

K has a value very similar to that which which can only support longitudinal waves. motion of a vibrational type in at least

is such that on the average a molecule or than about a minimum.

odel, the vibration of atom in liquid is id state structures with nearly the same

armonicity if we use Lennard-Jones model. n of liquid is not directly connected to of other structures (like body-centered le for the expansion, and the motion of e than would seem first from crude model. ructures into account. And this will be entropy of structural change).

The Equation of State of solid Helium.

J. S. DUGDALE

Division of Pure Physics, National Research Council - Ottawa

1. - Introduction.

Solid helium (*) has recently been used as a pressure-transmitting medium in experiments to find out how the electrical resistance of metals at low temperatures changes under pressure [1,2]. The method employed was to apply the pressure at such a temperature that the helium was fluid and then to cool the bomb, containing the specimen and the helium, under conditions of constant volume to the desired low temperature. By knowing the equation of state of solid helium the final pressure could be deduced (+). For the pressures so far used (up to 3000 atmospheres) the equation of state of the solid as determined experimentally by DUGDALE and SIMON [3] is sufficient, but if the pressure range is to be extended, more information on the equation of state is needed. The recent measurements of STEWART [4] provide the basis for obtaining this information. The method used to derive the equation of state and the results obtained will now be briefly described.

2. - The method and assumptions.

The steps in the calculation are as follows:

a) The first step is to use the isotherm measured at 4.2 °K to deduce U_0 , the internal energy at absolute zero, as a function of the volume, V .

(*) Unless otherwise stated, the helium referred to is ^4He .

(+) It should be possible to invert this procedure and investigate the equation of state of solid ^3He by using the electrical resistance of a suitable substance to determine the pressure in the solid as a function of temperature and volume.

(For this purpose 4.2 °K is effectively the absolute zero [3]). The change in internal energy, ΔU_0 , in altering the volume from V_1 to V_2 at 0 °K is given by:

$$\Delta U_0 = - \int_{V_1}^{V_2} p dV.$$

b) The second step is then to derive from the $U_0 - V$ curve so obtained the relationship between the Debye temperature of the solid, θ_D^2 , and the volume V . (Experiments [3] have shown that a Debye approximation is quite good for solid helium). To do this, it is assumed that $\theta_D^2 \propto d^2 U_0 / dr^2$, where r is the interatomic distance [5]. To evaluate the constant of proportionality, one value of θ_D was taken from specific heat measurements [3].

c) Thirdly the Lindemann melting formula relating θ , V , and the melting temperature, T_m , is used to find T_m as a function of V . A value for the Lindemann constant for helium was taken from the work of DUGDALE and SIMON [3], which had already shown that the Lindemann melting formula was valid for solid helium throughout the range of their experiments (up to 3000 atmospheres).

d) The last step is to use a Debye-Grüneisen model (*) of the solid to calculate the pressure corresponding to the volume, V , at the melting temperature. This gives the melting curve.

e) As a further check on the calculations, one can calculate the zero point energy $((9/8) R\theta_D)$ and subtract it from the internal energy. This gives the lattice energy, which may then be compared with that calculated from a suitable interatomic potential.

3. - The results.

The results are represented in Fig. 1 and 2. Fig. 1 shows the isochores (lines of constant volume) of solid helium calculated in the manner outlined above. It also shows the melting curve so derived: for comparison a melting curve based on experiment is also plotted. MILLS and GRILLY [6] have measured

(*) By this is meant a solid in which (a) the specific heat at constant volume, for example, is a function of θ/T , where θ depends only on volume, and (b) the temperature dependence of C_v is given by the Debye function. The calorimetric experiments of Dugdale and Simon showed that this was approximately true of solid helium.

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absolute zero [3]). The change in volume from V_1 to V_2 at 0 °K is given

dV .

from the $U_0 - V$ curve so obtained. The temperature of the solid, θ_D^2 , and the Debye approximation is quite good. It is assumed that $\theta_D^2 \propto d^2 U_0 / dr^2$, where d is the constant of proportionality, from the heat measurements [3].

formula relating θ , V , and the melting temperature of V . A value for the Lindemann constant was obtained from the work of DUGDALE and SIMON [3], and the Lindemann melting formula was valid for their experiments (up to 3000 atmo-

Grüneisen model (*) of the solid to the volume, V , at the melting tem-

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and 2. Fig. 1 shows the isochores calculated in the manner outlined above and derived: for comparison a melting curve derived from the work of MILLS and GRILLY [6] have measured

the specific heat at constant volume, for (a) only on volume, and (b) the temperature dependence. The calorimetric experiments of Debye are approximately true of solid helium.

the melting curve of helium up to 3500 atmospheres; they gave their results in the form of the following equation:

$$P + 17.80 = 17.315 T^{1.5554},$$

where P is the melting pressure in kg/cm² corresponding to the temperature T in °K. Points of this curve have been plotted up to 20000 atmospheres in Fig. 1. Other experimenters [7] have made measurements up to higher pressures (up to 9000 atmospheres) but their results are less accurate. In any case, all measurements so far are consi-

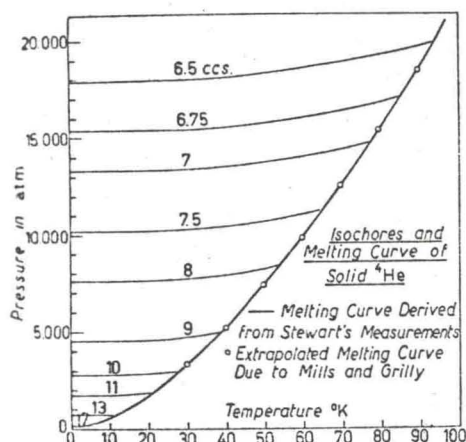


Fig. 1.

