Antiferromagnetism of $CuF_2 \cdot 2H_2O$ and MnF_3

R. M. BOZORTH AND J. W. NIELSEN Bell Telephone Laboratories, Murray Hill, New Jersey (Received January 20, 1958)

The molar susceptibility, χ_m , of CuF₂·2H₂O has been measured from T=1.3 to 260°K. It is antiferromagnetic with a Néel point of $\theta_N = 26$ °K. Above $T = \theta_N$ the Curie-Weiss law, $\chi_m = C_m/(T - \theta_p)$, is obeyed with $\theta_p = -37$ °K and $\mu_{eff} = 1.9$. Data for MnF₃ also show antiferromagnetism with $\theta_N = 47$ °, and with $C_m = 3.10$, $\theta_p = 8^\circ$, and $\mu_{eff} = 5.0$ above the Néel point.

THE compound $\operatorname{CuF}_2 \cdot 2\operatorname{H}_2O$ was prepared by adding reagent grade copper carbonate to an excess of 40% hydrofluoric acid.¹ This solution was kept in a polyethylene beaker and allowed to evaporate slowly at 71.5°C until a large number of crystals had formed. An x-ray diffraction photograph of freshly crushed crystals agreed with that reported by Wheeler and Haendler² for $\operatorname{CuF}_2 \cdot 2\operatorname{H}_2O$.

Measurements were made with the pendulum magnetometer previously described.³ The sample of $\operatorname{CuF}_2 \cdot 2H_2O$ was a coarse powder of about 1 g prepared from an agglomerate of freshly grown crystals. It was mounted in the apparatus in a gelatine capsule and placed next to the carbon resistor used for measurement of temperature.

The specimen of anhydrous MnF_3^4 was purchased from the Allied Chemical and Dye Corporation. The first measurements were made with the specimen enclosed in a gelatine capsule, and no antiferromagnetism was detected. It was pointed out to us by W. C.



Fig. 1. Molar susceptibility of $\rm CuF_2 \cdot 2H_2O,$ and its reciprocal, as dependent on temperature.

¹ Kurtenacker, Finger, an dHey, Z. anorg. allgem. Chem. 211, 83 (1933). ² C. M. Wheeler and H. M. Haendler, J. Am. Chem. Soc. 76,

² C. M. Wheeler and H. M. Haendler, J. Am. Chem. Soc. 76, 263 (1954).

⁴ The material was identified by Dr. S. Geller by x-ray diffraction.

Koehler and E. O. Wollan of Oak Ridge National Laboratory that their neutron diffraction measurements⁵ showed antiferromagnetism in this material with a Néel point near 45° K, and that our specimen may have hydrolyzed in contact with moisture. A fresh specimen was then carefully transferred to glass in a dry atmosphere and sealed. Antiferromagnetism was then found, as described below.

The field strength normally used was 10 800 oe, but higher and lower fields were used to test the proportionality between the field and magnetization.

Results for $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ are given in Fig. 1. The material becomes antiferromagnetic at $\theta_N = 26^\circ\text{K}$. The Curie-Weiss law, $\chi_m = C_m/(T - \theta_p)$, is obeyed above the Néel point, with the Curie constant per mole of $C_m = 0.46$ and paramagnetic Curie temperature of $\theta_p = -37^\circ\text{K}$. The effective Bohr magneton number is $\mu_{\text{eff}} = 1.9$, in good agreement with results for other Cu⁺⁺ salts.⁶ The Néel point is higher than for the other hydrated halides of iron-group elements (2 to 4°K) but lower than for most of these compounds in the anhydrous form (25 to 80°K, but 2° for MnCl₂).⁷ The ratio θ_N/θ_p is -0.7, not



FIG. 2. Molar susceptibility of MnF₃, and its reciprocal, as dependent on temperature.

³ Bozorth, Williams, and Walsh, Phys. Rev. **103**, 572 (1956); R. M. Bozorth and D. E. Walsh, J. Phys. Chem. Solids (to be published). ⁴ The material was identified by Dr. S. Geller by x-ray

⁶ Wollan, Child, Koehler, and Wilkinson (to be published). ⁶ American Institute of Physics Handbook (McGraw-Hill Book Company, Inc., New York, 1957), pp. 5-241. ⁷ Reference 6, pp. 5-226.

greatly different from this ratio for most of the other iron-group halogenides.

