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## Thermodynamics of Crystals and Melting

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The Helmholtz free energy,  $A$ , of a rigid body is a function of temperature, and of the six homogeneous strain components. If the crystal is to be rigid, three inequalities must be satisfied for the derivatives of  $A$  with respect to the six strain components, for a regular (cubic) lattice. This enables one to limit the pressure-temperature range for which the crystal is stable. The violation of the condition  $c_{44} > 0$ , that the crystal resist shearing, is interpreted as leading to melting. From a knowledge of the forces

between the molecules the phase integral, and therefore the free energy, may be calculated as a function of  $T$ ,  $V$ , and the six strain components. The numerical calculations are carried out for a body-centered cubic lattice. The product of all the frequencies is calculated directly, so that the assumption that the Debye equation for the frequency distribution holds, is not necessary. The melting curve, pressure against temperature, is then determined.

THERE exist many attempts to derive theoretically the laws of melting. I mention Lindemann's<sup>1</sup> formula, Grüneisen's<sup>2</sup> general thermodynamics of isotropic solids, the theories of Braunbeck,<sup>3</sup> Raschevsky<sup>4</sup> and of Herzfeld and Goepfert-Mayer.<sup>5</sup> The newest contribution to this problem is an ingenious paper of Lennard-Jones and Devonshire<sup>6</sup> who apply the "method of order and disorder" invented by Bragg and Williams.<sup>7</sup>

All these papers use different "criteria" of melting: e.g. Lindemann, the collision of a vibrating molecule with its neighbor; Raschevsky, the instability of a particle under the action of its neighbors; Braunbeck, the instability of the vibration of two rigid simple lattices against one another; Herzfeld and Goepfert-Mayer, the minimum of pressure with respect to changes of volume; Lennard-Jones, the transition of the structure from order into disorder.

In actual fact there can be no ambiguity in the definition of, or the criterion for, melting. The difference between a solid and a liquid is that the solid has elastic resistance against shearing stress while the liquid has not. Therefore, *a theory of melting should consist of an investigation of the stability of a lattice under shearing stress*. As far as I know, the only author who has made an

attempt to apply this natural definition of melting is Brillouin.<sup>8</sup> The short published account of his considerations indicates that he uses Debye's approximation for calculating the frequencies of the crystal; this method is objectionable, not only because it neglects the short waves, but because it does not lead to a reduction of the observable quantities to atomic forces.

Independently of this work of Brillouin, I have developed a method for treating thermodynamics of a crystal lattice in such a way that the formulae are valid over a wide range of temperature, in the hope that this range might include the melting point.

This theory is in some way the counterpart of Mayer's rigorous treatment<sup>9</sup> of condensing gases where the liquid state was reached from the other side, at least in so far as the existence of a condensation point could be proved with the methods of kinetic theory of gases.

The chief point in our method is the clear distinction between *molecular variables* and *molar parameters* as defined in statistical mechanics. The molecular variables are the generalized coordinates and conjugate momenta  $q_1, p_1; q_2, p_2; \dots$  which are distributed at random according to statistical laws. The molar parameters  $a_1, a_2, \dots$  describe the (macroscopic) external influences on the system (e.g. the volume of a gas). The energy of the system depends on both

<sup>1</sup> F. A. Lindemann, *Physik. Zeits.* **11**, 609 (1910).

<sup>2</sup> E. Grüneisen, *Ann. d. Physik* (4) **39**, 257 (1912).

<sup>3</sup> W. Braunbeck, *Zeits. f. Physik* **38**, 549 (1926).

<sup>4</sup> N. v. Raschevsky, *Zeits. f. Physik* **40**, 214 (1927).

<sup>5</sup> K. Herzfeld and M. Goepfert-Mayer, *Phys. Rev.* **46**, 995 (1934).

<sup>6</sup> J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. A* **169**, 317 (1939).

<sup>7</sup> W. L. Bragg and E. J. Williams, *Proc. Roy. Soc. A* **145**, 699 (1934); **151**, 540 (1935); **152**, 230 (1935).

<sup>8</sup> L. Brillouin, *Phys. Rev.* **54**, 916 (1938).

<sup>9</sup> J. Mayer, in collaboration with Ph. G. Ackermann and S. F. Harrison, *J. Chem. Phys.* **I**, 5, 67; **II**, 5, 74 (1937); **III**, 6, 87; **IV**, 6, 101 (1938).

See also M. Born and K. Fuchs, *Proc. Roy. Soc. A* **166**, 391 (1938); B. Kahn and G. E. Uhlenbeck, *Physica V* **4**, 399 (1938).

kinds of variables,  $\epsilon(q_1, p_1; q_2, p_2; \dots; a_1, a_2, \dots)$ . If it is given, we can construct the partition function which for high temperatures is given by the law of classical statistical mechanics:

$$Q(a_1, a_2, \dots; T) = \int \dots \int dq_1 dp_1 dq_2 \dots \times e^{-\epsilon(q_1, p_1; q_2, p_2; \dots; a_1, \dots)/kT}. \quad (1)$$

Then the free energy of the system is

$$A = -kT \log Q, \quad (2)$$

and all other thermodynamic properties are found by differentiation:

$$\begin{aligned} \text{the entropy} \quad S &= -\partial A / \partial T, \\ \text{the energy} \quad E &= A + TS, \end{aligned} \quad (3)$$

the generalized forces corresponding to the molar parameters:

$$F_r = -\partial A / \partial a_r. \quad (4)$$

If we want to apply this prescription to a crystal lattice we must clearly state which are the molar parameters. For the sake of simplicity let us consider only a cubic lattice of the Bravais type (simple, face-centered or body-centered). As thermodynamics has only to do with states of equilibrium (from the macroscopic, or molar, standpoint) we can restrict our considerations to homogeneous deformations. Then the cubic cell (with the side  $a$ ) becomes a general parallelepiped, described by three vectors  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$  with six essential parameters (invariant with respect to rigid motions), *viz.* three lengths and three angles, or the six scalar products of the vectors with one another

$$\mathbf{a}_1^2, \mathbf{a}_2^2, \mathbf{a}_3^2, \mathbf{a}_2 \cdot \mathbf{a}_3, \mathbf{a}_3 \cdot \mathbf{a}_1, \mathbf{a}_1 \cdot \mathbf{a}_2.$$

