Effect of Pressure on Néel Temperature of ZnCr₂Se₄

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This note is concerned with a measurement of hydrostatic pressure effect on the magnetic transition temperature of $ZnCr_2Se_4$ compound. It has the same spinel-type crystal structure as $Cd_{1-x}Zn_xCr_2Se_4$ compounds from $x=0$ to 0.4, which have been studied previously.[1] The former compound is a helical anti-ferromagnetic semiconductor with Néel temperature at 20 K and paramagnetic Curie temperature at 115 K, and the latter compounds are ferromagnetic semiconductors in which Curie temperatures are at 130 K for $x=0$ and decreasing linearly with increasing x.

As in the $Cd_{1-x}Zn_xCr_2Se_4$ compounds,[1] the specimen used was prepared by solid-vapor reaction between stoichiometric mixtures of the elements (99.99 % in purity). The compound thus obtained is of powder form. It was pressed into a cylindrical rod of 3.5 mm in diameter and 14 mm in length. The compressed one was sintered in vacuum at 700～800°C for 100 hours. The compound thus prepared was confirmed to be a single phase by an X-ray analysis. Measurements of magnetization were carried out by observation of low field mutual inductance under the pressure as described in a previous paper.[2]

Hydrostatic pressure was applied up to about 5 kbar by a standard Bridgman-type intensifier using petroleum ether as a transmitting medium. The temperature at which the measurement was done were obtained in the warming process after evaporation of liquid helium in a Dewar vessel. The warming
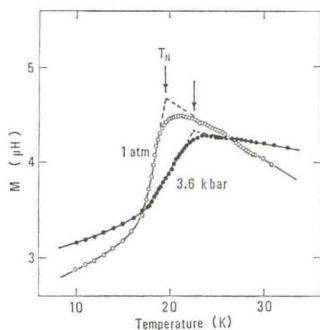
rate was 0.1 degree per minute.

In Fig. 1, the mutual inductance observed is plotted against temperature at both atmospheric pressure and 3.6 kbar. Néel temperature T_N is defined as the cusp of the curve. As pressure is increased, the Néel temperature is shifted to higher temperature. The pressure effect on T_N, $\Delta T_N/\Delta p$, is obtained as 0.90×10^{-3} (deg bar⁻¹). Lotgering has discussed the helical antiferromagnetic structure of $CdZn_2Se_4$.[3] According to his analysis, the antiferromagnetic superexchange interaction between the Cr ions through more than two Se ions is important together with the ferromagnetic superexchange interaction between the nearest neighbor Cr ions. Therefore, the increase of T_N with pressure may be explained by the assumption that the antiferromagnetic interaction exceeds the ferromagnetic interaction in their variations with decreasing atomic spacing. This assumption appears to suggest the NMR result[4] that the nearest neighbor ferromagnetic exchange depends mainly on the degree of covalence, while the antiferromagnetic more distant superexchange depends strongly on overlap of the Zn^{2+} ions with their neighboring Se^{2-} ions and Cr^{3+} ions.

On the basis of the molecular field theory, the pressure effect on T_N is given by

$$\frac{\Delta T_N}{\Delta p} = \frac{V T_N}{W_{m,0}}\left(\frac{\Delta V_0}{V_0}\right), \qquad (1)$$

where V is the molar volume and $(\Delta V_0/V_0)$ is the exchange striction at 0 K defined as the difference between the true volume and the volume which would exist in the absence of magnetoelastic interaction. $W_{m,0}$ is the magnetic energy at 0 K and can be approximated by

$$W_{m,0} = -\frac{3}{2} R T_N, \qquad (2)$$

where R is the gas constant. The value of $\Delta V_0/V_0$ was estimated as -6×10^{-4} by extrapolation of the empirical volume temperature curve from the paramagnetic region to 0 K obtained by R. Kleinberger and R. Kouchkovsky.[5] On substituting the values of T_N, $(\Delta V_0/V_0)$ and V into eq. (1) and eq. (2), the value of $\Delta T_N/\Delta p$ is estimated as 0.6×10^{-3} (deg bar⁻¹). The estimated value is in fair agreement with that obtained in the present experiment.

Fig. 1. Mutual inductance as a function of temperature at atmospheric pressure and 3.6 kbar for $CdZn_2Se_4$.

References

1) H. Fujii, T. Kamigaichi, Y. Hidaka and T. Okamoto: J. Phys. Soc. Japan **29** (1970) 244.
2) H. Fujii: J. Sci. Hiroshima Univ. A-II **33** (1969) 43.
3) F. K. Lotgering: Solid State Commun. **3** (1965) 347.
4) S. B. Berger, J. I. Budnick and J. Rurch: Phys. Rev. **179** (1962) 272; G.H. Stauss: Phys. Rev. **181** (1969) 636.
5) R. Kleinberger and R. Kouchkovsky: CR Acad. Sci. **260** (1966) 628.