Data for MnF₃ are shown in Fig. 2. The Néel point is 47°K with a possible error estimated at 2°. Above 50°K the Curie-Weiss law of the form $\chi_m = 3.10/(T-8)$ is obeyed, in fair agreement with the results of Klemm and Krose⁸ for temperatures above 90°K. The increase in χ_m with decreasing temperatures below 20°K indicates that a small part of the MnF₃ may have decomposed, with the decomposition products obeying the Curie law to low temperatures. Measurement of the material not protected from contact with moisture showed that it followed the law $\chi_m = 2.97/T$ to temperatures below 4°K, with a small irregularity, within the experimental error, near 50°K. The results on both of the specimens can be explained by the presence of the order of 90% decomposition in the first specimen and 10% decomposition in the second.

The value of μ_{eff} for MnF₃ is 5.0, to be compared ⁸ W. Klemm and E. Krose, Z. anorg. allgem. Chem. 253, 226

(1947).

with the value of 4.9 observed near room temperature by Hepworth, Jack, and Nyholm.⁹

It is surprising to find θ_N so much greater than θ_p in absolute magnitude, in this compound.

ACKNOWLEDGMENTS

We are indebted to Dr. R. G. Shulman for supplying the MnF₃, which was the same as that used in the experiments of Shulman and Jaccarino¹⁰ on the nuclear resonance shift in F¹⁹. We are also indebted to Dr. W. C. Koehler and Dr. E. O. Wollan of Oak Ridge National Laboratory for telling us of their neutron diffraction experiments on MnF₃ prior to publication.

Note added in proof.-Examination of a single crystal indicates that the spins are aligned along the c axis, the direction of nearest Cu-Cu neighbors according to the structure determined by Geller and Bond (to be published).

9 Hepworth, Jack, and Nyholm, Nature 179, 211 (1957). ¹⁰ R. G. Shulman and V. Jaccarino, Phys. Rev. 109, 1084 (1958).

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Oscillatory Galvanomagnetic Effects in *n*-Type Indium Arsenide*

H. P. R. FREDERIKSE AND W. R. HOSLER National Bureau of Standards, Washington, D. C. (Received January 30, 1958)

The Hall coefficient and the resistivity of n-type InAs, measured as a function of magnetic field strength at low temperatures, reveal de Haas-van Alphen type oscillations. The period is in good agreement with theoretical predictions. An electron effective mass of the order of $0.02 m_0$ is calculated from the field and temperature dependence of the amplitude.

INTRODUCTION

UANTIZATION of the orbital motion of electrons in a magnetic field gives rise to a quasi-periodic variation of the density of states as a function of energy.¹ Consequently the magnetic susceptibility and also the transport phenomena will show an oscillatory behavior as a function of the magnetic field strength. Such oscillations were first discovered in bismuth^{2,3} and later in several other metals.^{4,5}

A recent study of the magnetoresistance of InSb⁶ has shown that this oscillatory behavior can also be

effects; this paper contains a rather complete reference list).

⁴ D. Shoenberg, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1957), Vol. 2 (review of oscillatory susceptibility).
 ⁶ See, e.g., N. M. Nachimovich, J. Phys. U.S.S.R. 6, 111 (1942) (magnetoresistivity of 72).

(magnetoresistivity of Zn). ⁶ H. P. R. Frederikse and W. R. Hosler, Phys. Rev. 108, 1136

(1957).

observed in degenerate semiconductors. An additional interesting feature in the case of InSb is the fact that the conduction band is isotropic as opposed to the energy bands of all metals studied so far.

We have investigated the possibilities of observing the de Haas-van Alphen oscillations in other semiconductors. The conditions for observation of quantization effects in the transport phenomena are:

$$\omega \tau > 1,$$
 (1a)

$$\hbar\omega > kT, \tag{1b}$$

$$\zeta_0 > kT, \qquad (1c)$$

where $\omega = eH/m^*c =$ cyclotron frequency, $\tau =$ collision time, and ζ_0 = Fermi energy in the absence of a magnetic field. In germanium it is difficult to fulfill all three conditions. A high mobility [condition (1a)] requires a rather pure material; in that case, however, the electrons will condense in the impurity levels at low temperatures. It is perhaps possible to obtain germanium which is still degenerate at hydrogen tempera-

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¹ L. Landau, Z. Physik 64, 629 (1930).
² W. J. de Haas and P. M. van Alphen, Commun. Kamerlingh Onnes Lab. Univ. Leiden 212a (1930) (susceptibility).
³ J. Babiskin, Phys. Rev. 107, 981 (1957) (galvanomagnetic effects and product support s