Magnetism and Magneto-resistance of a CrO₂/RuO₂ Granular System

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After mixing RuO₂ and CrO₂ powders, (RuO₂)ₓ(CrO₂)₁₋ₓ was sintered at a low temperature of 473 K. The effects of using an RuO₂ spacer between CrO₂ grains were systematically studied for values of x between 0 and 1. The x-dependence of the averaged saturation magnetic moment \( \mu_s \) per transition metal ion abruptly decreased even at \( x = 0.03 \), and it linearly varied in the range 0.3 \( \leq x \leq 1 \), where the estimated magnetic moment per Cr ion was 1.43 \( \mu_B \), a 30% reduction from the value of 2 \( \mu_B \) for pure CrO₂. The magneto-resistance ratio (MRR) remained almost unchanged in the range 0 \( \leq x \leq 0.7 \).

Key words: half metal, CrO₂, RuO₂, magnetization, magneto-resistance

1. Introduction

The magnetism and magneto-resistance of CrO₂ have attracted the attention of many researchers because of the 100% spin polarization of 3d conduction electrons. In such a half-metallic CrO₂ system, the majority spins have a metallic band structure, while the minority spin band shows a semi-conductive energy gap at the Fermi level \( E_F \). Since the perfect spin polarization should result in a large magneto-resistance (MR), CrO₂ is expected to be a candidate material for the development of spintronics devices such as magnetic random access memory (MRAM) chips. In particular, we expect that all oxide composites based on CrO₂ will enable the development of very stable spintronics devices with high performance. However, the reported MR ratio of a CrO₂ granular system containing antiferromagnetic CrO₂ impurity at the grain boundaries was very low, with a value on the order of ~0.1% at room temperature \( T \). It is therefore necessary to search for a suitable oxide for the spacer substance between CrO₂ grains.

In previous reports, Bratkovsky \(^4\) calculated the band structure of a CrO₂/RuO₂/CrO₂ multilayer system within the linear muffin-tin orbitals method in a supercell geometry with [001] growth direction. Here, the half-metallic ferromagnet CrO₂ and the metallic Pauli paramagnet RuO₂ have a common rutile structure, and they have almost perfect lattice matching with each other. The calculated result showed a half-metallic density of state (DOS) at \( E_F \) for the CrO₂/RuO₂/CrO₂ film.

Miao et al. \(^5\) studied the MR of epitaxial CrO₂/RuO₂/CrO₂ thin-film heterostructures grown on the (100) plane of TiO₂ by chemical vapor deposition (CVD). However, they observed a very small MR ratio due to the existence of a disordered layer at the CrO₂/RuO₂ interface. To avoid such an intermixing between Cr and Ru, this system must be handled at low temperature. Monoharan et al. \(^6\) observed the MR of CrO₂/RuO₂ powder compact with a 1:1 weight ratio obtained by cold pressing, where the mole ratio of RuO₂ was about 0.4. Their results for the MR ratio were nearly the same as those obtained in CrO₂ powder compact.

As mentioned above, no experimental results with respect to the enhanced MR have yet been reported for the GMR system of CrO₂/RuO₂/CrO₂. In the present work, RuO₂ was mixed with CrO₂, and (RuO₂)ₓ(CrO₂)₁₋ₓ powders were sintered at low temperature. The effects of RuO₂ spacer between CrO₂ grains were systematically investigated for (RuO₂)ₓ(CrO₂)₁₋ₓ, where x is the mole ratio of RuO₂.

2. Sample preparation

Commercial RuO₂ and CrO₂ powders were mixed in an agate mortar for 30 minutes. They were then pressed and sintered in an electric furnace at 473 K for 3 hours under the atmospheric pressure of the air.

Fig. 1 XRD patterns of (RuO₂)ₓ(CrO₂)₁₋ₓ mixtures for x = 0 (bold solid line), 0.2 (thin solid line), and 0.5 (dotted line).

The coexistence of RuO₂ and CrO₂ was confirmed by CuKα powder x-ray diffraction (XRD) measurements. In Fig. 1, the XRD patterns of the x = 0, 0.2, and 0.5 samples are shown, where the intensity of the diffraction peaks of RuO₂ and CrO₂ vary monotonically with increasing x. The particle diameters \( d \), estimated from the half-widths of the XRD peaks, were about 40 nm and about 30 nm for RuO₂ and CrO₂, respectively, and were nearly independent of x.