The shape of the cell, i.e., these six parameters, are given by macroscopic (homogeneous) deformation and play the part of molar parameters. The actual positions of the particles can be described by displacement vectors relative to the deformed cell,  $\mathbf{u}^l$ , where the index  $l$  stands for three integers  $l_1, l_2, l_3$  defining a lattice point. The energy is a function of all the  $\mathbf{u}^l$  and the  $\mathbf{a}_1^2, \dots, \mathbf{a}_2 \cdot \mathbf{a}_3, \dots$ . If we develop it with respect to powers of the  $\mathbf{u}^l$  the linear terms vanish in consequence of the symmetry of the lattice, and the quadratic terms allow the introduction of

normal coordinates which can be used, instead of the  $\mathbf{u}^l$ , also in the higher terms. Then the integration in (1) can be performed, at least in principle, and leads to

$$A = A(T, \mathbf{a}_1^2, \mathbf{a}_2^2, \mathbf{a}_3^2, \mathbf{a}_2 \cdot \mathbf{a}_3, \mathbf{a}_3 \cdot \mathbf{a}_1, \mathbf{a}_1 \cdot \mathbf{a}_2). \quad (5)$$

It is evident that  $A$  is proportional to the number  $N$  of the particles (if surface effects are neglected). We introduce, instead of the  $\mathbf{a}_1^2, \dots, \mathbf{a}_2 \cdot \mathbf{a}_3, \dots$  the side of the cube of the original (undeformed) cell and the six dimensionless *strain components*\*

$$\begin{aligned} 2x_x = e_{11} &= (\mathbf{a}_1^2 - a^2)/a^2, & y_z = e_{23} &= \mathbf{a}_2 \cdot \mathbf{a}_3 / a^2, \\ 2y_y = e_{22} &= (\mathbf{a}_2^2 - a^2)/a^2, & z_x = e_{31} &= \mathbf{a}_3 \cdot \mathbf{a}_1 / a^2, \\ 2z_z = e_{33} &= (\mathbf{a}_3^2 - a^2)/a^2, & x_y = e_{12} &= \mathbf{a}_1 \cdot \mathbf{a}_2 / a^2, \end{aligned} \quad (6)$$

and write

$$A = Nf(T, a, x_x, y_y, z_z, y_z, z_x, x_y). \quad (7)$$

The function  $f$  depends on  $T$  and 7 geometrical variables, but only six of the latter are essential; there exists a linear identity between the seven first derivatives of  $f$ ,

$$a \partial f / \partial a = (2x_x + 1) \partial f / \partial x_x + \dots + 2y_z \partial f / \partial y_z + \dots.$$

By repeated differentiation one gets identities between the higher derivatives. We write down the two equations which hold for the first and second derivatives in the case  $x_x = 0, \dots, y_z = 0, \dots$ ,

$$\begin{aligned} a \frac{\partial f}{\partial a} &= \frac{\partial f}{\partial x_x} + \frac{\partial f}{\partial y_y} + \frac{\partial f}{\partial z_z}, \\ a^2 \frac{\partial^2 f}{\partial a^2} - a \frac{\partial f}{\partial a} &= \frac{\partial^2 f}{\partial x_x^2} + \frac{\partial^2 f}{\partial y_y^2} + \frac{\partial^2 f}{\partial z_z^2} \\ &\quad + 2 \frac{\partial^2 f}{\partial y_y \partial z_z} + 2 \frac{\partial^2 f}{\partial z_z \partial x_x} + 2 \frac{\partial^2 f}{\partial x_x \partial y_y}. \end{aligned} \quad (8)$$

If we develop  $f$  for a given value of  $a$  into a power series of the  $x_x, \dots, y_z, \dots$  the result must have, for a cubic lattice, the form

$$\begin{aligned} f &= f_0 + f_1 \cdot (x_x + y_y + z_z) \\ &\quad + \frac{1}{2} \{ f_{11} \cdot (x_x^2 + y_y^2 + z_z^2) \\ &\quad + 2f_{12} \cdot (y_y z_z + z_z x_x + x_x y_y) \\ &\quad + f_{44} \cdot (y_z^2 + z_x^2 + x_y^2) \} + \dots, \end{aligned} \quad (9)$$

\* We use two different notations, that of Voigt:  $x_x, \dots, y_z, \dots$ , and that of Brillouin:  $e_{11}, \dots, e_{23}, \dots$ . It is essential to define the strain components for finite deformations, as we have done here, not in the usual way for small displacements.

where  $f_0, f_1, f_{11}, f_{12}, f_{44}$  are functions of  $a$  and  $T$ ; the relations (8) become

$$a\partial f_0/\partial a = 3f_1, \quad a^2\partial^2 f_0/\partial a^2 = 3\{f_1 + f_{11} + 2f_{12}\}; \quad (10)$$

the latter can also be written

$$a\partial f_1/\partial a = 2f_1 + f_{11} + 2f_{12}. \quad (10a)$$

The density of free energy is  $A/V$  where  $V$  is the volume containing  $N$  particles. Let  $\gamma$  be the number of cells  $a^3$  corresponding to one particle, then  $V = \gamma Na^3$ . The value of  $\gamma$  differs for the different cubic lattices; if  $a$  is always the projection of the smallest distance on the side of the cube, we have for the simple cubic lattice:  $\gamma = 1$ ; body-centered:  $\gamma = 4$ ; face-centered:  $\gamma = 2$ . Now we get for the *density of free energy*

$$\begin{aligned} \frac{A}{V} = \frac{f}{\gamma a^3} = \frac{f_0}{\gamma a^3} - p \cdot (x_x + y_y + z_z) \\ + \frac{1}{2} \{c_{11}(x_x^2 + y_y^2 + z_z^2) \\ + 2c_{12}(y_y z_z + z_z x_x + x_x y_y) \\ + c_{44}(y_z^2 + z_x^2 + x_y^2)\} + \dots, \end{aligned} \quad (11)$$

where

$$-p = (1/\gamma a^3) f_1(a, T), \quad (12)$$

$$c_{11} = (1/\gamma a^3) f_{11}(a, T),$$

$$c_{12} = (1/\gamma a^3) f_{12}(a, T), \quad (13)$$

$$c_{44} = (1/\gamma a^3) f_{44}(a, T).$$

The derivatives of  $A/V$  with respect to  $x_x, \dots, y_z, \dots$  are the negative components of the stress tensor:

$$\begin{aligned} -X_x &= -p + c_{11}x_x + c_{12}(y_y + z_z) + \dots, \\ &\vdots \\ -Y_z &= c_{44}y_z + \dots. \end{aligned} \quad (14)$$

We see that the stress does not vanish for  $x_x = 0, \dots, y_z = 0, \dots$  but goes over into a uniform pressure  $p = X_x = Y_y = Z_z$ . This must be so as the constant  $a$  of the cubic lattice, to which the stress  $X_x, \dots, Y_z, \dots$  is applied, is not assumed to be that of equilibrium under zero pressure. Our theory corresponds exactly to the experimental conditions under which Bridgman and others<sup>10</sup> have recently worked, namely a combi-

nation of hydrostatic pressure and other stresses.

