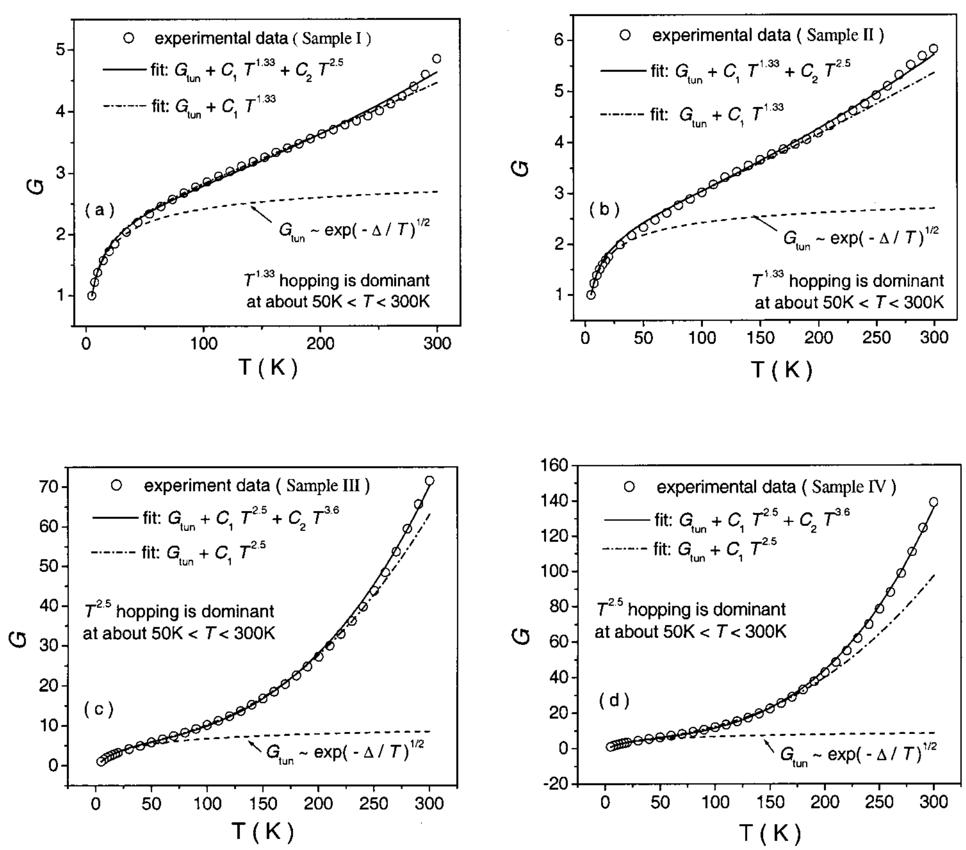


FIG. 5. Illustrations of the theoretical fits of $G$ as a function of $T$ obtained from Eq. (4) for samples I, II, III, and IV, respectively. At low temperature $G$ is mainly decided by the tunneling term; at high temperature, $G$ is dominated by higher-order hopping that follows a power law.

$$G = G_{\mathrm{SDT}} + G_{\mathrm{SI}} = C_1 \exp[-(\Delta/T)^{1/2}] + C_2 T^{\gamma}, \tag{4}$$

where $C_1$ and $C_2$ are free parameters. It is found that Eq. (4) fits our experimental data surprisingly well as will be discussed later.

Keeping in mind the power-law temperature dependence of the inelastic hopping conductance $G_N^{\mathrm{hop}} \propto T^{\gamma}$ and $\gamma = N - [2/(N+1)]$, the spin-independent conductance $G_{\mathrm{SI}}$ is due to the inelastic hopping of electrons through several ($N$) localized states in the barriers. That is, besides the elastic intergranular tunneling, the imperfections in the grain-boundary barriers provide a hopping conductance channel. The power-law term has previously been considered in simple magnetic tunnel junctions by Shang *et al.*;[11] however, the first term in Eq. (4) was not involved in those cases due to the nongranular nature of their junctions.

