measurements have been in the temperature range 1.3°K to 2.3°K, and it is felt that the results obtained may be of interest.

8 cc at N.T.P. of He^3 (96 percent) gas, kindly supplied by the U. S. Atomic Energy Commission, were condensed in an adiabatic calorimeter of volume 16 mm^3 fed by a tube of internal diameter 0.025 cm. The temperature of the calorimeter was measured with a carbon resistance thermometer and observations of the electrical "heating cycles" were made semi-automatically using the apparatus previously developed and used in other specific heat determinations.[7,8] A copper shield, mounted in vacuum, completely surrounded the calorimeter and was maintained continuously at a temperature of approximately 0.1°K above that of the calorimeter. This shield had attached thermally to it all the electrical leads leading to the calorimeter. This shield, moreover, formed the only low-temperature anchorage for the filling tube leading to the calorimeter and by this constructional arrangement unwanted condensation of vapor in the filling tube during a heating cycle was avoided.

Our preliminary results are shown in Fig. 1. Owing to the small quantities of liquid He^3 available for these experiments, we estimate that our errors could be as large as ±10 percent. Corrections had to be made for evaporation of liquid, for the heat capacity of the vapor and for the compression of the vapor during the heating cycles. These corrections totaled approximately 14 percent of the observed heat capacities. (Measurements were made, of course, also of the heat capacity of the empty calorimeter itself, which did not amount to more than a few percent of its total heat capacity when filled. Corrections, however, also have been made for this.)

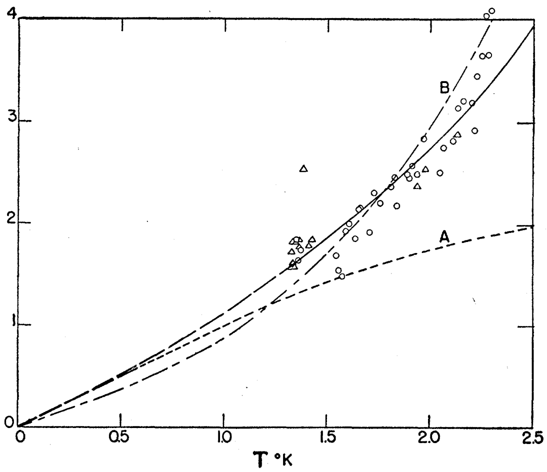

FIG. 1. The specific heat, C_{sat}, in cal/mole-deg, of liquid He^3 (96 percent He^3) as a function of the absolute temperature, T, in °K. The circles and triangles give the observed results. The full curve gives the formula (1) of this paper. The broken curve, A, gives the Fermi-Dirac contribution to formula (1) with $T^*=10°K$. The broken curve, B, gives formula: $C_{sat}=0.68T+0.2T^3$ cal/mole-deg (see text).

2.3°K was taken as the maximum useful temperature of observation consistent with manageable vapor corrections. The lower temperature of observation (1.3°K) was determined by initial technical considerations. We are now extending the observations to temperatures well below 1°K.

It will be seen that the observed specific heat increases monotonously from about 1.6 cal/mole-deg at 1.3°K to about 3.6 cal/mole-deg at 2.3°K. There is a singular observation at 1.38°K, giving $C_{sat}=2.53$ cal/mole-deg. We are unable, as yet, to decide whether this point represents an observational error or not.

The measured curve is convex towards the T axis and, moreover, C_{sat} at the higher temperatures is larger than $(3/2)R$. These two facts mean that it is impossible to describe the specific heat by a Fermi-Dirac function alone, no matter what degeneracy temperature T^* be chosen. As a crude first approximation our results could be described by the formula, $C_{sat}=0.68T+0.2T^3$ cal/mole-deg, which was proposed earlier[9] by one of us[5] and which was based on the results of the vapor pressure measurements on liquid He^3 by Abraham *et al.*[10] This is illustrated by one broken line B in Fig. 1.