The formula (12) is evidently the *equation of state* for the cubic crystal giving  $a$  as a function of  $p, T$ , hence the thermic expansion for any pressure.

$c_{11}, c_{12}, c_{44}$  are the elasticity constants in Voigt's notation for a given temperature and external hydrostatic pressure.

The stability conditions, which guarantee that the quadratic terms in (11) are positive definite,\* are

$$\frac{3}{\kappa} = c_{11} + 2c_{12} > 0, \quad c_{11} - c_{12} > 0, \quad c_{44} > 0, \quad (15)$$

where  $\kappa$  is the cubic compressibility. The identities (10), (10a) allow us to write the equation of state and the expression for the compressibility in the form

$$p = \frac{1}{3\gamma a^2} \frac{\partial f_0}{\partial a}, \quad \frac{3}{\kappa} = \frac{1}{\gamma a^3} \left( a \frac{\partial f_1}{\partial a} - 2f_1 \right) = \frac{\partial(a p)}{\partial a}, \quad (16)$$

which can be used for checking calculations.

We now discuss the different possibilities for instability of the lattice if temperature increases.

I. The normal case will be that where the stability against shearing stress vanishes first,  $c_{44} = 0$ . According to our previous considerations this means *melting*.

The *melting curve* is given by the two equations

$$f_1(a, T) = -a^3 \gamma p, \quad f_{44}(a, T) = 0. \quad (17)$$

The second one gives  $a(T)$ , and if we introduce this in the first equation we get  $p(T)$ .

II. It might happen that  $c_{11} = c_{12}$  is satisfied first so that the two equations

$$f_1(a, T) = -a^3 \gamma p, \quad f_{11}(a, T) - f_{12}(a, T) = 0 \quad (18)$$

are satisfied. This means the transition of the solid into a state in which the stress is a hydro-

\* Our minimum problem is not quite of the usual type because the variables  $a, x_x, \dots, y_z, \dots$  are not independent;  $x_x + y_y + z_z$  is the relative change of volume which can also be expressed as  $3\delta a/a$ . The orthodox way of treating the problem is this: We consider only 6 variables, say  $a, x_x, y_y, y_z, z_x, x_y$  by eliminating  $z_z$  with the help of  $x_x + y_y + z_z = 0$ . Then  $x_x, y_y$  are independent just as  $y_z, z_x, x_y$ . The linear terms in (11) vanish, and the quadratic terms can be written in the form

$$\frac{1}{2}(c_{11} - c_{12}) \cdot \{3(x_x + y_y)^2 + (x_x - y_y)^2\} + \frac{1}{2}c_{44}(y_z^2 + z_x^2 + x_y^2);$$

this gives the second and third of the conditions (15). The first follows directly by developing with respect to  $a$  and using (16).

<sup>10</sup> P. W. Bridgman, Am. J. Sc. **36**, 81 (1938). J. App. Phys. **9**, 517 (1938).

Mech. Eng. p. 107 (1939). Here a list of the literature is published.

static pressure (as in a liquid) but nevertheless an elastic resistance against shearing survives. I suggest calling this state a "gel."

Dr. K. Fuchs has directed my attention to the fact that there are indications of the existence of such a state even for metals. Measurements of the elastic constants of the *alkali metals* Na and K made by Bender<sup>11</sup> have shown that the difference  $c_{11}-c_{12}$  is unusually small. Bidwell<sup>12</sup> has measured electric resistance and thermoelectric power of these metals at various temperatures and found a change of slope at about 100° below the melting point indicating a transformation; but a study of the structure with the help of x-rays showed no change of the lattice type, but only an "obliteration" of the structure.

III. If  $c_{11}+2c_{12}=0$  is satisfied first so that

$$f_1(a, T) = -a^3\gamma p, \quad f_{11}(a, T) + 2f_{12}(a, T) = 0, \quad (19)$$

the lattice is completely unstable and has no cohesion at all.

This can be interpreted as *sublimation*; but a complete coincidence with the observed sublimation curve can hardly be expected because the representation of the phase space by the normal coordinates of a lattice excludes just that part of it which is characteristic for the gaseous state, namely the domain corresponding to free particles. The curve (19) will give a finite value of  $T_s$  for  $p \rightarrow 0$  (just as the melting curve (17)) whereas the real sublimation curve runs into the point  $T=0, p=0$ . Nevertheless I think that for high temperatures, near the melting curve, the formulae (19) might give a fair approximation of the sublimation curve.

If these curves intersect there exists a *triple point*, the solution of the three equations:

<sup>11</sup> O. Bender, Ann. d. Physik 5, 359 (1939), gives the following experimental data for Na and K (in units of  $10^{11}$  dynes/cm<sup>2</sup>), to which are added the theoretical values for Li (K. Fuchs, Proc. Roy. Soc. A157, 444 (1936)).

	$c_{11}-c_{12}$	$c_{44}$
Na	0.166	0.618
K	0.087	0.263
Li	0.341	1.329

This gives for  $(c_{11}-c_{12})/c_{44}$  the values 0.27, 0.33, 0.26 in Na, K, Li, respectively. In general the value of the ratio is about ten times larger, e.g. 2.7 for rocksalt, 5.4 for sylvite, 3.5 for fluorite.

<sup>12</sup> C. C. Bidwell, Phys. Rev. 23, 357 (1924); 27, 381 (1926).

$$f_1(a, T) = -a^3\gamma p, \quad f_{44}(a, T) = 0, \\ f_{11}(a, T) + 2f_{12}(a, T) = 0. \quad (20)$$

But it also is possible that these equations have no solution (for positive values of  $a, p, T$ ); such a crystal would never melt but only sublime (as diamond, for all attainable pressures).

Two other triple points can exist, with respect to the "gel" state.

Entropy  $S$  and energy  $E$  are obtained in the usual way:

$$S = -\left(\frac{\partial A_0}{\partial T}\right)_a = -N\left(\frac{\partial f_0}{\partial T}\right)_a, \\ E = A_0 + TS = N\left\{f_0 - T\left(\frac{\partial f_0}{\partial T}\right)_a\right\}. \quad (21)$$

The specific heats  $c_v, c_p$  can also be expressed by differentiating  $E$  with respect to  $T$  either with  $a=\text{const.}$ , or with  $p=\text{const.}$  using the equation of state (13).