In Fig. 2, the lattice constants of RuO₂ and CrO₂ phases are shown for all of the samples. The lattice parameters a and c are nearly constant around the dotted lines, which show the values reported in the literature. Here, RuO₂ has a tetragonal crystal...
structure with lattice parameters of $a=0.44931\text{nm}$ and $c=0.31064\text{nm}^3$, and CrO$_2$ also has a tetragonal crystal structure with $a$ of 0.4419nm and $c$ of 0.29154nm$^3$.

of 0.05 appeared in the field dependence of the magnetization, as shown in Fig. 4. In this figure, the magnetization curves show a nearly constant coercive field $H_C$ of about 800 Oe at 77 K for (RuO$_2$)$_x$(CrO$_2$)$_{1-x}$ in the range $0 \leq x < 1$. Meanwhile, the saturation magnetization nonlinearly decreased with increasing $x$.

3. Experimental results and discussion

3.1 Magnetization

Magnetization measurements were performed by means of a vibrating sample magnetometer from 77 K to 400 K under a magnetic field in the range of $\pm 10 \text{kOe}$. The temperature dependence of the magnetization $σ$ is shown in Fig. 3. As shown in this figure, the Curie temperature $T_C$ was constant at about 400 K for the (RuO$_2$)$_x$(CrO$_2$)$_{1-x}$ samples in the range $0 \leq x < 1$. However, it is very curious that the magnetization $σ$ steeply decreases even at $x = 0.03$. If (RuO$_2$)$_x$(CrO$_2$)$_{1-x}$ is a simple co-existing system composed of isolated RuO$_2$ and CrO$_2$ phases, the $σ$-value should be proportional to $1-x$.

Similar behavior of an abrupt decrease in $σ$ at a low $x$ value appeared in the field dependence of the magnetization, as shown in Fig. 4. In this figure, the magnetization curves show a nearly constant coercive field $H_C$ of about 800 Oe at 77 K for (RuO$_2$)$_x$(CrO$_2$)$_{1-x}$ in the range $0 \leq x < 1$. Meanwhile, the saturation magnetization nonlinearly decreased with increasing $x$.

Figure 5 shows the $x$-dependence of the averaged saturation magnetic moment $\bar{\mu}$ per transition metal (TM) ion, where the TMs are Ru$^{4+}$ and Cr$^{4+}$ in (RuO$_2$)$_x$(CrO$_2$)$_{1-x}$. At 77 K, an $x = 0$ sample of pure CrO$_2$ has a $\bar{\mu}$ value of $2\mu_B$, which is reasonable for a half metal with 3$d^2$ electrons. Therefore, we first expected that the $\bar{\mu}$ values would change according to the expression $2(1-x)\mu_B$, as illustrated by the dotted straight line in Fig. 5. However, the experimental $\bar{\mu}$-value abruptly decreased from $2\mu_B$ even at $x = 0.03$, and it linearly varied with $x$ in the range $0.3 \leq x \leq 1$. In this linear region, $\bar{\mu}$ at 77 K obeys the equation
Thus, the value of $\mu_B$ in the range $0.3 < x < 1$ means that the magnetic moment per Cr$^{4+}$ ion was reduced from $2 \mu_B$ to $1.43 \mu_B$ by coexisting RuO$_2$ particles.

Miao et al. assumed mixing of Ru$^{4+}$ and Cr$^{4+}$ at the interface of the RuO$_2$ and CrO$_2$ epitaxial films, and performed first-principles calculation for super-cells of Cr$_2$Ru$_2$O$_8$ composition. The result of their calculation showed that the magnetic moments of two neighboring Cr atoms were non-collinear, and aligned at an angle of about 150 degrees. Meanwhile, Ru had a small magnetic moment with a direction opposite to the total magnetic moments of Cr.

However, it is hard to confirm the existence of a mixed region from the XRD results for the present (RuO$_2$)$_x$(CrO$_2$)$_{1-x}$ system. Therefore, in our case, canting of the magnetic moment cannot be considered, since the magneto-resistance ratio (MRR) was not influenced by coexisting RuO$_2$ in the range $0 \leq x \leq 0.6$, as will be shown in a later section. We now think that the band structure of CrO$_2$ was changed by a certain reason so that it has minority spins with a small density of states at the Fermi energy level.

