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Magnetism and Magneto-resistance of Mo-doped CrO_2

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Mo-doping effects were studied for half metallic ferromagnet CrO_2. Mixed samples of $Mo_xCr_{1-x}O_y$ were prepared by planetary ball mill. X ray diffraction, magnetization M, resistivity ρ and magneto- resistance ratio MRR were measured for $x = 0$ to 1 with 0.1 step. Tetragonal phase of CrO_2-type transformed to monoclinic phase of MoO_3(II)-type at x above 0.7. M and $|MRR|$ rapidly decreased with increasing Mo content, and disappeared at x above 0.3. Above $x = 0.3$, trivalent Cr ions were assumed to be dominant for the magnetic property of present system.

Key Words : Half-metal, ferromagnetic oxide, Magnetization, Magneto-resistance

1. INTRODUCTION

CrO_2 has been known as a half metallic oxide with 100 % spin polarization of $3d$ conduction electrons. In this system, the band structure of majority spins is metallic, while the minority spin band has a semi-conductive energy gap at the Fermi level [1]. Since the perfect spin polarization should result in the large magneto-resistance (MR), CrO_2 is a candidate to develop the spintronics devises such as the spin valve and magnetic random access memory (MRAM). Reported MR ratio (MRR) for CrO_2 granular system, containing antiferromagnetic Cr_2O_3 impurity at grain boundaries, showed very small value on the order of – 0.1 % at room temperature [2]. Recently, we found that paramagnetic Cr_2O_5 barrier has a possibility to enhance the $|MRR|$ of CrO_2 system [3]. Recently, impurity doping effects were calculated for CrO_2 by DV-Xα method which showed that a slight increase of magnetic moment and Curie point T_c by Mo-doping [4].

In the present work, tri-oxide of MoO_3 was mixed with CrO_2, and the effects for the magnetism and conductivity were investigated. In the present experiments, MoO_3 has a monoclinic MoO_3(II) crystal structure with the lattice parameters of $a = 0.3954$ nm, $b = 0.3687$ nm, c = 0.7095 nm and $\beta = 103.75$ deg [5]. CrO_2 has a tetragonal crystal structure with a of 0.4419 nm and b of 0.29154 nm [6]. In the half-metallic CrO_2, all of $3d^2$ electrons exist in the majority up spin band and behave as the polarized conduction electrons.

Previous study on the effect of a few % doping of Mo^{6+} ($4d^0$) into CrO_2 revealed steep disappearance of ferromagnetism with reduction of magnetization and Curie point T_c [7]. We also expected so-called ferromagnetic quantum critical point (FQCP) [8] for the doping of Mo^{6+} into the CrO_2-phase in the $(MoO_3)_x(CrO_2)_{1-x}$ mixed system.

At 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_3 /CrO_2 mixtures.

2. SAMPLE PREPARATION AND EXPERIMENTAL

Commercial CrO_3, $Cr(OH)_3 \cdot nH_2O$ and MoO_3 were used as the precursor for $Mo_xCr_{1-x}O_y$ samples, where the x-values are between 0 and 1. First, we obtained $CrOOH \cdot 0.5H_2O$ by sintering $Cr(OH)_3 \cdot nH_2O$ at 523 K for 1 hour in air. Then the powder mixture of CrO_3, $CrOOH \cdot 0.5H_2O$ and MoO_3 with the mole ratio of $(1-x)/3 : 2(1-x)/3 : 1$ was milled for 1 hour by the planetary ball mill (Fritch Pulverisette-7, Germany) with Cr-steel vials. The inner diameter and volume of each vial were 40 mm and 45 cm^3, respectively, and the Cr-steel balls with 15 mm diameter 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. Rotation speed was kept as 700 rpm.

The ground products were followed by annealing at 573 K for 4 hours in the flow of oxygen gas, and they were characterized as the solid solutions of $Mo_xCr_{1-x}O_y$ by x-ray powder diffraction (XRD) as mentioned below. Then they were mixed with aqueous solution of Polyvinyl Alcohol (PVA) and pressed to be a 1 mm thick pellet with 5 mm diameter.