A calculation of the latent heat of melting\* is not possible without a knowledge of the corresponding formulae for the liquid state which our theory does not provide.

The thermodynamical properties of the crystal isolated or in equilibrium with its liquid can be expressed in terms of the functions  $f_0, f_1, f_{11}, f_{12}, f_{44}$  of  $a$  and  $T$  and their derivatives. We proceed now to derive explicit expressions for these. For this purpose we have to make *approximations of a different kind*.

The first approximation is the assumption that the *thermic motion can be considered as harmonic*. To justify this step we recall the simple model of Debye consisting of one particle moving in a nonlinear field of force. He uses this to explain the thermal expansion as the shift of the mean position due to the asymmetry of the amplitude in the nonharmonic field, and he shows that the vibration about this (shifted) mean position can be considered as harmonic. The situation becomes much clearer in the case of a real lattice if we distinguish sharply between molar pa-

\* L. Brillouin, reference 8, says that a theory which considers melting as vanishing of shearing elasticity does not lead to a latent heat. This is quite correct insofar as an approach to any equilibrium from one side is insufficient for calculating the latent heat; but such a theory is not in contradiction with the existence of a latent heat (as, for instance, is the case for some types of so-called  $\lambda$ -point transitions).

rameters—the dimensions of the cell (corresponding to the mean position in Debye's model)—and the vibrating coordinates proper. Even if we assume the law of force for the latter to be linear, the averaged force acting on the molar parameters becomes nonlinear, and this suffices to explain thermic expansion. We shall show, moreover, that it also suffices to give a qualitative explanation of melting. Whether these formulae are accurate enough for quantitative purposes can only be judged after a thorough investigation which we shall carry out later. In any case, there is no difficulty in principle in developing the free energy for nonharmonic vibrations.

For harmonic vibrations a well-known procedure leads to the following expression for the free energy:<sup>13</sup>

$$|[x, y]| = \begin{vmatrix} \sum_l \varphi_{xx}^l (e^{-i(l\alpha)} - 1) & \sum_l \varphi_{xy}^l (e^{-i(l\alpha)} - 1) & \sum_l \varphi_{xz}^l (e^{-i(l\alpha)} - 1) \\ \sum_l \varphi_{yx}^l (e^{-i(l\alpha)} - 1) & \text{---} & \text{---} \\ \sum_l \varphi_{zx}^l (e^{-i(l\alpha)} - 1) & \text{---} & \text{---} \end{vmatrix} \quad (25)$$

where  $l$  is the index of the cell, representing really three integers  $l_1, l_2, l_3$ ;  $(l\alpha) = l_1\alpha_1 + l_2\alpha_2 + l_3\alpha_3$ , and  $\varphi_{xx}^l, \varphi_{xy}^l, \dots$  the second derivatives of the potential energy between two lattice points in the relative position given by  $l(l_1, l_2, l_3)$ .

The determinant (25) can be written as a triple sum; one finds after some calculations:

$$|[x, y]| = 64 \sum_{(l>0)} \sum_{(l'>0)} \sum_{(l''>0)} \times \{ll''\} \sin^2 \frac{(l\alpha)}{2} \sin^2 \frac{(l'\alpha)}{2} \sin^2 \frac{(l''\alpha)}{2}, \quad (26)$$

where  $\sum_{(l>0)}$  indicates that the sum is to be extended only over half of the lattice points, in such a way that of two points  $l_1, l_2, l_3$  and  $-l_1, -l_2, -l_3$  one is to be omitted. The coefficient  $\{ll''\}$  depends on the indices of 3 points,  $l(l_1 l_2 l_3)$ ,  $l'(l'_1 l'_2 l'_3)$ ,  $l''(l''_1 l''_2 l''_3)$ , and can be written in such a way that it is expressed by the invariants of the distance vectors  $\mathbf{r}^l, \mathbf{r}^{l'}, \mathbf{r}^{l''}$  of these three points (where  $\mathbf{r}^l = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3$ ), namely  $(\mathbf{r}^l)^2$ ,

$$A = \Phi_0 + 3NkT \log \frac{\hbar \bar{\omega}}{kT}, \quad (22)$$

where  $\Phi_0$  is the potential energy of the non-vibrating, but homogeneously deformed lattice,  $\bar{\omega}$  a mean frequency (per  $2\pi$  seconds) given by

$$\log \bar{\omega} = \frac{1}{6} \langle \log |[x, y]| \rangle_{\mu} - \frac{1}{2} \log \mu. \quad (23)$$

Here  $\mu$  is the mass of the particles; the average is taken over the phases  $\alpha_1, \alpha_2, \alpha_3$  of the waves,

$$f = \frac{1}{(2\pi)^3} \int_{-\pi}^{+\pi} \int_{-\pi}^{+\pi} \int_{-\pi}^{+\pi} f(\alpha_1, \alpha_2, \alpha_3) d\alpha_1 d\alpha_2 d\alpha_3, \quad (24)$$

and  $|[x, y]|$  is the determinant of the secular equation for the waves with phases  $\alpha_1, \alpha_2, \alpha_3$ . For a simple lattice one has

$(\mathbf{r}^{l''} \times \mathbf{r}^{l'})^2 (\mathbf{r}^l \cdot (\mathbf{r}^{l''} \times \mathbf{r}^{l'}))^2$ . We introduce the operator

$$D = (1/r)(d/dr) \quad (27)$$

and write  $[D\varphi(r)]_{r=r^l} = D\varphi^l$ . Then we obtain:

$$\begin{aligned} \{ll''\} &= D\varphi^l \cdot D\varphi^{l'} \cdot D\varphi^{l''} + (\mathbf{r}^l)^2 D^2\varphi^l \cdot D\varphi^{l'} \cdot D\varphi^{l''} \\ &\quad + \frac{1}{2}(\mathbf{r}^{l'} \times \mathbf{r}^{l''})^2 \cdot D\varphi^l \cdot D^2\varphi^{l'} \cdot D^2\varphi^{l''} \\ &\quad + \frac{1}{6}(\mathbf{r}^l \cdot (\mathbf{r}^{l'} \times \mathbf{r}^{l''}))^2 \cdot D^2\varphi^l \cdot D^2\varphi^{l'} \cdot D^2\varphi^{l''}. \end{aligned} \quad (28)$$

The invariants of the distance vectors depend only on the scalar products of the vectors  $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ , therefore, on account of (5), on the strain components  $x_1, \dots, y_3, \dots$ . Introducing (28) in (26) we get  $|[x, y]|$  as a function of the  $x_1, \dots, y_3, \dots$  and of  $\alpha_1, \alpha_2, \alpha_3$ ; averaging  $\log |[x, y]|$  over these angles (as defined by (24)) leads to the value of  $\bar{\omega}$ , (23), as a function of  $x_1, \dots, y_3, \dots$ . This procedure, though quite definite and simple in principle, is in practice very involved and leads to formidable integrals. Therefore I shall use here a rather rough approximation, which is sufficient to show that our theory represents the main features of lattice thermodynamics.