The SDT channel (tunneling) and SI channel (hopping) have different temperature dependences, and they are the dominant conduction mechanisms over different temperature regions. The SDT channel dominates the conductance at low temperature and the SI channel dominates at high temperature. The enhanced role of the latter at high temperature explains the rapid decrease in the MR.

According to the analysis of Glazman and Matveev[12] and Xu, Ephron, and Beasley,[13] the order of electron inelastic hopping $N$ can be increased by increasing temperature or bias voltage. Higher level of impurity and a thicker barrier can also result in a higher order of inelastic hopping. In our data, it is found that both the second-order hopping ($\gamma = 1.33$) and third-order hopping ($\gamma = 2.5$) exist, and the fourth-order hopping ($\lambda = 3.6$) become non-negligible at temperatures higher than 250 K for the longer time-annealed samples III and IV.

The conductance of our samples can be fitted generally by

$$G = C_1 \exp[-(\Delta/T)^{1/2}] + C_2 T^{1.33} + C_3 T^{2.5} + C_4 T^{3.6}. \tag{5}$$

In the first term of the spin-dependent tunneling channel $\exp[-(\Delta/T)^{1/2}]$, the $\Delta$ values are determined from the slopes in Fig. 4. The second, third, and fourth terms represent the spin-independent channel $G_{\mathrm{SI}}$ of power-law $T^{\gamma}$ with $\gamma$ equal to 1.33 (second-order hopping), 2.5 (third-order hopping), and 3.6 (fourth-order hopping), respectively. It is found that, for samples I and II, the $T^{3.6}$ term is never needed and the $T^{2.5}$ term can be omitted except at very high temperatures. In other words, the hopping conductance is dominated by the second-order hopping ($T^{1.33}$). For the annealed samples III and IV, the $T^{1.33}$ term can be omitted and the hopping conductance is dictated by the $T^{2.5}$ term. An even better fit can be obtained at high temperatures if we take into account a higher-order term $T^{3.6}$. Figures 5(a)–5(d) show the details of the theoretical fits of the temperature dependence of the conductance using different terms described above for all four samples. It can be seen that Eq. (5) works very well in describing the phenomena.

The increase in the $\gamma$ value with annealing reflects the increase in the order of the inelastic hopping possibly due to the changes in effective barrier thickness, which is associated with the increases of the number of localized states $N$. Increasing temperature also favors higher-order hopping in agreement with the theory of Glazman and Matveev.

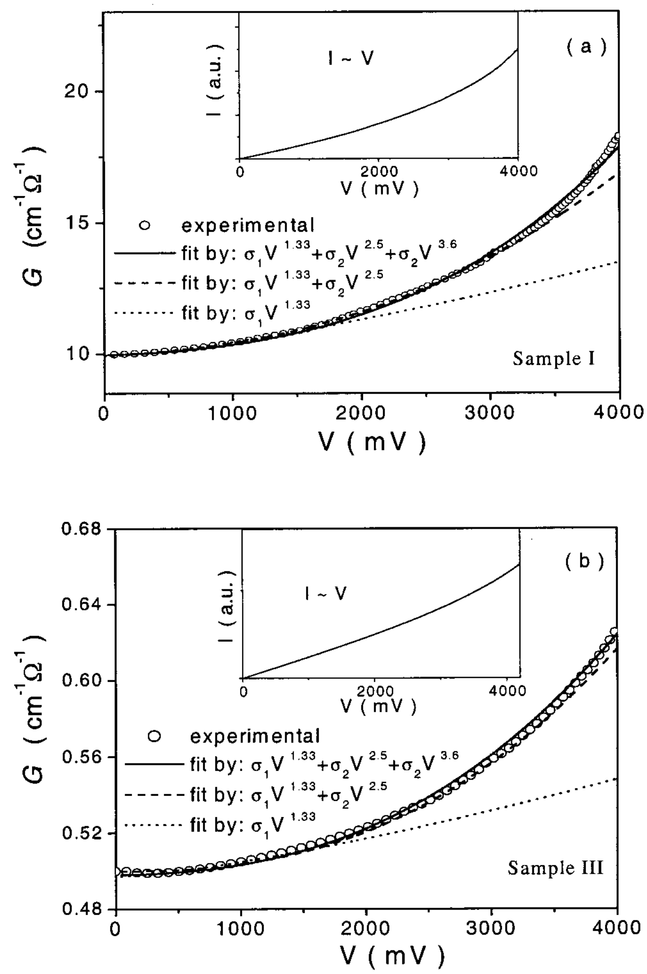


FIG. 6. Conductance as functions of voltage at $T = 300$ K for samples I and III. Both the experimental data and theoretical fits according to Eq. (6) are given.

