EFFECT OF PRESSURE ON THE CURIE TEMPERATURE OF $CoCr_2O_4$

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The pressure effect on the Curie temperature T_C of $CoCr_2O_4$ was measured under pressures up to 11.5 kbar. The pressure derivative of T_C is found to be +0.25 K/kbar. On the basis of this result, the relationship between the magnetic transition temperature and volume is discussed.

Bloch [1] reported that there is an emperical rule for the relationship between the magnetic transition temperature $T_{C,N}$ (T_C: Curie temperature, T_N: Néel temperature) and volume V in insulating magnetic compounds such as CoO, FeO, several garnets and ferrites:

$$\mathrm{d}\log T_{C,N}/\mathrm{d}\log V = -\tfrac{10}{3}\,, \qquad (1)$$

or

$$\mathrm{d}T_{C,N}/\mathrm{d}p = \tfrac{10}{3}\kappa T_{C,N}\,, \qquad (1')$$

in which κ expresses the isothermal compressibility.

Recently, Kanomata et al. [2] also reported that the value of $\mathrm{d}\log T_{C,N}/\mathrm{d}\log V$ for chalcogenide spinels $FeCr_2S_4$ and $CoCr_2S_4$ are given by about $-\frac{10}{3}$. Furthermore they reported that eq. (1) is obtained by assuming that the dominant part of the superexchange interaction is the kinetic one and the band width W (the transfer integral t) is proportional to $V^{-5/3}$. However, it is not clear at present whether Bloch's rule is adaptable for all insulating magnetic compounds. So, it is necessary to examine systematically the pressure effect on the transition temperature of many magnetic compounds besides those mentioned above.

The compound $CoCr_2O_4$ crystalizes in the spinel lattice with a normal cation distribution, where Co^{2+} ions locate at tetrahedral (A) sites and Cr^{3+} ions at octahedral (B) sites. It becomes ferrimagnetic below the Curie temperature (T_C) of 97 K [3]. There is a magnetic phase transition (T_s) around 27 K [3]. The spontaneous magnetization at 4.2 K is about 0.1 μ_B per formular unit [3], which is so low that it cannot be explained by the simple Néel model. Menyuk et al. [4] and Plumier [5] proposed a ferrimagnetic spiral structure with three magnetic sublattices A, B-I and B-II for $CoCr_2O_4$ from their neutron diffraction (N.D.) experimental data. Then, Tsuda et al. [6] observed the NMR signals from Co^{59} and Cr^{53} nuclei in $CoCr_2O_4$. From the magnetic field dependence of these resonance frequencies up to 50 kOe, they estimated the half cone angles of the ferrimagnetic spiral for low temperature magnetic phase to be $18° \pm 7°$, $123° \pm 4°$ and $123° \pm 4°$ for Co, Cr-I and Cr-II sublattices, respectively. These angles are somewhat different from those determined by N.D. Furthermore, they reported that the local moment of Co^{2+} in the high temperature magnetic phase seems to be parallel to the net magnetization. The main purpose of the present note is to measure the pres-

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sure change of the Curie temperature of $CoCr_2O_4$ and to investigate the interatomic distance dependence of the superexchange interaction of $CoCr_2O_4$.

For the preparation of the sample, desired proportions of powdered Co_3O_4 and Cr_2O_3 were mixed in alcohol, and, after preheating at 900°C for six hours and 1000°C for twelve hours, this product was fired at 1400°C in air for a day and then quenched to room temperature.

The X-ray diffraction pattern which was obtained at room temperature using copper radiation indicated a single-phase, normal spinel structure. The lattice parameter and u parameter are found to be 8.322 Å and 0.386, respectively. This value of the u parameter is in good agreement with that previously observed by Menyuk et al. [4].

The value of dT_C/dp was measured with the magnetic induction method at hydrostatic pressures described in a previous work [7]. Initial permeability versus temperature curves for $CoCr_2O_4$ were obtained at different pressures: initial permeability decreases rapidly just below T_C with increasing temperature and then takes a nearly constant value with further rise in temperature. T_C was defined as the point of intersection of linear extrapolations from both high and low temperature ranges. The Curie temperature for $CoCr_2O_4$ was found to shift from 100.2 K at normal pressure to 103.1 K under a pressure of 11.5 kbar. The Curie temperature at normal pressure is somewhat larger than the value (97 K) reported by Menyuk et al. [3]. The pressure shift of T_C is shown against applied pressure in fig. 1. For the present compound, the Curie temperature was found to increase linearly with applied pressure in the pressure range investigated. The value of dT_C/dp determined from the results in fig. 1 is found to be +0.25 K/kbar. This value is smaller than those of Mn–Zn and Ni–Zn ferrites. That is, dT_C/dp of Ni–Zn ferrites range from $+0.73\pm0.06$ to $+1.16\pm0.07$ K/kbar [8]. Furthermore, dT_C/dp of $Mn_{0.5}Zn_{0.5}$-Fe_2O_4 was found to be $+0.9\pm0.04$ K/kbar [9]. The value of $d\log T_C/d\log V$ for $CoCr_2O_4$ was obtained to be -3.1 using the present result on dT_C/dp. In this calculation, we used the compressibility $\kappa=(0.80\pm0.21)\times10^{-3}$ kbar^{-1} for $CoCr_2S_4$ [2] as the compressibility of $CoCr_2O_4$. In fig. 2, we plot $dT_{C,N}/dp$ against $\kappa T_{C,N}$ for $CoCr_2O_4$ together with those for CoO [10,12], FeO [11,12], MnO [12,13],