<sup>13</sup> See, for instance, M. Born, *Atomtheorie des festen Zustandes* (Leipzig, 1923), p. 677. The method used here is due to O. Stern, Ann. d. Physik (4), 51, 237 (1916).

If we assume  $\varphi(r)$  as a power series in  $1/r$ , beginning with  $r^{-m}$  where the exponent  $m$  is large, we see that in the neighborhood of the minimum of  $\varphi$  the higher derivatives of  $\varphi$  will predominate. We proceed on the assumption that we can omit in (28) all terms except the last one which contains the highest derivatives and is proportional to the square of the volume of the parallelepiped determined by three lattice points:

$$\{\mathcal{W}l''\} \simeq \frac{1}{6}(\mathbf{r}^l \cdot (\mathbf{r}^{l'} \times \mathbf{r}^{l''}))^2 \cdot D^2\varphi^l \cdot D^2\varphi^{l'} \cdot D^2\varphi^{l''}. \quad (29)$$

We assume further that the potential  $\varphi(r)$  decreases so quickly with the distance that only the few next neighbors have to be taken into account. We shall—rather arbitrarily—take the first and second neighbors in the static terms ( $\Phi_0$ ), but only the first neighbors in the vibrational terms ( $\bar{\omega}$ ).

Finally, to fix our ideas, we consider one special case of a cubic lattice. The simple lattice is statically unstable if only the first neighbors are effective, and becomes stabilized only by the action of the second neighbors; this is the reason why this type practically never occurs in nature. The body-centered and the face-centered lattices occur in nature. I have decided (rather unfortunately, as was found later) to perform the calculations for the *body-centered lattice* since it has the coordination number 8 (instead of 12 for the face-centered lattice), and this number of the first neighbors determines the number of terms in the sum (26).

Then one obtains after some calculation

$$|[x, y]| = 64 \times 16 |\mathbf{a}_1 \mathbf{a}_2 \mathbf{a}_3|^2 \cdot (A_1 R_1 + A_2 R_2 + A_3 R_3 + A_4 R_4), \quad (30)$$

where  $A_\kappa$ ,  $R_\kappa$  have the following meaning: The distances and phases for 4 of the 8 neighbors are:

$$\begin{aligned} l=1(1 \ 1 \ 1) & \quad r_1 = a_1 + a_2 + a_3 \\ 2(-1 \ 1 \ 1) & \quad r_2 = -a_1 + a_2 + a_3 \\ 3(1 \ -1 \ 1) & \quad r_3 = a_1 - a_2 + a_3 \\ 4(1 \ 1 \ -1) & \quad r_4 = a_1 + a_2 - a_3 \end{aligned} \quad (31)$$

$$\begin{aligned} (1, \alpha) &= \alpha_1 + \alpha_2 + \alpha_3, \\ (2, \alpha) &= -\alpha_1 + \alpha_2 + \alpha_3, \\ (3, \alpha) &= \alpha_1 - \alpha_2 + \alpha_3, \\ (4, \alpha) &= \alpha_1 + \alpha_2 - \alpha_3. \end{aligned}$$

Then

$$\begin{aligned} A_1 &= \sin^2 \frac{(2, \alpha)}{2} \sin^2 \frac{(3, \alpha)}{2} \sin^2 \frac{(4, \alpha)}{2}, \\ R_1 &= D^2\varphi_2 \cdot D^2\varphi_3 \cdot D^2\varphi_4, \\ A_2 &= \sin^2 \frac{(3, \alpha)}{2} \sin^2 \frac{(4, \alpha)}{2} \sin^2 \frac{(1, \alpha)}{2}, \\ R_2 &= D^2\varphi_3 \cdot D^2\varphi_4 \cdot D^2\varphi_1, \\ A_3 &= \sin^2 \frac{(4, \alpha)}{2} \sin^2 \frac{(1, \alpha)}{2} \sin^2 \frac{(2, \alpha)}{2}, \\ R_3 &= D^2\varphi_4 \cdot D^2\varphi_1 \cdot D^2\varphi_2, \\ A_4 &= \sin^2 \frac{(1, \alpha)}{2} \sin^2 \frac{(2, \alpha)}{2} \sin^2 \frac{(3, \alpha)}{2}, \\ R_4 &= D^2\varphi_1 \cdot D^2\varphi_2 \cdot D^2\varphi_3, \end{aligned} \quad (32)$$

where  $D^2\varphi_1 = D^2\varphi(r_1)$  etc.

The functions  $R_\kappa$  have to be developed with respect to the  $x_z, \dots y_z, \dots$ . For this purpose it is convenient to use the fact that any function of the distance,  $f(r)$ , in which  $r$  is replaced by  $(r^2 + 2\rho)^{\frac{1}{2}}$ , has the following development:

$$f(r^2 + 2\rho)^{\frac{1}{2}} = f(r) + Df(r) \cdot \rho + \frac{1}{2} D^2 f(r) \cdot \rho^2 + \dots, \quad (33)$$

just as a Taylor series where differentiation is replaced by the operator  $D$ .

