

advanced by Mastrangelo and Aston,⁸ but the pressure used by them seems to have a rather different character.

It may be necessary to supplement this picture by considering the zero-point energy, as was done by Bijl, de Boer, and Michels.⁹ Although the zero-point energy is known to be much larger than the value appearing in their theory, this does not exclude the possibility of a small superimposed variation with film thickness. Using the simplifying assumptions of the Debye theory of solids, the zero-point energy of the longitudinal Debye waves in the film can be shown to be

$$Z(d) = Z(\infty) \left[1 - \frac{1}{6} \frac{c}{v_c \infty d} + \frac{1}{32} \left(\frac{c}{v_c \infty d} \right)^2 + \dots \right], \quad (3)$$

where c is the velocity of first sound and $v_c \infty$ the cut-off frequency in the bulk liquid. The resulting relationship between film thickness and height is

$$H = \alpha / g d^3 + (4 \times 10^{-6} / d)^2. \quad (4)$$

The zero-point energy is responsible for the term in $1/d^2$, which is seen to be important for thick saturated films but less important for the thinner unsaturated films. It should be emphasized that only that part of the zero-point energy associated with the longitudinal Debye waves has been included in this treatment, and the remaining part may be equally important.

A more complete account will appear in the *Canadian Journal of Physics*.

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Anomalous Paramagnetic Resonance in Copper Propionate

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ANOMALOUS resonance absorption by Cu^{++} in copper acetate has been observed by Bleaney and Bowers^{1,2} and in our laboratory.^{3,4} In this salt, the spins of two copper ions are strongly coupled to form an equivalent spin $S=1$.

I have recently observed similar anomaly in copper propionate monohydrate $\text{Cu}(\text{CH}_2\text{CH}_2\text{COO})_2 \cdot \text{H}_2\text{O}$. This crystal is monoclinic with $a:b:c=0.874:1:0.886$ and $\beta=94^\circ 22'$.⁵ The wavelength of the microwave used is 10.7 mm. When the static magnetic field H_s is applied in the ac plane, six resonance peaks are observed. Three pairs of lines can be obtained from these peaks when H_s is rotated in the ac plane. Each line observed in the ac plane splits into two lines in any plane which is perpendicular to the ac plane. In addition to these, one line is observed almost independent of the direction of H_s , at about half of the mean magnetic field for other peaks.

These observed spectra can be explained by superposition of six sets of spectral lines which are expressed by the Hamiltonian

$$\mathcal{H} = [g] \beta \mathbf{H} \cdot \mathbf{S} + DS_z^2 + E(S_x^2 - S_y^2), \quad (1)$$

under the condition that $S=1$, where x , y , and z denote the axes of the crystalline field. Values of g , D , and E for three pairs are listed in Table I, the three remaining pairs being given by mirror reflection about the ac plane. ψ in the table means the angle between the c axis and the plane containing two z axes, and α is the angle between one of the z axes and the ac plane. D^* stands for the D value to be given in order to satisfy mainly the experimental data in the x and y directions. g , D , and E for pair (3) in Table I are less reliable than the others because the resonance peaks for this pair could not be observed for some range of angle of H_s .

TABLE I. Parameters occurring in Eq. (1) for the paramagnetic spectra of copper propionate monohydrate.

	Pair (1)	Pair (2)	Pair (3)
g_z	2.34 ₈	2.35 ₆	(2.29 ₆)
g_x	2.09 ₃	2.10 ₀	2.09 ₂
g_y	2.09 ₅	...	2.09 ₈
D (in oersteds)	3460	3460	(3730)
D^*	3620	3650	3580
E	~ 0	~ 0	~ 0
ψ (in degrees)	106	158	174
α (in degrees)	28.5	16	52

From these results, the following conclusions may be derived: (1) The unit cell of this crystal contains six inequivalent pairs of Cu^{++} ions, whereas we have two pairs in copper acetate, so far as the microwave spectra are concerned. (2) Each pair of ions in the unit cell is in a very similar environment except that the orientations of the axes of the crystalline field are different. (3) The origin of the anomaly may be assumed to be the extraordinarily short distance between Cu^{++} ions in a pair; a distance of 2.6 Å between copper ions has been found in copper acetate by van Niekerk and Schoening.⁶

Single crystals of copper formate dihydrate $\text{Cu}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ and tetrahydrate were also examined.⁷ The anomalous splitting could not be found, and only one resonance peak was observed, the g value of which ranges from 2.06 to 2.32, just as in the ordinary copper salts. Kiriyama at Osaka University has analyzed the structure of these salts by means of x-rays.⁸ The arrangement of atoms in these crystals is quite different from that in copper acetate.

