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# Pressure derivatives of the Curie temperature of spinel-type $CoCr_2O_4$ and $CoMn_2O_4$

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The magnetic permeability of  $CoCr_2O_4$  and  $CoMn_2O_4$  at high pressures has been measured in a piston-cylinder apparatus. The Curie temperature or the temperature of the Hopkinson peak of  $CoCr_2O_4$  increases with pressure at a rate of  $-0.1 \pm 0.1$  to  $-0.3 \pm 0.2$  K GPa<sup>-1</sup> or  $-0.26 \pm 0.06$  to  $-0.17 \pm 0.09$  K GPa<sup>-1</sup>, respectively; namely, these are negative pressure derivatives and those of  $CoCr_2O_4$  increase with pressure at a rate of  $1.5 \pm 0.2$  to  $2.7 \pm 0.2$  K GPa<sup>-1</sup> or  $1.37 \pm 0.08$  to  $1.9 \pm 0.4$  K GPa<sup>-1</sup>, respectively.

#### 1. Introduction

Recently, the negative pressure derivative  $(-3.3 \text{ to } -3.47 \text{ K GPa}^{-1})$  of the Curie temperature was found [1] for spinel-type MnCo<sub>2</sub>O<sub>4</sub>. This fact had not been seen for the other magnetic oxides.

The magnetic permeability of spinel-type  $CoCr_2O_4$  and  $CoMn_2O_4$  were measured at high pressures using a piston-cylinder apparatus and an epoxy-sealed cell with the use of 1-pentene [2]  $(CH_3CH_2CH_2CH:CH_2)$  as the pressure-transmitting medium, and the negative pressure derivative (-0.1 to -0.3 K GPa<sup>-1</sup>) of the Curie temperatule and that (-0.26 to -0.17 K GPa<sup>-1</sup>) of the temperature of the Hopkinson peak was found for  $CoCr_2O_4$ . This result indicates that for spinel-type magnetic oxides, the negative pressure derivative of the Curie temperature of the Hopkinson peak is not a unique case for MnCo<sub>2</sub>O<sub>4</sub>.

Cobalt chromite,  $CoCr_2O_4$ , is known to have a cubic normal-spinel structure, namely,  $Co^{2+}$  ions locate at tetrahedral (A) sites and  $Cr^{3+}$  ions at octahedral (B) sites. The magnetic structure

Correspondence to: S. Tamura, National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305, Japan. between  $24.5 \text{ K} (T_s)$  and Curie temperature  $(T_c)$  is a collinear ferrimagnet model (quasi Néel type) and a long range order of the transverse spin component is realized [3] (cone structure) below  $T_s$ . A cancellation of angular momenta occurs at 82.5 K  $(T_1)$  and a deviation from the proper conical spin structure at 10.5 K  $(T_1)$  is expected [3]. The easy axis is [0 0 1] at 77 K and any magnetic anisotropy at 90 K cannot be found within an experimental error of  $\pm 5\%$  [4].

As  $MnCo_2O_4$  has a negative pressure derivative of the Curie temperature [1], it is interesting to study a pressure derivative of the Curie temperature of  $CoMn_2O_4$ . A positive pressure derivative of the Curie temperature of the temperature of the Hopkinson peak was found for  $CoMn_2O_4$ .

The inversion parameter  $\nu$  is defined as  $(Co_{1-\nu}Mn_{\nu})[Co_{\nu}Mn_{2-\nu}]O_4$ , where () and [] represent tetrahedral A and octahedral B sites of a spinel lattice, respectively. When  $\nu = 1$ , it is a fully inverse spinel and when  $\nu = 0$ , it is a fully normal spinel. The ferrimagnetic tetragonal (c/a > 1) [5] spinel CoMn<sub>2</sub>O<sub>4</sub> has an incomplete normal structure [5] (table 1). Brabers and Van Setten [6] reported that the Co ion is divalent and the Mn ion is trivalent for CoMn<sub>2</sub>O<sub>4</sub> and the Co ion in the tetrahedral site is divalent, the Co

Table 1

The conditions of the sample preparation for  $CoCr_2O_4$  or  $CoMn_2O_4$  and the inversion parameter for  $CoMn_3O_4 \nu$ , i.e. manganese quantity in tetrahedral site from the data by Boucher et al. [5].

Sample	Temperature (K)	Time (h)	Atmosphere	v
CoCr,O, A	1673	24	In air	_
В	1273	72	In air	_
	After 1673	24	In air	
CoMn <sub>2</sub> O <sub>4</sub> C	1523	15	In air	0.39
D	1273	47	In air	0.33
	After 1523	15	In air	

ion in the octahedron site is trivalent and the Mn ion is trivalent for  $MnCo_2O_4$  by an X-ray photoelectron spectroscopic study, but Blasse [7] proposed that the Co ion is divalent and the Mn ion is tetravalent from a study of the magnetic susceptibility of  $MnCo_2O_4$ .