For the four neighbor points (31) we have  $r_1 = r_2 = r_3 = r_4 = a\sqrt{3}$  where  $a$  is the smallest coordinate difference in the lattice. The changes of  $r^2$  for a deformation  $x_x, \dots y_x, \dots$  are

$$\begin{aligned} \rho_1 &= a^2(x_x + y_y + z_z + y_z + z_x + x_y), \\ \rho_2 &= a^2(x_x + y_y + z_z + y_z - z_x - x_y), \\ \rho_3 &= a^2(x_x + y_y + z_z - y_z + z_x - x_y), \\ \rho_4 &= a^2(x_x + y_y + z_z - y_z - z_x + x_y). \end{aligned} \quad (34)$$

With the help of (33) and (34) it is easy to develop the  $R_\kappa$ . The square of the determinant  $|\mathbf{a}_1 \mathbf{a}_2 \mathbf{a}_3|$  is equal to the determinant of the scalar products  $\mathbf{a}_r \cdot \mathbf{a}_z$  and hence is expressible by the  $x_x, \dots y_x, \dots$ ; one obtains for the terms up to the second order

$$|\mathbf{a}_1 \mathbf{a}_2 \mathbf{a}_3| = a^3 \{ 1 + (x_x + y_y + z_z) - (y_z^2 + z_x^2 + x_y^2) + (y_y z_z + z_x x_x + x_y y_y) + \dots \}. \quad (35)$$

These developments must be substituted in (30) and then the averaging performed, as prescribed

in (23). We omit the very lengthy calculations and write down only the result:\*

$$\begin{aligned}
 f_0 &= 4\varphi_3 + 3\varphi_4 + 3kT\left\{\frac{1}{2}\log(D^2\varphi_3) - \log T + \log a + C\right\}, \\
 f_1 &= -\gamma a^3 p = 4a^2 D\varphi_3 + 4a^2 D\varphi_4 + kT\left(1 + \frac{3}{2}a^2 \frac{D^3\varphi_3}{D^2\varphi_3}\right), \\
 f_{11} &= \gamma a^3 c_{11} = 4a^4 D^2\varphi_3 + 16a^4 D^2\varphi_4 + kT\left\{-2 + \frac{3}{2}a^4 \left[\frac{D^4\varphi_3}{D^2\varphi_3} - \left(\frac{D^3\varphi_3}{D^2\varphi_3}\right)^2\right]\right\}, \\
 f_{12} &= \gamma a^3 c_{12} = 4a^4 D^2\varphi_3 + kT \cdot \frac{3}{2}a^4 \left[\frac{D^4\varphi_3}{D^2\varphi_3} - \left(\frac{D^3\varphi_3}{D^2\varphi_3}\right)^2\right], \\
 f_{44} &= \gamma a^3 c_{44} = 4a^4 D^2\varphi_3 + kT\left\{-1 + \frac{3}{2}a^4 \left[\frac{D^4\varphi_3}{D^2\varphi_3} - \frac{16I_2 + 5}{9} \left(\frac{D^3\varphi_3}{D^2\varphi_3}\right)^2\right]\right\},
 \end{aligned}$$

where the constant  $C$  is given by

$$C = \log \frac{2^{5/3} \hbar I_0^{1/6}}{k\mu^{\frac{1}{2}}}. \quad (36a)$$

Here the lower indices, as in  $\varphi_3$ ,  $\varphi_4$ ,  $D\varphi_3$  etc., indicate the square of the distance (in units  $a$ ) for which the function is to be taken, e.g.

$$\begin{aligned}
 \varphi_3 &= \varphi(a\sqrt{3}), \quad \varphi_4 = \varphi(a\sqrt{4}), \\
 D\varphi_3 &= \frac{1}{a\sqrt{3}} \frac{\partial \varphi(a\sqrt{3})}{\partial a\sqrt{3}}, \quad \dots
 \end{aligned} \quad (37)$$

According to our convention we have taken the first and second neighbors for the static terms, the first only for the kinetic terms.

In these expressions some numerical integrals appear,  $I_0$  and  $I_2$ . As  $I_0$  is only contained in the constant  $C$  its value is of no interest. The other constant is

$$I_2 = \frac{1}{(2\pi)^3} \int \int \int_{-\pi}^{+\pi} \frac{A_1^2}{(A_1 + A_2 + A_3 + A_4)^2} d\alpha_1 d\alpha_2 d\alpha_3. \quad (38)$$

I have not succeeded† in finding an accurate value of  $I_2$ ; but it is easy to see that it lies

\*The formulae contain the well-known result that central forces, treated statically ( $T=0$ ), lead to the Cauchy relation  $c_{12}=c_{44}$ ; but they show at the same time that for  $T>0$  this is not the case. This is worth noting as deviations from the Cauchy relation are usually considered as a criterion for noncentral forces which is not necessarily true.

†Note added in proof.—T. du Cros has found by numerical calculation that  $I_2=1.85/16$ ,  $\epsilon=2.15/16$ , for the body-centered lattice.

between  $\frac{1}{16}$  and  $\frac{1}{4}$ . We shall write

$$I_2 = \frac{1}{4} - \epsilon, \quad \text{where } 0 < \epsilon < \frac{3}{16}. \quad (38a)$$

One can check the long calculations with the help of the formulae (13a) which are indeed satisfied (observe the meaning of  $D\varphi_3$ ,  $D\varphi_4$  ... etc. as explained in (37)).

The last step now consists in choosing a suitable function  $\varphi(r)$ . We take a law of the form

$$\varphi = u \frac{nm}{n-m} \left( -\frac{1}{m} \left( \frac{r_0}{r} \right)^m + \frac{1}{n} \left( \frac{r_0}{r} \right)^n \right), \quad (39)$$

then

$$\frac{d\varphi}{dr} = \frac{u}{r_0} \frac{nm}{n-m} \left( \left( \frac{r_0}{r} \right)^{m+1} - \left( \frac{r_0}{r} \right)^{n+1} \right)$$

vanishes for  $r=r_0$ ;  $r_0$  is therefore the equilibrium distance for two particles. The frequency  $\nu_0$  of vibration of one particle about this equilibrium, if the other particle is fixed, is given by

$$4\pi^2 \mu \nu_0^2 = \left( \frac{d^2\varphi}{dr^2} \right)_{r=r_0} = \frac{u}{r_0^2} mn.$$

$u = -\varphi(r_0)$  is the *dissociation energy* of a molecule formed of two particles, which can also be expressed as a temperature  $\Theta = u/k$ . We introduce further instead of  $r_0$  its projection  $a_0$  on the cubic axes, given by  $3a_0^2 = r_0^2$ , and the corresponding volume  $V_0 = N\gamma a_0^3$  which the crystal would have at zero temperature if only first neighbors interacted (the real volume at  $T=0$  is a little smaller). We shall use further



a quantity of the dimensions of pressure,  $p_0 = R\Theta/V_0$ , where  $R = kN$  is the gas constant.

Our law of force contains four constants, the numbers  $m$ ,  $n$  and any two of the quantities  $r_0$  (or  $a_0$ , or  $V_0$ ),  $v_0$ ,  $u$ ,  $\Theta$ ,  $p_0$ , which are connected by

$$V_0 = N\gamma a_0^3 = N\gamma \frac{r_0^3}{3\sqrt{3}}, \quad u = k\Theta = \frac{4\pi^2}{mn} \mu v_0^2 r_0^2, \quad (40)$$

$$p_0 V_0 = R\Theta.$$

We shall use a *final simplification* by choosing

$$n = 2m. \quad (41)$$

Lennard-Jones<sup>14</sup> has found this assumption successful in the theory of the virial coefficient of gases, for the special value  $m=6$ ; and he has used it also in his new order-disorder theory of melting, quoted above.

