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Magnetic Susceptibility of $MnIn_2S_4$*

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Recent magnetic resonance results suggest that $MnIn_2S_4$ is antiferromagnetic with a Néel point near liquid helium temperature, in disagreement with previously reported dc (direct current) susceptibility measurements. The resonance data suggest that these susceptibility measurements were made at an applied dc field comparable to or greater than the critical field. This would tend to obscure observation of a magnetic transition, since some of the spins would be "flopped." The susceptibility measurements have been repeated at a much lower applied field. From these new measurements, a Néel temperature of 4.9°K is obtained, in agreement with the resonance data, and an exchange parameter of 1430 is computed.

Introduction

Manganese indium thiospinel has been shown by Schlein and Wold to be a mixed spinel $Mn_xIn_{1-x}(In_{1+x}Mn_{1-x})S_4$ (*1*). Their dc magnetic susceptibility measurements on a powdered specimen with a 10 kOe applied magnetic field intensity indicate that this material exhibits Curie–Weiss behavior over the temperature range 4.2–298°K with $\theta = -78°K$. No apparent ordering temperature was found, although a slight curvature in the inverse susceptibility vs temperature plot was observed at the lower temperatures.

Goodenough has commented (*2*) that all interactions in this compound are expected to be antiferromagnetic, and expressed surprise that no ferrimagnetism had been observed above 4.2°K. Recently, however, this compound has been studied with magnetic resonance techniques (*3*), and the results indicate that a transition to the antiferromagnetic state occurs near 6°K. The zero applied field resonance frequency yields an effective internal field of 3.59 kOe at 4.2°K based on the Néel two-sublattice model. The effective internal field should increase as temperature is decreased, but it is unlikely that, even at absolute zero, this field greatly exceeds 10 kOe—the applied field used in the original susceptibility measurements. It was thus felt that the low-temperature susceptibility behavior may have been obscured in those measurements, as explained below. Consequently, we have reexamined the susceptibility of this compound using lower applied field values (~1.3 kOe), and employing a magnetometer whose low temperature sensitivity is much greater than that of the instrument used for the original measurements.

Effect of Applied Magnetic Field on Powder Susceptibility

Low-Field Case

Susceptibility measurements on an antiferromagnetic substance are usually performed in a dc magnetic field H which is small compared to the effective internal field at absolute zero $H_c = (2H_E H_A)^{1/2}$, where H_E and H_A are the exchange field and the anisotropy field,

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respectively, at absolute zero. In a powdered specimen of an antiferromagnetic substance with one preferred axis, for example, the low-field powder susceptibility χ_p is given (*4*) by

$$\chi_p = 1/3\chi_\parallel + 2/3\chi_\perp \qquad (H \ll H_c), \qquad (1)$$

where $\chi_\parallel$ and $\chi_\perp$ are single crystal susceptibilities measured with the applied magnetic field parallel and perpendicular to the preferred axis, respectively. The temperature dependences of χ_p $(H \ll H_c)$, $\chi_\parallel$ and $\chi_\perp$ are shown in Fig. 1 for $T < T_N$ (*5*), where T_N is the Néel temperature.

High-Field Case

The effect of an applied magnetic field H on any crystallite in a powdered specimen can be considered qualitatively by decomposing H into two orthogonal components, one parallel to and the other perpendicular to the easy direction of the particle, $H_\parallel$ and $H_\perp$. If $H_\parallel$ is comparable to or greater than H_c, the sublattice magnetizations of the crystallite will flop (*4*) into an orientation perpendicular to the easy direction. This phenomenon will increase the contribution of $\chi_\perp$ to χ_p in Eq. (1). Thus, for $T < T_N$, χ_p measured with $H \sim H_c$ is greater than that with $H \ll H_c$. As examples, Fig. 1 also shows the temperature dependence of the powder susceptibility of a uniaxial antiferromagnet for $H = H_c$ and $H = \sqrt{3}H_c$ (*5*). Clearly, the effect of the magnetic field on the susceptibility curve is to smooth out the peak at T_N, making the determination of T_N less certain. The effect becomes more pronounced as the field is increased, so care should be taken to ensure that the field applied during susceptibility measurements is sufficiently low.

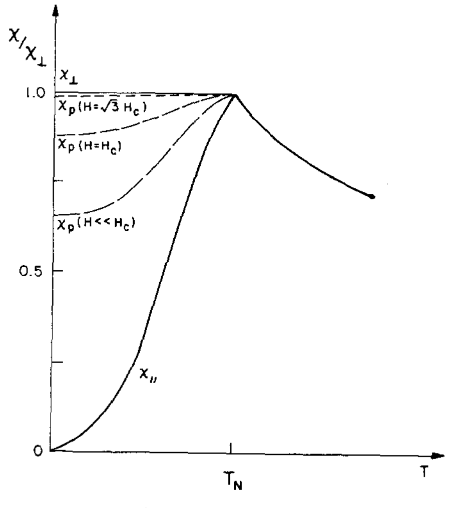

FIG. 1. Uniaxial antiferromagnetic susceptibilities.

Experimental Procedure and Results

Material Preparation

The $MnIn_2S_4$ used in this study was prepared using the procedure described in Ref. (*1*). X-ray diffraction measurements showed the material to be single phase—having a mixed spinel structure with a cell edge of 10.72 Å.

Low-Field Susceptibility Measurements

Susceptibility data were obtained with a Faraday Balance over the temperature range 2.5–300°K at a field of 1.27 kOe. The results from 2.50 to 20°K are shown in Fig. 2. The data indicate antiferromagnetic ordering below a Néel point of 4.9°K, in agreement with the resonance data. At temperatures above T_N, the susceptibility follows the Curie–Weiss law $\chi = C/(T-\theta)$ with $C(\text{molar}) = 4.26$ and $\theta = -75°K$, in fair agreement with the previously reported susceptibility measurements. The exchange parameter $\lambda = 1/\chi_\perp$ with $\chi_\perp$ in cgs/cm³. Since $\chi_\perp$ is given by the maximum of the powder susceptibility (6.5×10^{-2} cgs/mole from Fig. 2), an exchange parameter $\lambda = 1430$ is calculated using the X-ray density.

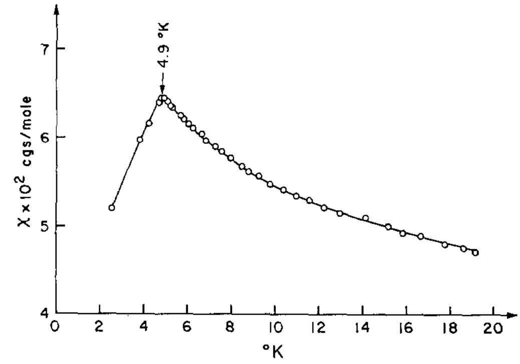

FIG. 2. $MnIn_2S_4$ powder susceptibility.

Acknowledgment

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References

1. W. Schlein and A. Wold, *J. Solid State Chem.* 4, 286 (1972).
2. J. B. Goodenough, *J. Solid State Chem.* **4**, 292 (1972).
3. C. I. Hsu, E. A. DeMeo, G. S. Heller, and A. Wold, to be published.
4. See, e.g., T. Nagamiya, K. Yosida, and R. Kubo, *Adv. Phys.* **4**, 32 (1955).
5. See, e.g., F. Keffer and W. O'Sullivan, *Phys, Rev.* **108**, 637 (1957).