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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

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

where c is the velocity of first sound and ν_c^{∞} the cut-off frequency in the bulk liquid. The resulting relationship between film thickness and height is

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

M. Polanyi, Verhandl. deut. physik. Ges. 15, 55 (1916).
 T. L. Hill, Advances in Catalysis (Academic Press, New York, 1952),
 Vol. IV.
 W. G. McMillan and E. Teller, J. Chem. Phys. 19, 25 (1951).
 K. R. Atkins, Ph.D. thesis, Cambridge University, 1948 (unpublished).
 L. Schiff, Phys. Rev. 59, 838 (1941).
 J. Frenkel, J. Phys. (U.S.S.R.) 2, 345 (1940).
 F. A. Long and L. Meyer, Advances in Physics 2, 1 (1953).
 S. V. R. Mastrangelo and J. G. Aston, J. Chem. Phys. 19, 1370 (1951).
 Bijl, de Boer, and Michels, Physica 8, 655 (1941).

Anomalous Paramagnetic Resonance in **Copper Propionate**

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NOMALOUS resonance absorption by Cu++ in copper A 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 Cu(CH₃CH₂COO)₂·H₂O. 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

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

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	2.348	2.356	(2.295)
gz	2.093	2.10_{0}	2.092
gy	2.095	•••	2.098
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 2.6A between copper ions has been found in copper acetate by van Niekerk and Schoening.6

Single crystals of copper formate dihydrate Cu(HCOO)₂·2H₂O 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 Ôsaka 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.

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- ¹ B. Bleaney and K. D. Bowers, Phil. Mag. **43**, 372 (1952). ² B. Bleaney and K. D. Bowers, Proc. Roy. Soc. (London) **214**, 451
- ² B. Bleaney and K. D. Bowers, 1100, 1007, 2007, (1952).
 ⁴ Kumagai, Abe, and Shimada, Phys. Rev. 87, 385 (1952).
 ⁴ H. Abe and J. Shimada, Phys. Rev. 90, 316 (1953).
 ⁵ P. Groth, *Chemische Kristallographie* (Teubner, Leipzig, 1910), Vol. 3, 202
- p. 202. ⁶ J. N. van Niekerk and F. R. L. Schoening, Acta Cryst. 6, 227 (1953). ⁷ Shimada, Abe, and Ôno, J. Phys. Soc. Japan (to be published).
 ⁸ Kiriyama, Ibamoto, and Matsuo, Acta Cryst. (to be published).

Specific Heat of He³ between 1.3°K and 2.3°K⁺

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PURE liquid He³, unlike liquid He⁴, 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 He³ and He⁴, it is known that He3, exactly like He4, 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 He3.) There consequently remains the possibility that liquid He³ undergoes a liquid-liquid transformation at a sufficiently low temperature. Such a transformation would not be one into a superfluid phase, as in liquid He4; 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 calorlmetric determinations of the specific heat of liquid He³ (He³ content 96 percent; He⁴ content 4 percent) with a view to resolving this problem experimentally. Our initial