In interpreting our results in more detail, we have tentatively tried to use the following formulation for C_{sat}:

$$C_{sat}=F(T/T^*)+aT^3 \text{ cal/mole-deg}, \qquad (1)$$

where $F(T/T^*)$ is the Fermi-Dirac specific heat function corresponding to a degeneracy temperature T^*, and where the T^3 function would be due to compressional Debye waves.[11] Putting $T^*=10.0°K$ and $a=0.125$ cal/mole-deg^4, we obtain the full line of Fig. 1, which is a fair approximation of the experimental results. (One broken line A in Fig. 1 gives the function $F(T/10°K)$ alone, which will be seen to have a slope given by 1.0 cal/mole-deg^2 at $T\rightarrow 0$.)

The apparently appropriate F–D degeneracy temperature, $T^*=10°K$, is high compared with that which can be computed for a F–D gas with the liquid He^3 number density of particles (4.85°K). The absolute magnitude of the cubic[12] term of Eq. (1) is approximately 5 times larger than that in liquid He^4, as measured by Kramers *et al.*[13]

Equation (1), if considered as an appropriate extrapolation for the specific heat *below* 1.3°K, leads to an entropy of 1.1 cal/deg^{-1} $mole^{-1}$ at 1°K. This is 1.1 cal/deg^{-1} $mole^{-1}$ *less* than that calculated by Abraham *et al.*[10] from the vapor pressure data if the nuclear entropy is also included. It seems peculiar that the magnitude of the discrepancy is approximately $R\ln 2$, the nuclear entropy. It seems necessary to conclude, therefore, that Eq. (1) may *not* be extrapolated below 1°K with any confidence and that at best it must be regarded as an *interpolation formula* in the temperature range covered by our measurements *only*.

[†] Assisted by a contract between the U. S. Atomic Energy Commission and The Ohio State University Research Foundation.

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[11] Strictly, C_v should be used in this formulation rather than C_{sat}. In view of the relatively large possible experimental errors in the values of C_{sat} given here, it has been considered unnecessary to make the corrections for this difference.

[12] The Debye θ for compressional modes only, corresponding to the term a of Eq. (1) equal to 0.125 cal/mole-deg,[4] is 10.8°K. Strictly, therefore, the specific heat would not be exactly cubic at 2.3°K.

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Interpretation of Hall Effect and Resistivity Data in PbS and Similar Binary Compound Semiconductors

WAYNE W. SCANLON
U. S. Naval Ordnance Laboratory, White Oak, Maryland

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THE width of the forbidden energy gap in a semiconductor is an important parameter appearing in theories of photoconductivity and other semiconductor phenomena. For the elementary semiconductors, such as germanium and silicon, there is good agreement among the various workers on the value of this energy. In the case of certain binary compound semiconductors, the values reported in the literature are not consistent. In lead sulfide, for example, values are reported ranging from 0.3 to 1.17 ev[1] for the forbidden band width (ΔE) as obtained from the slope of the high-temperature resistivity and Hall effect data. The most recent value, 1.17 ev, based upon Hall effect data at temperatures between 700°C and 900°C, reported by Putley and Arthur,[2] is difficult to reconcile with information gained from either photoconductivity or infrared absorption studies which indicate an energy gap of about 0.4 ev.[3]

This note will point out a source of error in the interpretation of Hall effect and resistivity data on compound semiconductors which may account for the diversity of values given for the energy gap in some of these materials.