### 3.2 Magneto-resistance

Measurements of magneto-resistance were performed by the usual 4-terminal method in dc magnetic fields between $-1 \text{ T}$ and $1 \text{ T}$. The $1/T^{1/2}$-dependence of resistivity $\rho$ was plotted for an $x = 0.20$ sample in Fig. 6 by using a semi-logarithmic scale. The relation of $\ln \rho \propto \sqrt{\Delta/T}$ holds in the range $77 \text{ K} < T < 300 \text{ K}$, and the tunneling energy barrier $\Delta$ is estimated to be about 2.5 K. Similar behaviors for $\rho$ values of 0.1–0.5 $\Omega \text{ cm}$ were observed in the other samples in the range $0 \leq x \leq 0.7$. Though we could not confirm our suspicions from the XRD experiments, these results suggest the existence of some tunneling barriers such as Cr$_2$O$_3$ impurity phase in the grain boundaries between CrO$_2$ particles.

In Fig. 7, the field dependences of the magneto-resistance ratio (MRR) at $77 \text{ K}$ are shown for three samples where $x = 0$, 0.6 and 0.8. The MRR is defined by

$$[\rho (H) - \rho (H_0)]/\rho (H_0)$$

where $\rho (H)$ is the field-dependent resistivity and $H_0$ is the peak field at which $\rho (H)$ becomes maximum.

As shown by the solid curves in Fig. 7, the spin polarization coefficient $P$ was derived by fitting the equation

$$MRR = -P^2 m^2/(1+P^2 m^2)$$

where $m$ is the normalized magnetization of $(\mu / \mu_B)^g$. The values of $P$ were 0.2–0.24 in the range $0 \leq x \leq 0.7$. As shown by eq. (3), the MRR-value is not determined by $\mu_B$, but by $m$. Therefore, reduction of $\mu_B$ due to

![Fig. 6](image)

Fig. 6

$\ln \rho$ vs. $T^{1/2}$ for an $x = 0.20$ sample. The tunneling barrier $\Delta$ was estimated as 2.5 K.

![Fig. 7](image)

Fig. 7

Field dependence of the magneto-resistance ratio at $77 \text{ K}$ for three samples where $x = 0$, 0.6, and 0.8.

![Fig. 8](image)

Fig. 8

Peak field $H_p$ and coercive field $H_c$ of (RuO$_2$)$_x$(CrO$_2$)$_{1-x}$. 

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the coexistence of RuO$_2$ does not immediately bring low $|\text{MRR}|$ when the parallel alignment of magnetic moments gives $m_1$ under a high magnetic field.

The value of the peak field $H_p$ and coercive field $H_c$ estimated from the magnetization curves are shown in Fig. 8. Both $H_p$ and $H_c$ are almost constant in the range $0 \leq x \leq 0.8$, and each value of $H_p$ nearly coincides closely with $H_c$. These results are one of the characteristics of the giant-magneto-resistance (GMR) effect. However, from the experimental results shown in Figs. 6 and 7, we think that these results show the tunneling-magneto-resistance (TMR) effect due to the Cr$_2$O$_3$ impurities.

In Fig. 9, the $x$-dependences of the magneto-resistance ratio $MRR$ at 8, 77, and 300 K are shown. The $|MRR|$ at 8 K, 77 K, and 300 K are about 11%, 5% and 0.2%, respectively, for pure CrO$_2$. The $|MRR|$ is almost constant in the range $0 \leq x \leq 0.7$ and then decreases as the RuO$_2$ content increases in the range $0.8 \leq x \leq 1$.

Corresponding to the behaviors of the polarization coefficient $P$. At $x \sim 0.4$, our value of $|MRR|$ agrees with the experimental result reported by Monoharan et al. [6]. Above $x = 0.8$, $|MRR|$ becomes negligibly small due to the disappearance of ferromagnetism.

4. Conclusion

The (RuO$_2$)$_x$(CrO$_2$)$_{1-x}$ system was sintered at a low temperature of 473 K, and the effects of RuO$_2$ spacer between CrO$_2$ grains were systematically studied for $x$ between 0 and 1. However, the $x$-dependence of the averaged saturation magnetic moment $\bar{\sigma}$ abruptly decreased even at small $x$, and varied linearly in the range $0.3 \leq x \leq 1$. Meanwhile, the magneto-resistance ratio (MRR) remained almost unchanged in the range $0 \leq x \leq 0.7$.

From these results, it was assumed that the magnitude of the magnetic moment of CrO$_2$ was reduced by the electrons with minority spins. The nearly constant $MRR$ values in the range $0 \leq x \leq 0.7$ may be due to Cr$_2$O$_3$ impurities.

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References


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