The I–V characteristics have been measured at room temperature and it is also found that the conductance $G$ as a function of bias voltage $V$ can be approximately fitted by a power law. Figure 6 gives the I–V curves and $G$ as a function of $V$ for samples I and III. The conductance can be fitted by

$$G = \sigma_0 + \sigma_1 V^{1.33} + \sigma_2 V^{2.5}, \tag{6}$$

where $\sigma_0$, $\sigma_1$, and $\sigma_2$ are free parameters. Better fits at the high-bias end can be obtained if one includes a higher-order term of $V^{3.6}$. Similar bias dependence of $G$ has been observed in samples II and IV but is not shown here for the sake of clarity. For sample I, where the temperature dependence follows $T^{1.33}$, $G$ could not be expressed simply as $V^{1.33}$ [see Fig. 6(a)]. Instead, it is necessary to add the $V^{2.5}$ term particularly at high-bias voltage. This behavior can be explained considering that a higher bias should lead to a higher order of hopping in addition to the fact that the experiment is done at a relatively high temperature, which also promotes higher-order hopping. It should be mentioned, although the power-law dependence of the inelastic hopping conductance on bias $V^{\gamma}$ is predicted under condition $eV \gg k_B T$, the theory explicitly states that increasing temperature or bias voltage favors hopping along chains with more localized states ($N > 2$) resulting in an increasing nonlinear dependence of the conductance on temperature and voltage.[12,13] Our experimental results show that the power-law relationship between the hopping conductance and bias voltage still holds in our cold-pressed powder systems at room temperature.

Besides the inelastic hopping, there are several other mechanisms that have been proposed to be responsible for the rapid reduction in MR at high temperature. Coey *et al.*[7] suggested the existence of spin-flip processes introduced by the excitation of antiferromagnetic magnons in the interface layer or maybe the weakly exchange coupled $Cr^{3+}$ ions at the interfaces. The study of Watts *et al.*[17] showed the two-band magnetotransport in $CrO_2$ films and suggested a temperature-dependent spin-flip scattering corresponding to the temperature dependence of carrier mobilities and MR. It is also possible that the MR is reduced by the suppression of spin polarization $P$ at high temperature due to thermally excited spin waves.[11] Itoh *et al.*[18] presented a double-exchange model showing that $P$ decreases with increasing temperature, their calculated results also indicated that MR decreases more rapidly than $P$ but can still be large at high temperatures. To explain the rapid decrease of the MR with temperature, one needs to take into account the inelastic hopping conduction channel. The suppression of MR at high temperature is mainly due to the rapid increase of the spin-independent hopping channel with increasing temperature. However, the mechanisms introduced in Refs. 7, 11, 17, and 18 may still play important roles.

## IV. CONCLUSIONS

We have studied the conductance and magnetoresistance of $CrO_2$ powder compacts. Besides the intergranular tunneling conductance, a spin-independent conductance has been found due to the inelastic higher-order hopping through the localized states in the grain boundaries. At low temperature, the integranular spin-dependent tunneling is the major conduction mechanism. When temperature is higher, the inelastic hopping plays a more important role. The suppression of the MR at high temperature is correlated to the increase of the spin-independent hopping channel with temperature. It is suggested that in order to maintain a large MR ratio at high temperature, one may need to consider reducing the spin-independent channel. For example, reducing the imperfections in the grain boundaries, changing the granule size and adjusting the Coulomb charging gap may be helpful to enhancing the magnetoresistance of the $CrO_2$ materials.

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