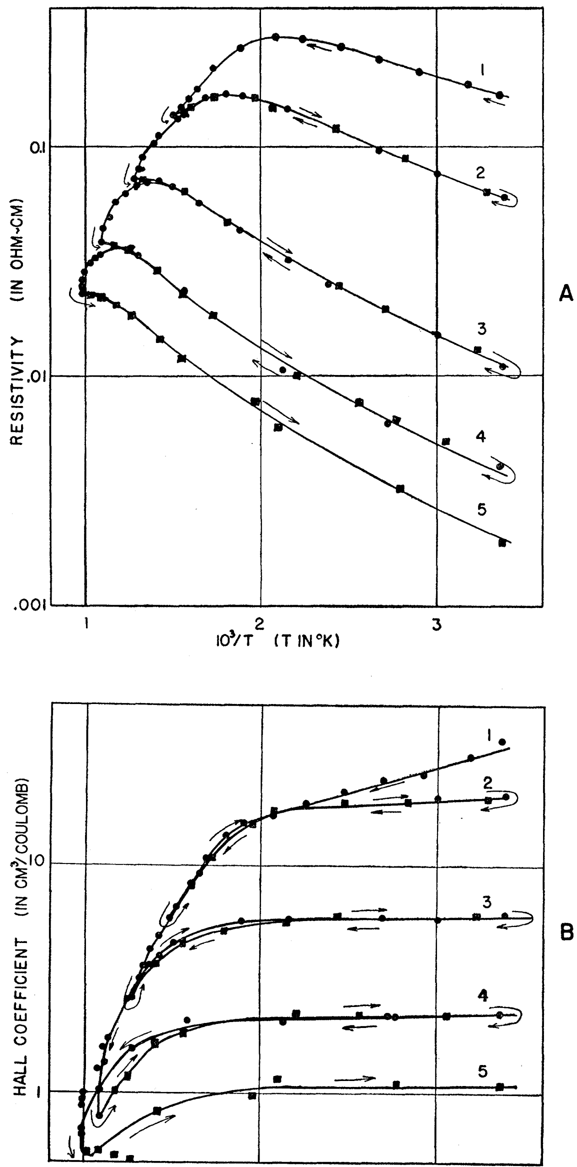

FIG. 1. (A) Resistivity, and (B) Hall effect in a PbS single crystal for heating cycles to the following maximum temperatures: Curve 1, 680°K; Curve 2, 788°K; Curve 3, 919°K; and Curve 4, 1023°K. Points on heating curve ●●●. Points on cooling curve ■■■.

The electrical properties of a binary compound semiconductor, such as PbS, are governed by deviations from stoichiometric proportions of Pb and S in the crystal. An excess of Pb results in *n*-type conductivity, while an excess of S results in *p*-type conductivity. In our experiments on single crystals of PbS, we find that the concentration of excess Pb or S atoms remains unchanged in temperature cycles up to about 500°K, as shown by the reversibility of the curves of Hall effect and resistivity. Upon heating the crystal above this temperature irreversible behavior is observed. We have observed similar irreversible behavior in single crystals of PbSe and PbTe. Effects of this type have also been noted by Chasmar and Putley in PbTe.[4]

In Fig. 1A are the curves of resistivity taken on a natural *n*-type PbS crystal for a series of temperature cycles between room temperature and maximum temperatures of about 700°, 800°, 900°, and 1000°K. The sample was in an inert atmosphere of pure argon[5] throughout the experiment. Curves 1 and 2, where the maximum temperature was about 700°K, begin to show composition changes. Curves 2 and 3, where the maximum temperature was about 800°K, show further composition changes to the extent that the cooling curve for resistivity no longer has a knee leading from the intrinsic conductivity region. At about 750°K a change in the slope of the heating curve can be seen. Curves 4 and 5 provide further evidence of changing composition of the PbS with no evidence of intrinsic conductivity appearing on the cooling curves. A series of four measurements made on the sample, while it was held at 1023°K for about an hour, show a continuous change in composition giving the resistivity curve an apparent infinite slope.

The Hall effect, which was measured at the same time as the resistivity, is plotted in Fig. 1B. The irreversible character of the data with temperature cycles can be seen. The cooling curves from the higher maximum temperatures do not show intrinsic semiconductor behavior. The data for curves 4 and 5 at high temperatures are somewhat scattered due to the small Hall effect, and they are not as reliable as the corresponding resistivity data.

