Magnetization and Magnetoresistance in an MoO$_2$/CrO$_2$ Mixed System

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Mixtures of metallic Pauli paramagnetic MoO$_2$ and half-metallic ferromagnet CrO$_2$ were prepared by planetary ball milling. The magnetization $M$, resistivity $\rho$, and magnetoresistance ratio $MRR$ were measured for (MoO$_2$)$_x$(CrO$_2$)$_{1-x}$ from $x = 0$ to 1. $M$ and $|MRR|$ rapidly decreased with increasing MoO$_2$ content. Rpm-dependence of the coercive force $H_c$ was observed in the $x = 0.05$ sample.

Key words: half metal, dioxide, magnetization, magnetoresistance

1. Introduction

CrO$_2$ is known to be a half-metallic oxide with 100% spin polarization of 3$d$ conduction electrons. In this system, the band structure of majority spins is metallic, while the minority spin band has a semiconductive energy gap at the Fermi level [1,2]. Since the perfect spin polarization should result in large magnetoresistance (MR), CrO$_2$ is a candidate material for the development of spintronic devices such as spin valves and magnetic random access memories (MRAMs). The same situation exists for Fe$_3$O$_4$, in which only 3$d$ electrons with minority spin can be conductive [3,4].

The reported MR ratio ($MRR$) for CrO$_2$ granular systems with and without antiferromagnetic Cr$_2$O$_3$ impurity at grain boundaries showed very small values on the order of ~0.1% at room temperature [5-10]. Recently, we found that a paramagnetic Cr$_2$O$_3$ barrier can enhance the $|MRR|$ of a CrO$_2$ system [11]. Impurity doping effects calculated for CrO$_2$ by the DV-X$\alpha$ method have shown that Mo$^{4+}$ doping causes a slight increase in the magnetic moment and Curie temperature $T_C$ [12].

In the present study, metallic dioxide of MoO$_2$ was mixed with CrO$_2$, and the effects on the magnetism and conductivity of the latter were investigated. MoO$_2$ has a monoclinic crystal structure with lattice parameters of $a = 0.56096$ nm, $b = 0.4857$ nm, $c = 0.56259$ nm, and $\beta = 120.912$ deg [13]. CrO$_2$ has a tetragonal crystal structure with $a = 0.4419$ nm and $b = 0.29154$ nm [14]. Both MoO$_2$ and CrO$_2$ belong to the Rutile structure family, but they have different energy band diagrams [15]. In metallic MoO$_2$, one of the $4d^2$ electrons is used for the metal-metal $\sigma$-bonding and the other $4d^2$ electron partially fills the metal-oxygen $\pi^*$ band. In half-metallic CrO$_2$, all of the $3d^2$ electrons exist in the majority up spin band and behave like as polarized conduction electrons.

A previous study of the effect of doping CrO$_2$ with a few percentage points of Mo$^{4+}$ ($4d^2$) revealed a steep disappearance of ferromagnetism along with a reduction in magnetization and a lowering of the Curie temperature $T_C$ [16]. We also expected to observe a so-called ferromagnetic quantum critical point (FQCP) [17] as a result of slight doping of CrO$_2$-phase in an (MoO$_2$)$_x$(CrO$_2$)$_{1-x}$ system with Mo$^{4+}$. At the FQCP, the ferromagnetism of CrO$_2$ disappears and, for example, a possibility of $p$-type superconductivity may occur. Here we will report the effects of mechanical milling on the conductivity and magnetism of MoO$_2$/CrO$_2$ mixtures.

2. Sample preparation and experiment

Commercial 99.9% CrO$_2$ (Aldrich Chemical Company, Inc.) and 99.9% MoO$_2$ (Soekawa Chemicals) were used as the precursor for (MoO$_2$)$_x$(CrO$_2$)$_{1-x}$ mixed powder, where $x$ is the molar concentration of MoO$_2$. The $x$-values are between 0 and 1 with step of 0.1. The powder mixture of CrO$_2$ and MoO$_2$ was milled with a planetary ball mill (Fritsch Pulversette-7, Germany) using Cr-steel vials. The inner diameter and volume of each vial were 40 mm and 45 cm$^3$, respectively, and Cr-steel balls with a diameter of 15 mm were used as the grinding media. About 2 g of powder mixture was the starting material. The volume ratio of balls and powder was about 30:1. The rotation speed was controlled between 100 and 700 rpm, and the rotation time was 30 min.