Vibrating sample magnetometer (VSM) and the super-conducting quantum interference devise (SQUID) were used for the magnetization measurements. Measurements of resistivity and magneto-resistance were performed for dried samples by usual 4-terminals method in DC magnetic field between –1 T and 1 T.

3. EXPERIMENTAL RESULTS

3.1 X-ray diffractions

Powder Cu$K\alpha$ -XRD were measured for the milled

samples of nominal $(MoO_3)_x(CrO_2)_{1-x}$. We obtained the XRD pattern like as that of CrO_2 in $0 \le x \le 0.7$ accompanied by the decreasing of diffraction angle of 2θ as x increased. Meanwhile, in $0.7 \le x \le 1.0$, the XRD pattern was similar to that of MoO_3(II). At $x = 0.7$, two XRD patterns like as CrO_2 and MoO_3 coexisted. As depicted in Fig. 1, the diffraction angle of (110) reflection of CrO_2 shifts to lower value, according to the increasing of Mo content. Above $x = 0.7$, diffraction angle 2θ of (110)-reflection becomes nearly constant as shown in Fig.1.

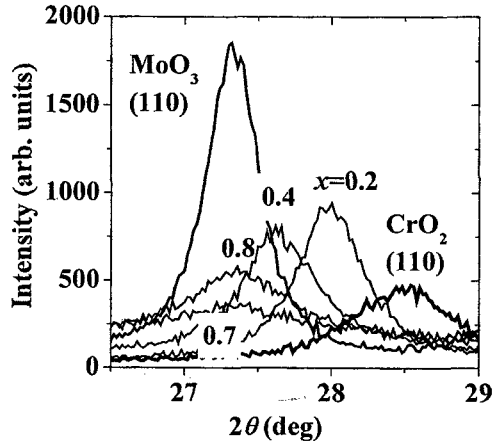

Fig.1 (110) main peaks of CrO_2 and MoO_3 in $0 \le x \le 1.0$.

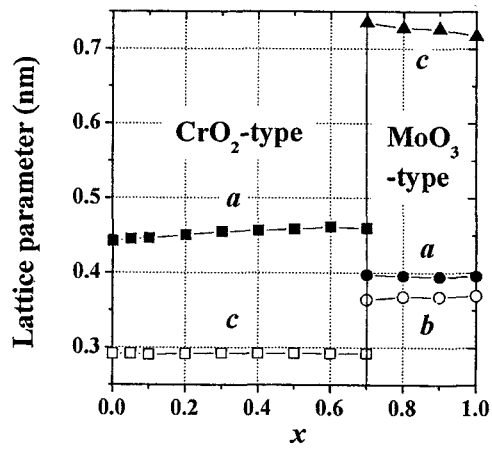

Fig.2 Lattice parameters of tetragonal phase in $0 \le x \le 0.7$, and monoclinic phase in $0.7 \le x \le 1.0$.

In Fig. 2, calculated lattice parameters from XRD results are shown. They show that the extension of a-axis in the tetragonal phase below $x = 0.7$, and the shrinking of c-axis in the monoclinic phase above $x = 0.7$ as x increases. The β of monoclinic phase was almost constant at about 104 deg in $0.7 \le x \le 1.0$.

From the above results, we convinced of the successful doping of Mo^{6+} to the CrO_2 phase in $1 \le x \le 0.6$, considering the larger ion radius of Mo^{6+} than that of Cr^{4+}. However, above x=0.8, the stable crystalline phase changed to the MoO_3(II)-type. In $0.8 \le x \le 1$, we can assume that the Cr^{3+}-ions are mainly doped into MoO_3 from the electric and magnetic properties as will be discussed below. In anyway, we can express the prepared samples as $Mo_xCr_{1-x}O_y$, where $x = 0 \sim 1$ and $y = 2 \sim 3$. From the half widths of XRD peaks, the grain sizes of $Mo_xCr_{1-x}O_y$ were estimated as 10~20 nm, which means that the present system is composed of the $Mo_xCr_{1-x}O_y$ nano-particles.