As a result of the heat treatments, the composition of the PbS changed from 4×10^{17} to 7×10^{18} donor atoms/cm³. This increase in the lead concentration in the crystal may be accomplished at elevated temperatures by the loss of sulfur atoms, which leave their positions in the lattice and diffuse out through the surface. Hintenburger[6] and Eisenmann[7] have shown in similar experiments that sulfur may be added or removed from PbS by heat treatments.

The analysis of resistivity and Hall effect data from a semiconductor which undergoes composition changes is complicated by the presence of two mechanisms for increasing the concentration of electrons in the conduction band. At elevated temperatures, the loss of sulfur from PbS crystals apparently becomes so rapid as to produce changes in the concentration of electrons at a rate exceeding those produced by thermal excitation of intrinsic electrons. Furthermore, while the latter reaches an equilibrium condition rapidly, the former will proceed toward an equilibrium at a rate which depends upon the temperature of the crystal and the sulfur vapor pressure outside the crystal. In the extreme case where the sulfur pressure is maintained at zero, the PbS could eventually convert to lead. Thus, in measurements of this kind the time required to obtain a single curve becomes an important factor. Measurements carried out slowly will be more affected by the loss of sulfur than those carried out rapidly.

We believe that Putley and Arthur's[2] interpretation of the slope of the Hall effect curves, from 700° to 900°K, failed to take into account the thermal changes of composition in the material. Their published value of 1.17 ev for the width of the forbidden energy gap in lead sulfide may be due more to composition changes than to intrinsic behavior.

If, however, Hall effect data are taken on samples of relatively pure PbS only up to about 500°K, where composition changes are not observed, a calculation of the forbidden energy gap may be made using the conventional intrinsic semiconductor equation $R=AT^{-\frac{3}{2}}\exp(\Delta E/2kT)$. The value of ΔE obtained on six single crystals of PbS, with impurity concentrations from 10^{16} to 10^{17}/cc and for data taken only up to about 500°K , was found to be 0.37 ±0.01 ev. This energy gap is in better agreement with optical data and indicates that in PbS the valence band is the primary source of photoconductive electrons. This clarifies the question raised by

Smith[3] regarding the difficulty of understanding the source of primary photoconductive electrons in PbS and possibly also in PbSe and PbTe.

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Thermal Anomalies Associated with the Antiferromagnetic Ordering of FeF_2, CoF_2, and NiF_2

J. W. STOUT AND EDWARD CATALANO*
Institute for the Study of Metals and Department of Chemistry, University of Chicago, Chicago, Illinois

(Received October 28, 1953)

FROM measurements of the magnetic susceptibility of powdered materials, Bizette[1] concluded that MnF_2 and FeF_2 are antiferromagnetic, but that the isomorphous compounds CoF_2 and NiF_2 are not. The neutron diffraction studies of Erickson[2] show, however, that at low temperatures all four compounds are antiferromagnetically ordered and magnetic anisotropy measurements[3] on a single crystal of CoF_2 indicate an antiferromagnetic behavior. We have measured the heat capacity of FeF_2, CoF_2, and NiF_2 over the temperature range 12–300°K. Each of these salts shows a pronounced thermal anomaly of the lambda-shape characteristic of processes where there is cooperative ordering. The experimental heat capacity data in the neighborhood of the anomalies are shown in Figs. 1, 2, and 3 for FeF_2, CoF_2, and NiF_2, respectively. In order to determine the shape of the curves, the points in the regions of rapidly changing heat capacity were taken with small temperature increments (about 0.1°). The temperatures of the heat capacity maximum are: FeF_2, 78.3°K; CoF_2, 37.7°K; NiF_2, 73.2°K. A similar anomaly in MnF_2 with a heat capacity maximum at 66.5°K has been reported previously.[4] There seems to be no doubt that these anomalies represent the loss in entropy upon passing from the disordered paramagnetic state to the ordered antiferromagnetic state.