#### 2. Experiments

The starting substances were Co<sub>3</sub>O<sub>4</sub> (99.999%, Johnson Matthey Chemicals) and Cr<sub>2</sub>O<sub>3</sub> (99.999%, Johnson Matthey Chemicals) for  $CoCr_2O_4$ .  $Co_3O_4$  and  $Cr_2O_3$  were mixed in a 1:3 molar ratio by using an agate mortar and pestle under acetone for 1 h and pressed at  $0.26 \text{ GN m}^{-2}$  into ring shapes. When ring-shaped samples were prepared at room temperature, polyvinyl alcohol  $[(-CH_2CHOH_)_n, n \approx 1500]$  of 4 wt% was used as binder, because of the difficulty in moulding rings of these mixtures. The mixture was heated at 873 K for 16 h in air to evaporate the binder and it was fired at 1503 K for 53 h as the preheating. The conditions for the sample preparation are shown in table 1. The samples (A and B), which were ring shaped, were quenched from these conditions to room temperature.

The starting substances were MnO<sub>2</sub> (99.999%, Johnson Matthey Chemicals) and Co<sub>3</sub>O<sub>4</sub> 99.999%, Johnson Matthey Chemicals) for CoMn<sub>2</sub>O<sub>4</sub>. The method of preparing ring-shaped sample is similar to that in the literature [1]. CoMn<sub>2</sub>O<sub>4</sub> is stable in the range of temperature from 1120 K to 1630 K in air [8]. The coorditions of the sample preparation and the values [5] of  $\nu$ 

are shown in table 1. The samples (C and D), which were ring shaped, were quenched from these conditions to room temperature.

To measure the magnetic permeability, coils of 400 turns were wound on the ring-shaped sam-ID = 3.8 - 4.0 mm.(OD = 6.9 - 8.0 mm)ples height = 2.9-3.0 mm) and 10 kHz current was passed through them to measure the self-inductance of the coils, which is proportional to the magnetic permeability of the samples. The selfinductance was measured in a magnetic field of about  $400 \text{ Am}^{-1}$  (~5 Oe) with a digital LCR meter (Ando, model AG-4311); the EMF of the Chromel-Alumel thermocouple in contact with the sample was measured with a digital voltmeter (Keithley, model 182). The equipment was controlled using a personal computer (NEC, model PC-9801 UV2) by means of a general-purpose interface bus (GP-IB). The EMF of the thermocouple was calibrated with a platinum resistance thermometer (Scientific Instruments Inc., model P3AB) at normal pressure and was calibrated at high pressure at 83 K (near liquid nitrogen temperature). The measurements were made while the temperature was increased at the natural heating rate  $(1.5-0.3 \text{ K min}^{-1})$ .

#### 3. Results and discussions

The relative magnetic permeability,  $\mu_r$  (magnetic permeability of the sample over the magnetic permeability of a vacuum) at 1.59 GPa of sample A (CoCr<sub>2</sub>O<sub>4</sub>) or 1.34 GPa of sample D (CoMn<sub>2</sub>O<sub>4</sub>) are plotted against temperature in figs. 1 and 2. The Curie temperature ( $T_c$ ) was



Fig. 1. Temperature dependence of the relative magnetic permeability (magnetic permeability of the sample over the magnetic permeability of vacuum) of  $CoCr_2O_4$  (sample A) at 1.59 GPa.  $T_C$ , Curie temperature;  $T_{II}$ , temperature of the peak (Hopkinson effect).



Fig. 2. Temperature dependence of the relative magnetic permeability of  $CoMn_3O_4$  (sample D) at 1.34 GPa.

determined as the point of intersection of the tangent to the sharply ascending part of the relative magnetic permeability-temperature curve with the line to which this curve tended in the high temperature region. The peak at  $T_{\rm H}$  (below  $T_{\rm C}$  by about 1 K for sample A, below  $T_{\rm C}$  by about 4 K for sample D) is attributed to the Hopkinson effect.

Figures 3 and 4 show the relation between  $T_C$  of sample A (CoCr<sub>2</sub>O<sub>4</sub>) or sample D (CoMn<sub>2</sub>O<sub>4</sub>) and pressure, respectively. The fits obtained by the least-squares method are

$$T_{\rm C}({\rm K}) = (95.8 \pm 0.1) - (0.1 \pm 0.1)p \,({\rm GPa})$$
 (1)

for sample A ( $CoCr_2O_4$ ) and

$$T_{\rm C}$$
 (K) = (96.1 ± 0.2) - (0.3 ± 0.2)p (GPa) (2)



Fig. 3. Relation between the Curie temperature  $T_{\rm C}$ , for sample A (CoCr<sub>2</sub>O<sub>4</sub>), and pressure *p*.