The ground products were characterized by x-ray powder diffraction (XRD), and were then mixed with an aqueous solution of polyvinyl alcohol (PVA) and pressed into a 1-mm-thick pellets with a diameter of 5 mm.

Measurements of the resistivity and magnetoresistance were performed for dried samples by the usual 4-terminals method in dc magnetic fields between ~1 T and 1 T. A vibrating sample magnetometer (VSM) and a superconducting quantum interference device (SQUID) were used for the magnetization measurements.

3. Results and discussion

Figure 1 shows the Cu$K\alpha$ x-ray powder diffraction patterns of (MoO$_2$)$_{0.03}$(CrO$_2$)$_{0.97}$ prepared by mechanical milling at 100, 400, and 700 rpm for 30 min. The
(110)-peak of CrO$_2$ was greatly broadened at 400 and 700 rpm. The sharpness of the (110)-peak of MoO$_2$-phase was kept at 400 rpm, but was followed by broadening at 700 rpm.

If we use Sherrer's formula for the half-width of XRD peaks, the mean crystallographic correlation length $d$ of CrO$_2$ can be estimated as 5-10 nm as a result of milling at 400 rpm. This shows that either CrO$_2$ nano-particles or amorphous phase is produced in this sample. The $d$ value of MoO$_2$ particles did not decrease for rotation speeds up to 700 rpm, indicating that MoO$_2$ particles are much harder than CrO$_2$ particles.

X-ray powder diffraction patterns of $x = 0.05$, which were milled at 290 rpm for 30 min., are depicted in Fig. 2. The (110) diffraction peak of CrO$_2$ rapidly broadened at $x = 0.4$ and disappeared at $x = 0.8$. On the other hand, the (110) peak intensity of MoO$_2$ rose as $x$ increased, without broadening. This means that $d$ in CrO$_2$ was steeply reduced by milling with the harder MoO$_2$ particles. At $x = 0.8$, the CrO$_2$ crystal phase becomes unstable, and may be completely transformed into amorphous phase.

In Fig. 3, the field dependences of magnetization $M$ at 300 K are shown for the samples of $x = 0, 0.2, 0.4$, and 0.6 prepared after 290 rpm milling for 30 min. According to the x-ray results of Fig. 2, the ferromagnetic magnetization of CrO$_2$ rapidly decreased as the MoO$_2$ content increased. At $x = 0.6$, the sample showed very weak ferromagnetism or super-paramagnetism, which may be due to the production of CrO$_2$ nano-particles or amorphous CrO$_2$-phase by mechanical milling.

The $x$-dependences of the saturation magnetization $M_s$ and remanent magnetization $M_r$ at 77 K and 300 K are shown in Fig. 4 for $x = 0$-1.0 samples, prepared by 290 rpm milling for 30 min. The $M_s$ and $M_r$ decreased

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Fig. 1. X-ray powder diffraction patterns of the $x = 0.05$ sample after milling at 100-700 rpm for 30 min.

Fig. 2. X-ray powder diffraction patterns of $x = 0, 0.1, 0.4$, and 0.8 samples after 290 rpm milling for 30 min.

Fig. 3. Field dependence of the magnetization $M$ at 300 K for $x = 0, 0.2, 0.4$, and 0.6 samples after 290 rpm milling for 30 min.

Fig. 4. $x$-dependence of the saturated magnetization $M_s$ and remanent magnetization $M_r$ at 77 K and 300 K for the $x = 0$-1 samples after 290 rpm milling for 30 min.
non-linearly with x. At values of x above 0.6, the \( M_r \) nearly disappeared but the \( M_s \) kept a finite value. This may be due to the production of CrO\(_2\) nano-particles or small crystalline CrO\(_2\)-phase by mechanical milling with MoO\(_2\).

The same situation was observed in the temperature dependences of \( M \) as shown in Fig. 5. For the \( x = 0, 0.2, \) and 0.4 samples, the Curie temperature \( T_c \) could be identified as about 400 K from the inflection point of the \( M-T \) curve, but the \( T_c's \) were very ambiguous for \( x = 0.6 \) and 0.8 samples. We can therefore assume that the ferromagnetism of half-metallic CrO\(_2\) disappeared at \( x \sim 0.7 \).