If we divide Eqs. (36) by  $k\Theta$ , the right-hand terms are dimensionless, independent of  $r_0$ . On the left-hand side the coefficient of  $-\dot{p}$ ,  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$  becomes

$$\frac{\gamma a^3}{R\Theta} = \frac{\gamma a_0^3}{R\Theta} \frac{a^3}{a_0^3} = \frac{V_0}{R\Theta} \left(\frac{r}{r_0}\right)^3 = \frac{1}{p_0} \left(\frac{r}{r_0}\right)^3.$$

We choose now  $r_0$  as unit of length and replace the variable  $a = r/\sqrt{3}$  by

$$\xi = 1 - \frac{1}{r^m} = 1 - \left(\frac{1}{a\sqrt{3}}\right)^m. \quad (42)$$

Then the domain  $1 \leq r \leq \infty$ , extending from the equilibrium position of the first neighbors to infinity, corresponds to the range

$$0 \leq \xi \leq 1. \quad (42a)$$

As

$$\frac{1}{r^n} = \frac{1}{r^{2m}} = (1 - \xi)^{2m}$$

$\varphi$  and all derivatives,  $D\varphi_3$ ,  $D^2\varphi_3$ ,  $\dots$   $D\varphi_4$ ,  $\dots$  are polynomials in  $\xi$ ; for instance

$$\frac{a^2}{u} D\varphi_3 = \frac{r^2}{3u} D\varphi(r) = \frac{2m}{3} (1 - \xi) \cdot \xi.$$

The result of a long series of reductions is the

following expressions:

$$\begin{aligned} -\frac{\dot{p}}{p_0} \frac{1}{(1-\xi)^{3/m}} &= F_1(\xi) + G_1(\xi) - \frac{T}{\Theta} H_1(\xi), \\ \frac{c_{11}}{p_0} \frac{1}{(1-\xi)^{3/m}} &= F_2(\xi) + G_2(\xi) - \frac{T}{\Theta} (2 + H_2(\xi)), \\ \frac{c_{12}}{p_0} \frac{1}{(1-\xi)^{3/m}} &= F_2(\xi) - \frac{T}{\Theta} H_2(\xi), \\ \frac{c_{44}}{p_0} \frac{1}{(1-\xi)^{3/m}} &= F_2(\xi) - \frac{T}{\Theta} (1 + H_2(\xi) - 2H_3(\xi)), \end{aligned} \quad (43)$$

where

$$F_1(\xi) = \frac{8m}{3} (1 - \xi) \cdot \xi, \quad (44)$$

$$F_2(\xi) = \frac{8m^2}{9} (1 - \xi) \cdot \left(1 - 2\frac{m+1}{m}\xi\right);$$

$$G_1(\xi) = 2\left(\frac{3}{4}\right)^{m/2} m^2 (1 - \xi) \cdot \left\{1 - \left(\frac{3}{4}\right)^{m/2} + \left(\frac{3}{4}\right)^{m/2} \xi\right\},$$

$$G_2(\xi) = 2\left(\frac{3}{4}\right)^{m/2} m^2 (1 - \xi) \quad (45)$$

$$\cdot \left\{1 - 2\frac{m+1}{m} \left[1 - \left(\frac{3}{4}\right)^{m/2}\right] - 2\frac{m+1}{m} \left(\frac{3}{4}\right)^{m/2} \xi\right\};$$

$$H_1(\xi) = \frac{4+3m}{2} \frac{1 - \frac{4(m+1)^2}{m(3m+4)}\xi}{1 - 2\frac{m+1}{m}\xi},$$

$$H_2(\xi) = \frac{m^2 - 4}{3} \frac{\left(1 - \frac{m+1}{m}\xi\right) \cdot \left(1 + \frac{8(m+1)}{m(m-2)}\xi\right)}{\left(1 - 2\frac{m+1}{m}\xi\right)^2}, \quad (46)$$

$$H_3(\xi) = \frac{8(m+2)^2}{3} \frac{\left[1 - \frac{4}{3}\frac{m+1}{m}\xi\right]^2}{\left[1 - 2\frac{m+1}{m}\xi\right]}.$$

<sup>14</sup> J. E. Lennard-Jones, *Physica* (IV) 10, 941 (1937).

TABLE I.\*

$\xi$	$\sqrt{1-\xi}$	$F_1(\xi)$	$F_2(\xi)$	$G_1(\xi)$	$G_2(\xi)$	$H_1(\xi)$	$H_2(\xi)$	$H_3(\xi)$
-0.25	1.118	-5.00	63.3	2.99	-3.91	9.53	2.29	131
-0.20	1.095	-3.84	56.3	3.00	-5.54	9.73	3.26	136
-0.15	1.027	-2.76	49.7	3.00	-7.03	9.96	4.47	142
-0.10	1.049	-1.76	43.4	2.99	-8.37	10.24	6.00	150
-0.05	1.025	-0.84	37.5	2.96	-9.56	10.58	8.00	159
0	1.000	0	32.0	2.93	-10.60	11.00	10.67	171
0.05	0.975	0.76	26.9	2.88	-11.49	11.53	14.37	186
0.10	0.949	1.44	22.1	2.83	-12.23	12.22	19.72	207
0.15	0.922	2.04	17.7	2.76	-12.82	13.15	28.1	237
0.20	0.894	2.56	13.7	2.68	-13.26	14.50	42.2	285
0.25	0.866	3.00	10.0	2.59	-13.56	16.60	68.9	367
0.30	0.837	3.36	6.72	2.50	-13.70	20.33	131.0	539
0.35	0.806	3.64	3.81	2.39	-13.69	28.8	341.	1054
0.40	0.775	3.84	1.28	2.27	-13.54	67.0	2477.	5486
0.45	0.742	3.96	-0.88	2.14	-13.23	-73.0	4154.	6144

\* I have to thank Dr. E. W. Kellermann for computing these tables and for helping me in the subsequent numerical work.

Table I contains the numerical values of these functions for  $m=6$ ; this value corresponds to London's quantum-mechanical explanation of van der Waals force and has been successfully used by Lennard-Jones, as mentioned above.