The author wishes to express his sincere thanks to Professor H. Kumagai for his continuous guidance. A more detailed report will appear in the *Journal of the Physical Society of Japan*.

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Specific Heat of He^3 between 1.3°K and 2.3°K†

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PURE liquid He^3 , unlike liquid He^4 , has been found to show no signs of superfluidity. The experimental indications of this marked difference in behavior were evident first in the early work on solutions by Daunt and co-workers,¹ and then by the observations of the pure liquid down to 1.0°K by Osborne, Weinstock, and Abraham² and down to 0.2°K by Daunt and Heer.³ Despite this established difference in the flow properties of liquid He^3 and He^4 , it is known that He^3 , exactly like He^4 , does not become solid under its saturated vapor pressure even at the lowest possible temperatures. (See Osborne *et al.*⁴ for data on the melting curve of He^3 .) There consequently remains the possibility that liquid He^3 undergoes a liquid-liquid transformation at a sufficiently low temperature. Such a transformation would not be one into a superfluid phase, as in liquid He^4 ; but it would be, if it existed, evident from observations of the specific heat. A discussion of the many speculations by various authors regarding this possible transformation has already been given by one of us,⁵ and this will not be repeated here.⁶

We have carried out calorimetric determinations of the specific heat of liquid He^3 (He^3 content 96 percent; He^4 content 4 percent) with a view to resolving this problem experimentally. Our initial

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 He³ (96 percent) gas, kindly supplied by the U. S. Atomic Energy Commission, were condensed in an adiabatic calorimeter of volume 16 mm³ 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 He³ 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

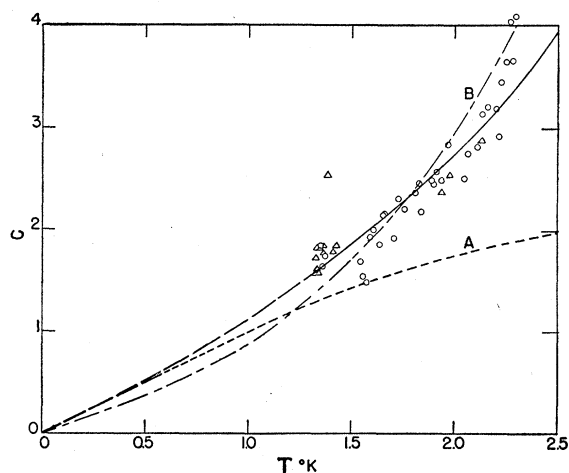


FIG. 1. The specific heat, C_{sat} , in cal/mole-deg, of liquid He³ (96 percent He³) as a function of the absolute temperature, T , in °K. The circles and triangles give the observed results. The full curve gives the formula (1) of this paper. The broken curve, A, gives the Fermi-Dirac contribution to formula (1) with $T^* = 10^\circ\text{K}$. The broken curve, B, gives formula: $C_{sat} = 0.68T + 0.2T^3$ cal/mole-deg (see text).

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.)

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 earlier⁹ by one of us⁶ and which was based on the results of the vapor pressure measurements on liquid He³ 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} :

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

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 $T^* = 10.0^\circ\text{K}$ and $a = 0.125$ cal/mole-deg⁴, 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 $F(T/10^\circ\text{K})$ alone, which will be seen to have a slope given by 1.0 cal/mole-deg² at $T \rightarrow 0$.)

The apparently appropriate F-D degeneracy temperature, $T^* = 10^\circ\text{K}$, is high compared with that which can be computed for a F-D gas with the liquid He³ number density of particles (4.85°K). The absolute magnitude of the cubic¹² term of Eq. (1) is approximately 5 times larger than that in liquid He⁴, 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.

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

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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 for the forbidden band width (ΔE) as obtained from the slope