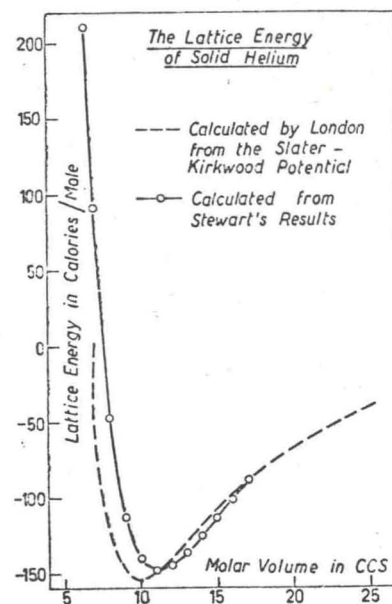


Fig. 2.

istent with the equation given by MILLS and GRILLY. It is seen that the agreement between the extrapolated experimental curve and the melting curve deduced, as described above, from Stewart's experiments is very close indeed.

Fig. 2 shows the lattice energy of solid helium calculated as described together with London's calculation of the lattice energy assuming a Slater-Kirkwood potential [8]. The agreement for large molar volumes is satisfactory: at the minimum of energy and at molar volumes smaller than this the agreement is not good. It is of course known that the Slater-Kirkwood potential does not predict altogether correctly the properties of the gas phase [9]; moreover, the values of θ_D which have been taken were chosen to represent the low temperature specific heats [3] reasonably well and they may differ signi-

ficantly from the values of θ_∞ , which strictly are needed for calculating the zero point energy [10]. For completeness, the Debye temperature, the Grüneisen parameter γ ($\gamma = -d \log \theta / d \log V$), and the melting temperature as calculated for various values of the volume are listed in Table I.

TABLE I. - *The Debye temperature, the Grüneisen γ and melting temperature of solid helium calculated for various values of volume.*

V (cm ³)	θ_D (°K)	γ	T_m (°K)
16	44	2.71	4.9
15	52	2.49	6.6
14	62	2.31	8.8
13	73	2.17	11.7
12	86	2.06	15.5
11	102	1.96	20.8
10	123	1.87	28.0
9	149	1.8	38.5
8	184	1.74	53.9
7	230	1.68	77.7
6.5	261	1.65	94.5

4. - Conclusions.

From the remarkably close agreement between the extrapolated experimental melting curve and that calculated by the methods outlined in this paper, one may draw the following conclusions:

a) that the calculated melting curve and isochores of the solid can be accepted with considerable confidence;

b) that in spite of the large zero point motion of the atoms composing it, a relatively simple model of solid helium is sufficient to account quite well for its properties provided that the effect of the zero point energy is taken into account at the very outset of the calculations (*); and

c) that the Lindemann melting formula appears to be valid over an enormous region of the melting curve, a fact which deserves close theoretical attention.

(*) To carry out the calculation from first principles, the U_0 - V relationship should be derived from the interatomic potential. This has already been attempted with some success [11] but the difficulty is that a really satisfactory theoretical interatomic potential for helium does not yet exist.

* * *

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REFERENCES

- [1] J. S. DUGDALE and J. A. HULBERT: *Can. Journ. Phys.*, **35**, 720 (1957).
 [2] J. S. DUGDALE and D. GUGAN: *Proc. Roy. Soc.*, A **241**, 397 (1957).
 [3] J. S. DUGDALE and F. E. SIMON: *Proc. Roy. Soc.*, A **218**, 291 (1953).
 [4] J. W. STEWART: *Journ. Phys. Chem. Solids*, **1**, 146 (1956).
 [5] C. DOMB: *Changements de Phases* (Paris, 1952), p. 338.
 [6] R. L. MILLS and E. R. GRILLY: *Phys. Rev.*, **99**, 480 (1955).
 [7] For a summary of this work, see: C. DOMB and J. S. DUGDALE: *Progress in Low Temperature Physics*, vol. 2 (Amsterdam, 1957), p. 338.
 [8] F. LONDON: *Proc. Roy. Soc.*, A **153**, 576 (1936).
 [9] J. L. YNTEMA and W. G. SCHNEIDER: *Journ. Chem. Phys.*, **18**, 646 (1950).
 [10] C. DOMB and L. S. SALTER: *Phil. Mag.*, **43**, 1083 (1952).
 [11] J. S. DUGDALE and D. K. C. MACDONALD: *Phil. Mag.*, **45**, 811 (1954).

INTERVENTI E DISCUSSIONI

— C. DOMB:

Dr. DUGDALE's observation that the θ values used in estimating the Lindemann constant C need to be revised would mean a far smaller variation of C with A^* than indicated in my paper. It may help to account for the apparent discrepancy noted between solid hydrogen and solid helium.

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