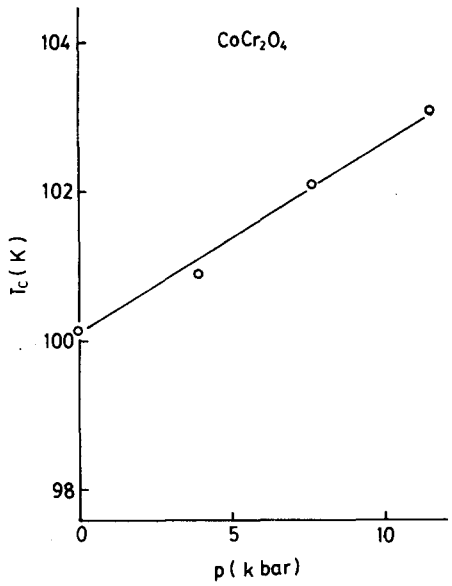

Fig. 1. Shift of the Curie temperature versus pressure curve.

NiO [12,14,15], La_2CuO_{4-y} [16,17], Mn–Zn ferrite [9], $FeCr_2S_4$ [2], $CoCr_2S_4$ [2] and the rare earth iron garnets [10,18]. The relation (1′) suggested by Bloch is expressed by the straight line in fig. 2. As shown in fig. 2, the relation between $dT_{C,N}/dp$ and $\kappa T_{C,N}$ for the present compound is well consistent with the relation proposed by Bloch [1]. For the compressibility of Mn–Zn ferrite, GdIG and ErIG, we assumed that the compressibility of these compounds are equal to that of YIG [18].

As mentioned above, the spin arrangement of $CoCr_2O_4$ is a complicated ferrimagnetic spiral type.

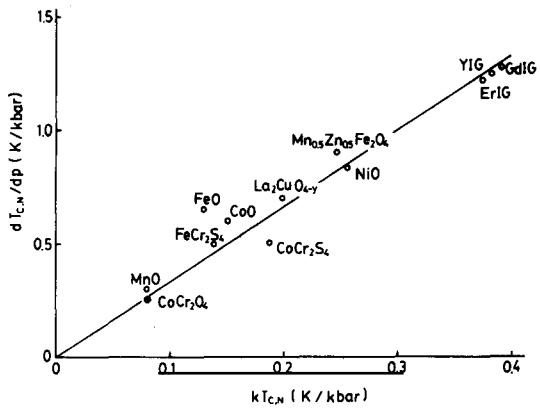

Fig. 2. Plots of $dT_{C,N}/dp$ against $\kappa T_{C,N}$.

Lyons and Kaplan [19] studied theoretically the ground state spin configuration of cubic normal spinels. They proposed a ferrimagnetic spiral structure with three magnetic sublattices A, B-I and B-II, when the isotropic exchange interaction between the nearest neighbour B–B ions becomes comparable with that between nearest neighbour A–B ions. Tsuda et al. [6] discussed the relation between the ferrimagnetic spiral structure and the exchange parameters for $CoCr_2O_4$ on the basis of the experimental results of their NMR measurement. According to their results, the nearest neighbour A–B and B–B interactions are almost equal and are consistent with the theoretical result by Lyons and Kaplan. These two interactions are an order of magnitude larger than many other exchange interactions between distant neighbour ions in this oxide. Therefore, the pressure dependence of the Curie temperature is probably caused by the variation in the nearest neighbour A–B and B–B interactions. The nearest neighbour A–B interaction is the 125° Co–O–Cr superexchange which has one intervening oxygen ion. The nearest neighbour B–B interaction is the 90° Cr–O–Cr superexchange one via one oxygen ion. As seen above, both A–B and B–B interactions are superexchange interactions. Thus, the present results also indicate that Bloch's rule is valid for the magnetic compounds with superexchange interactions. In fact, the characteristics of exchange interactions in all compounds as shown in fig. 2 are: (1) the dominant exchange interactions in compounds are superexchange and (2) the superexchange interactions have only one intervenient anion.

On the other hand, there exist a number of magnetic compounds in which the dominant exchange interactions are the superexchange via two or more intervening anions. The compounds $CoAl_2O_4$ [20] and $CoRh_2S_4$ [21] crystallize in the spinel lattice with a normal cation distribution. They are antiferromagnetic below the Néel temperature of 4 K ($CoAl_2O_4$) and 400 K ($CoRh_2S_4$). The spin arrangement of these compounds [20,22] is a simple Néel type in which each A site Co ion is tetrahedrally surrounded by four nearest neighbour same site Co ions with oppositely directed moment. In these compounds, the only magnetic interactions of antiferromagnetic spinels are those of A site Co ions. The distance between A site Co ions is very large and the A–A interaction involves two or three intervening ions in superexchange interactions. In this case, it is interesting to investigate whether the relationship between the magnetic transition temperature and volume follows Bloch's empirical rule mentioned above.

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