The temperature dependences of the electrical resistivity \( \rho \) are shown in Fig. 6. The transverse axis was taken as \( T^{1/2} \) and the vertical axis as \( \log_{10} \rho \), because the tunneling magneto-resistance (TMR) theory for the granular system [18] gives the resistivity as

\[
\rho = \frac{\rho_0}{1 + P^2 m^2} \exp \left( \frac{\Delta}{\sqrt{2 T}} \right),
\]

where \( \rho_0 \) and \( \Delta \) are constant values, \( P \) is the spin polarization coefficient of conduction electrons, and \( m \) is defined by \( M/M_s \). The parameter \( \Delta \) is defined by \( \sqrt{2m^* (V - E_F) / h^2} \) and \( C = sE_c = \text{const} \). The parameter \( m^* \) is the effective mass of electrons, \( V \) is the barrier potential, \( E_F \) is the Fermi energy, \( s \) is the barrier thickness, and \( E_c \) is the charging energy. Equation (1) is derived from the condition that \( s \) gives the maximum transmission coefficient of conduction electrons [19].

The linearity of \( \log \rho \) vs. \( T^{1/2} \) was found for \( x = 0 \) and 0.1 samples, but non-linear hopping-like behavior appeared in \( x = 0.3 \) and 0.5 samples. The \( \Delta \) values of \( x \)

\[\begin{array}{c}
\text{Fig. 5. Temperature dependence of the magnetization } M \\
\text{for } x = 0, 0.2, 0.4, 0.6, \text{ and } 0.8 \text{ samples between 77 K and 300 K.}
\end{array}\]

\[\begin{array}{c}
\text{Fig. 6. } T^{1/2}-\text{dependence of the electrical resistivity } \rho \\
\text{for } x = 0, 0.1, 0.3, 0.5, 0.7, \text{ and } 0.9 \text{ samples.}
\end{array}\]

\[\begin{array}{c}
\text{Fig. 7. } x-\text{dependence of the magneto-resistance ratio (MRR) at 77 K.}
\end{array}\]
The field dependences of the $MRR$ of the $x = 0, 0.1, 0.3, 0.5$, and $0.7$ samples at 77 K are shown in Fig. 7. The $MRR$ is defined here as $\frac{\rho(H) - \rho(0)}{\rho(H)}$, where $H_p$ is the peak field at which $\rho(H)$ becomes maximum. The $|MRR|$ at 77 K was about 6% for pure CrO$_2$, and it decreased steeply as the amount of MoO$_2$ was increased. At $x = 0.7$, $|MRR|$ became negligibly small. By the theory of TMR in a granular system [10], $MRR$ is derived from Eq. (1) as

$$
P^2 m^2 \rho \leq (H_p)^2$$

at constant temperature.

For an external field of 1 T, the magnetization nearly saturated for all of the samples in the range $0 \leq x \leq 0.9$. Therefore the decrease in $|MRR|$ indicates a reduction of the electron spin polarization coefficient $P$ in the grain boundary between CrO$_2$ nano-particles or in the amorphous phase boundary between small crystalline parts.

![Fig. 8. $x$-dependence of the coercive force $H_c$ at 77 K and peak field $H_p$ of the $MRR$ curve at 77 K.](image)

In Fig. 8, the coercive force $H_c$ is plotted for each sample milled at 290 rpm for 30 min, in the range $0 \leq x \leq 0.9$, together with the peak field $H_p$ at which $\rho(H)$ became maximum. Both of $H_c$ and $H_p$ of the samples agreed well with each other in $0 \leq x \leq 0.6$ at 290 rpm for 30 min. This represents one of the characteristics of TMR in half-metallic CrO$_2$. Nearly constant $H_c$ values above $x > 0.6$ show that the magnetism of CrO$_2$ nano-particles or small crystalline parts is not super-paramagnetic but weakly ferromagnetic.

Here it should be noted that an enhancement of $H_c$ was observed for $x = 0.05$ samples milled at 100 and 200 rpm for 30 min. Though there is no reasonable explanation for this result at the present time, it might be due to the slight doping of the CrO$_2$-phase with Mo$^{4+}$.

4. Summary

Mixtures of metallic Pauli paramagnet MoO$_2$ and half-metallic ferromagnet CrO$_2$ were prepared by planetary ball milling. The magnetization $M$, resistivity $\rho$, and magnetoresistance ratio $MRR$ were measured for (MoO$_2$)$_x$(CrO$_2$)$_{1-x}$ from $x = 0$ to 1. $M$ and $|MRR|$ steeply decreased with increasing MoO$_2$ content and disappeared at $x \sim 0.7$, where the CrO$_2$ nano-particles or small crystalline parts contributed to weak ferromagnetism. At $x = 0.05$, anomalous rpm-dependence was observed for the coercive force $H_c$ in this system.

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References

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