Fig. 4. Relation between the Curie temperature  $T_c$ , for sample D (CoMn<sub>2</sub>O<sub>4</sub>), and pressure p.

for sample B ( $CoCr_2O_4$ ).

$$T_{\rm C}({\rm K}) = (103.4 \pm 0.2) + (1.5 \pm 0.2)p \,({\rm GPa})$$
 (3)

for sample C (CoMn<sub>2</sub>O<sub>4</sub>) and

$$T_{\rm C}({\rm K}) = (103.5 \pm 0.1) + (2.7 \pm 0.2)p \,({\rm GPa})$$
 (4)

for sample D (CoMn<sub>2</sub>O<sub>4</sub>). The Curie temperatures at 0 GPa of samples A and B agree with each other within the experimental errors and the pressure derivatives of  $T_{\rm C}$  for sample A and B are nearly equal. Although the variation of  $T_{\rm C}$ of CoCr<sub>2</sub>O<sub>4</sub> at each pressure is smaller that that of MnCo<sub>2</sub>O<sub>4</sub> [1] which has a negative pressure derivative of  $T_{\rm C}$  by a factor of about 1/34,  $T_{\rm C}$ decreases with increasing pressure. This fact is a very rare case for magnetic oxides.

From Anderson's theory [9] of superexchange interaction (kinetic exchange), the strength of

that is a certain average of  $|b_{\rm mm'}|^2 U$ , where  $b_{\rm mm'}$ is a parameter of an electron transfer and U is an excited energy when two electrons, both on the same ion, repel each other. It is unlikely that the effect of U which increases with increasing pressure surpasses that of  $|b_{\rm mm'}|^2$  which increases with increasing pressure. An effective exchange integral, J, of localized spins is the summation of the kinetic exchange part,  $J_{\rm kin}$ , and the potential exchange (direct exchange) part [9],  $J_{\rm pot}$ . A pressure variation of  $J_{\rm pot}$  which gives ferromagnetic interaction always may surpass that of  $J_{\rm kin}$ which gives antiferromagnetic interaction, therefore CoCr<sub>2</sub>O<sub>4</sub> and MnCo<sub>2</sub>O<sub>4</sub> [1] have negative pressure derivatives of the Curie temperature.

The Curie temperatures at 0 GPa of samples C and D agree with each other within the experimental errors and the pressure derivative of  $T_{\rm C}$  for sample D (inversion parameter,  $\nu = 0.33$ ) is larger than that for sample C ( $\nu = 0.39$ ) by a factor of 1.8, namely, the pressure derivative of  $T_{\rm C}$  increases with increasing v.  $T_{\rm C}$  of CoMn<sub>2</sub>O<sub>4</sub> increases with increasing pressure and this fact differs from the case of inverse spinel-type  $Co[MnCo]O_4$  [1] which has a negative pressure derivative of  $T_{C}$  [] indicates the ions in the octahedral site. This seems to be related to the fact that  $dT_C/dp$  of CoMn<sub>2</sub>O<sub>4</sub> is sensitive to v. When the ratio of Co/Mn in the octahedral site approaches 1,  $dT_c/dp$  decreases and MnCo<sub>2</sub>O<sub>4</sub> has a negative value.

The temperature  $(T_{\rm H})$  at which the relative



Fig. 5. Pressure dependence of the temperature,  $T_{\rm H}$ , of the peak (Hopkinson effect) of the permeability-temperature curve for sample A (CoCr<sub>2</sub>O<sub>4</sub>).



Fig. 6. Pressure dependence of the temperature,  $T_{\rm H}$ , of the peak (Hopkinson effect) of the permeability-temperature curve for sample D (CoMn,O<sub>4</sub>).

permeability has a peak (Hopkinson effect) for sample A ( $CoCr_2O_4$ ) or sample D ( $CoMn_2O_4$ ) is plotted against pressure in figs. 5 and 6, respectively. The fits obtained by the least-squares method are

$$T_{\rm H}$$
 (K) = (95.11 ± 0.06) - (0.26 ± 0.06)p (GPc)  
(5)

for sample A ( $CoCr_2O_4$ ),

$$T_{\rm H}$$
 (K) = (95.10 ± 0.09) - (0.17 ± 0.09)p (GPa)  
(6)

for sample B ( $CoCr_2O_4$ ),

$$T_{\rm H}$$
 (K) = (87.7 ± 0.4) + (1.9 ± 0.4)p (GPa) (7)

for sample C ( $CoMn_2O_4$ ) and

$$T_{\rm H}$$
 (K) = (99.57 ± 0.06) + (1.37 ± 0.08)p (GPa)  
(8)

for sample D (CoMn<sub>2</sub>O<sub>4</sub>).  $dT_{\rm H}/dp$  decreases with increasing pressure for CoCr<sub>2</sub>O<sub>4</sub> and  $dT_{\rm H}/dp$ dp increases with increasing pressure for CoMn<sub>2</sub>O<sub>4</sub>. These results are similar to that of  $T_{\rm C}$ .  $T_{\rm H}$  at 0 GPa of sample A (CoCr<sub>2</sub>O<sub>4</sub>) and B (CoCr<sub>2</sub>O<sub>4</sub>) agree with each other and the pressure derivative of  $T_{\rm H}$  for sample A is larger than that for sample B by a factor of 1.5. For CoMn<sub>2</sub>O<sub>4</sub>,  $T_{\rm H}$  at 0 GPa increases with decreasing  $\nu$  and  $dT_{\rm H}/dp$  decreases with decreasing  $\nu$ .

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