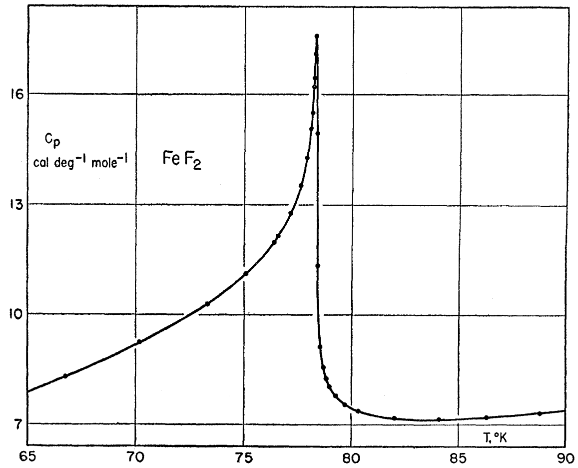

FIG. 1. Molal heat capacity of ferrous fluoride *versus* temperature.

The antiferromagnetic Curie temperatures deduced by Erickson[2] from the temperature variation of the magnetic structure factor are higher than those of the maximum in heat capacity by factors ranging from 1.1 to 1.3. However, the neutron diffraction measurements are a relatively imprecise method for determining the Curie temperature and also it seems probable that near the Curie point the magnetic form factor is varying much more rapidly with temperature than the Brillouin function used by Erickson in his extrapolation. We do not believe, therefore, that there is a significant disagreement.

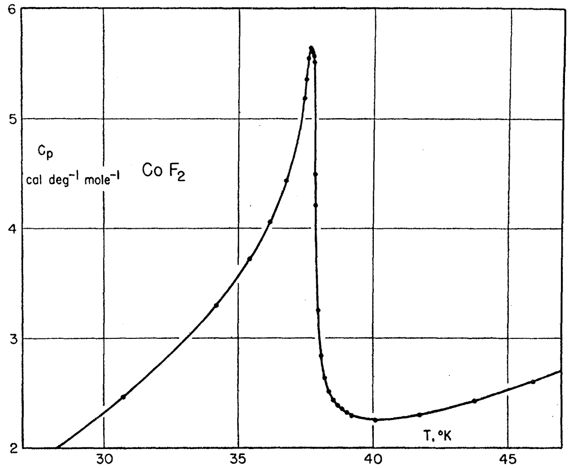

FIG. 2. Molal heat capacity of cobalt fluoride *versus* temperature.

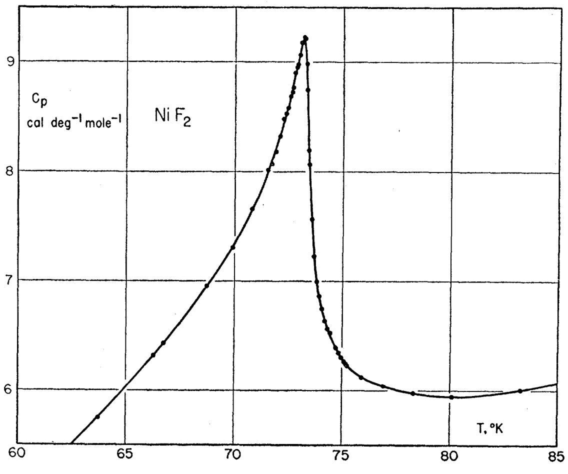

FIG. 3. Molal heat capacity of nickel fluoride *versus* temperature.

We have also made heat capacity measurements on the diamagnetic salt ZnF_2, which is isomorphous with the four antiferromagnetic fluorides. The data on ZnF_2 will permit an estimate of the entropy and heat capacity arising from lattice vibrations in the antiferromagnetic salts and thus enable the separation of the thermal effects caused by the magnetic ordering. The data and calculations will be published in detail elsewhere.

* Eastman Kodak Company Fellow 1951–52; Allied Chemical and Dye Corporation Fellow 1952–53.
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