3.2 Magnetization

Magnetization curves at 77 K are shown in Fig. 3. The saturation magnetization M_s rapidly decreased at $x = 0.2$, and kept low values above $x = 0.3$.

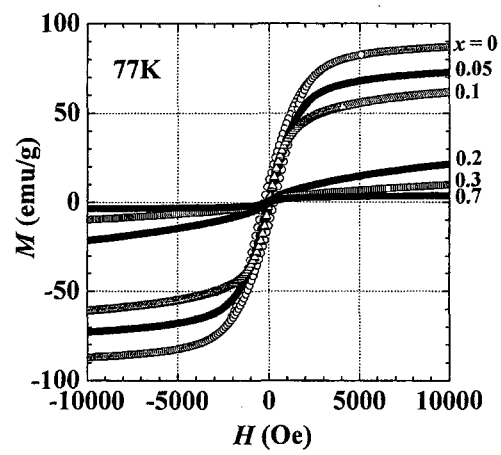

Fig.3 Magnetization curves of $Mo_xCr_{1-x}O_y$ at 77 K.

Temperature dependences of magnetization M under the field of 5 kOe are shown in Fig.4. The M were nearly saturated at 77 K in $0 \le x \le 0.3$, but the M-value at 77 K steeply decreased at $x = 0.2$. The vertical arrows are indicating the inflection points of the M(T)-curves which roughly give the ferromagnetic Curie point T_c. As shown in Fig. 4, rapid decreasing of T_c was observed at $x = 0.2 \sim 0.3$. The above results mean that the ferromagnetism, which is induced from large electron spin polarization,

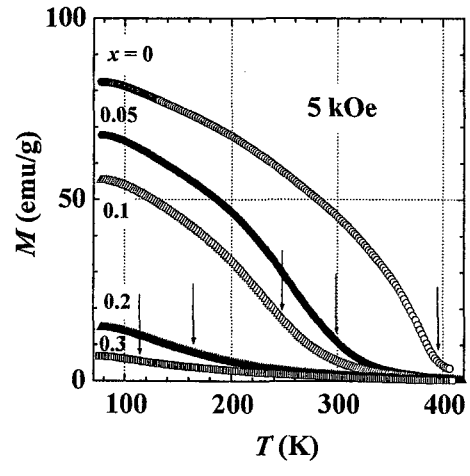

Fig.4 Temperature dependence of magnetization at 5 kOe.

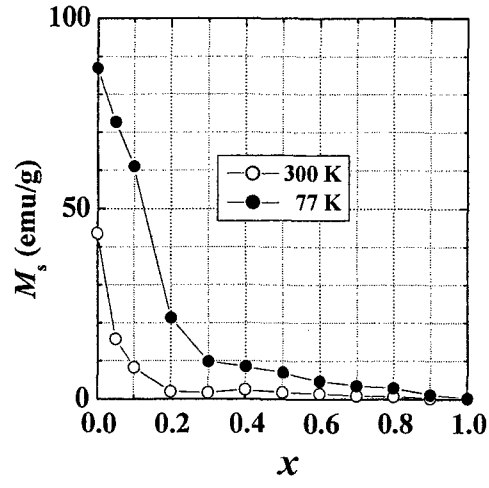

Fig. 5 x-dependence of saturation magnetization M_s at 77 K and 300 K.

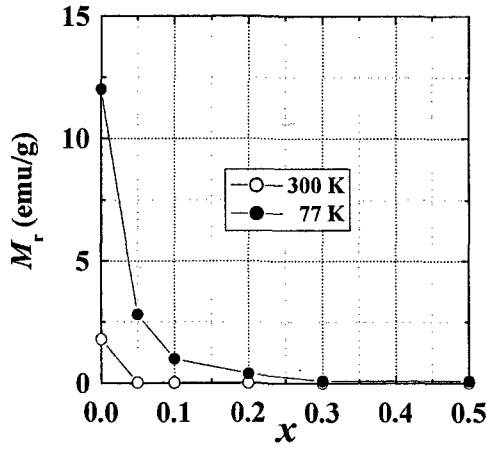

Fig.6 x-dependence of remanent magnetization M_r at 77 K and 300 K.

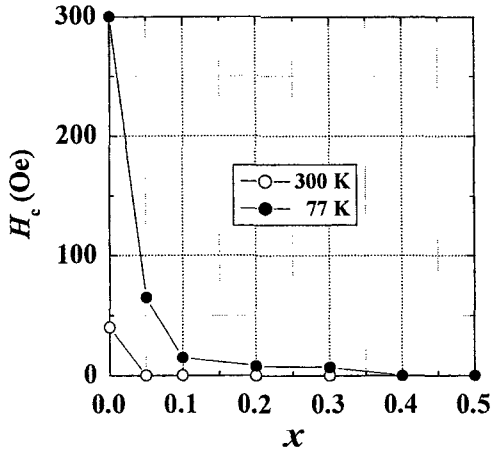

Fig.7 x-dependence of coercive force H_c at 77 K and 300 K.

smeared out by the Mo^{6+}-doping above x = 0.3. The x-dependence of saturation magnetization M_s, remanent magnetization M_r and coercive force H_c at 77 K and 300 K are shown in Fig. 5, 6 and 7, respectively. All of the magnetic quantities become very small at x = 0.2 ~0.3. Therefore we can identify the vanishing point of half metallic ferromagnetism in $Mo_xCr_{1-x}O_y$ ($y \sim 2$) as $x \sim 0.3$.

3.3 Resistivity and magneto-resistance effect

In Fig. 8, temperature dependence of electrical resistivity ρ is shown for x = 0 ~ 0.5 samples. Since pure CrO_2 showed the tunneling magneto-resistance (TMR) at 77 K and 300 K [3] by the spin polarized 3d electrons, we plotted $\log \rho$ for $1/T^{1/2}$ following the TMR theory [9]. As shown in Fig. 8, $\log \rho$ is linear with $1/T^{1/2}$ up to x = 0.5 between about 150 K and 350 K. This result looks like as that the half metallic property does not disappear completely at x = 0.5. However the magnitude of ρ, which is also shown in Fig. 9, shows steeply increases above x = 0.3 and becomes one thousand time larger than that of CrO_2 (x = 0) at x = 0.5. The increasing of ρ corresponds to the disappearance of ferromagnetism in this system.

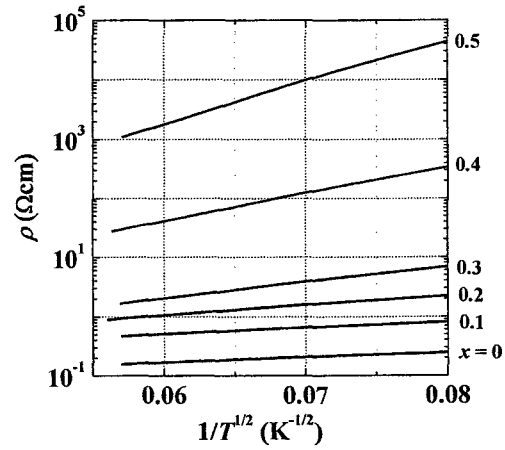

Fig.8 Temperature dependence of electrical resistivity.

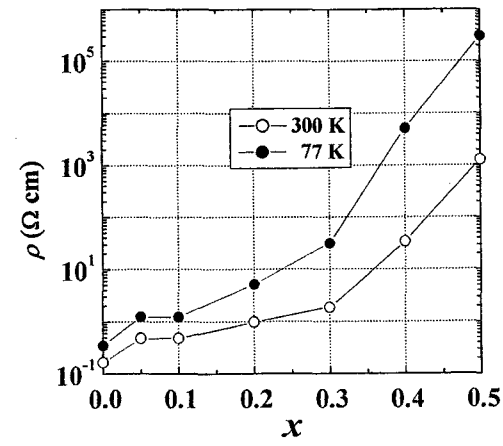

Fig.9 x-dependence of electrical resistivity at 77 K and 300 K.

In Fig. 10, magneto-resistance ratio (*MRR*) of $Mo_xCr_{1-x}O_y$ are shown, where *MRR* is defined here as $[\rho(H_p)-\rho(H)]/\rho(H_p)$, where H_p is the peak field at which $\rho(H)$ becomes maximum. The $|MRR|$ at 77 K was about 4 % for pure CrO_2, but it steeply decreased as the Mo-content increased. Above x = 0.3, $|MRR|$ becomes negligibly small, which also shows the disappearance of ferromagnetism.

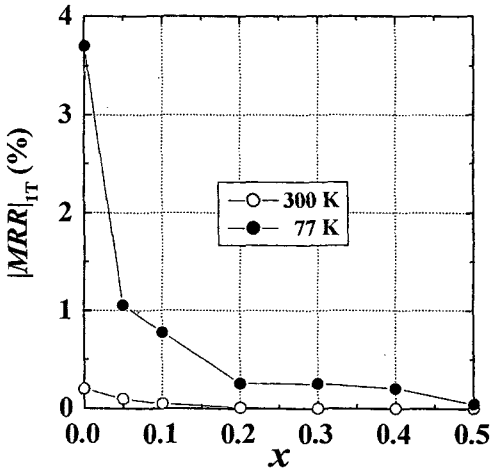

Fig.10 x-dependence of magneto-resistance ratio at 77 K and 300 K.

DISCUSSION

Now we discuss the ionic states of Cr based on the above experimental results. From the XRD results, we confirmed that the successful doping of Mo^{6+} to the CrO_2 phase in $1 \le x \le 0.6$. Meanwhile, the MoO_3-type crystalline phase was observed in $0.8 \le x \le 1$. Here we think that the Cr^{3+}-ions play the important role in the present $Mo_xCr_{1-x}O_y$ system as following.

For example, the $Mo_xCr_{1-x}O_y$ can be assumed as $(Mo^{6+})_x(Cr^{4+})_{1-3x}(Cr^{3+})_{2x}O_2$ in $0 \le x \le 1/3$. In that case, no Cr^{4+} ion exists at x =1/3 (~ 0.3), where the half-metallic ferromagnetism disappears. In the region of $1/3 \le x \le 2/3$, $(Mo^{6+})_{4x/[3(1+x)]}(Cr^{3+})_{4(1-x)/[3(1+x)]}\square_{(3x-1)/[3(1+x)]}O_2$ is possible considering $\square$ as the vacancy in CrO_2-type crystal structure. In $2/3 \le x \le 1$, we can assume $(Mo^{6+})_x(Cr^{3+})_{1-x}O_{3-\delta}$ where $\delta = 3(1-x)/2$ is the oxygen deficiency. Then the coexistence of two phases of $Mo^{6+}_{0.53}Cr^{3+}_{0.27}\square_{0.2}O_2$ (CrO_2-type) and $Mo^{6+}_{0.67}Cr^{3+}_{0.33}O_{3-0.5}$ (MoO_3-type) is capable at x =2/3 (~0.7).

The above example shows one of the possibilities, but the importance of Cr^{3+}, which composes an antiferromagnetic oxide of Cr_2O_3, can be sufficiently elucidated for the present system.

If there is the ferromagnetic quantum critical point (FQCP) of $Mo_xCr_{1-x}O_y$ near x = 0.3, p-type superconductivity can be expected at very low temperature [9]. Therefore, electronic and magnetic properties below 77 K is very interesting, and they shall be reported in the near future.

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