The functions  $F_1$ ,  $F_2$  represent the statical effect of the first neighbors;  $G_1$ ,  $G_2$  that of the second neighbors. As  $G_1$  is not small compared with  $F_1$  the omission of all the more distant neighbors seems rather doubtful. Further,  $G_2$  is negative, therefore  $c_{11}$  is smaller than  $c_{12}$  and  $c_{44}$  (at least for  $T=0$ , but really, as we shall see, throughout). Here it turns out that the choice of the body-centered lattice is unfortunate; for  $c_{11} < c_{12}$  means instability (of the type leading to a "gel" state). In fact, one sees without calculation that for central forces acting only between first and second neighbors the face-centered lattice (densest packing) will be the most stable arrangement.\*

I have, nevertheless, calculated graphs for all physical quantities. (We may assume that the stability with respect to the condition  $c_{11} > c_{12}$  is maintained by other forces, not taken into account.) We shall concentrate our attention on  $c_{44}$  and investigate whether our thesis that  $c_{44}=0$  means melting gives reasonable results.

It is easy to compute the quantities (43) as functions of  $p$  and  $T$  with the help of Table I, as the expressions (43) are linear in  $T/\Theta$ . I have used a graphical method in which these linear functions are represented by straight lines; it is obviously sufficient to calculate two points of each line from the table. From these systems of straight lines (one for each of the quantities

$p$ ,  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$ ) one can construct curves which give  $\xi$  (or the molar volume  $V$ ) and the elastic constants as functions of  $p$  and  $T$ .

Figure 1 represents the isobars of thermic expansion,  $\xi$  (or  $V$ ) for constant  $p$  as function of  $T/\Theta$ . The  $V$ -scale is given in two forms; in the first one  $V$  is referred to  $V_0$  as unit, the quantity used in the theoretical considerations (representing the volume of the lattice which it would have for  $T=0$ ,  $p=0$  if only the first neighbors interact); in the second scale  $V$  is referred to  $V(0)$ , the actual (calculated) volume for  $T=0$ ,  $p=0$ . The figure shows that  $\xi$  increases first linearly with  $T/\Theta$ , but later much quicker, until the increase becomes infinite. This extreme point is, of course, the absolute limit of stability; we have, nevertheless, continued the curves as dotted lines beyond these points.

Figure 2 shows the effect of compression with the help of some isotherms  $\xi$  (or  $V$ ) as function of  $p/p_0$ .

Figures 3, 4, 5 and 6 represent the elasticity constants as functions of  $T/\Theta$  for different hydrostatic pressures. As I could not determine the real value of the integral  $\epsilon$  I have calculated  $c_{44}$  for two values of  $\epsilon$ , namely  $\epsilon=0$  (the lower limit) and  $\epsilon=\frac{1}{16}$ , which presumably is not far from the correct value. All constants decrease first linearly with  $T/\Theta$ , but turn downward at last and reach the zero line at steep angles; the values of  $T/\Theta$  where  $c_{44}$  vanishes should be the melting points for different pressures. We see that the behavior of the curves for  $c_{44}$  is rather different for  $\epsilon=0$  and  $\epsilon=\frac{1}{16}$ ; in the latter case, Fig. 6, the zero points of  $c_{44}$  are not the maximum values reached by  $T/\Theta$  on the curves.

There is an arc on every curve on which to each value of  $c_{44}/p_0$  there belong two values of  $T/\Theta$ —a feature which could not well be foreseen from the general formulae (36). Those parts of the curves where  $c_{44}$  is not unique correspond apparently not to stable states of the lattices (or at least only to metastable, "overheated" states). The value of  $c_{44}$  jumps by a finite amount to zero at the melting point. Fig. 7 represents the melting curve  $p(T)$ , as taken from the zero points of  $c_{44}$  for  $\epsilon=0$  and  $\epsilon=\frac{1}{16}$ ; they do not differ much, but the latter is probably nearer to the truth. We see a slight increase of melting temperature with pressure.

\* The calculation for the face-centered lattice will be performed by my collaborator, Mr. Teissier du Cros.

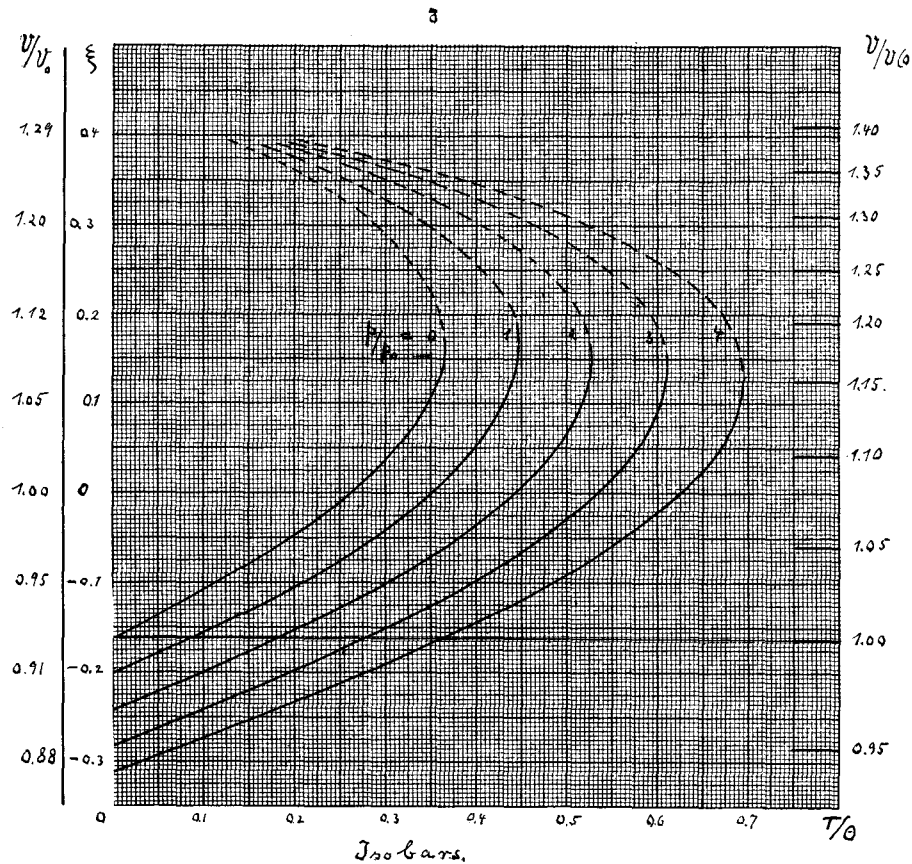


FIG. 1.

If we now compare the curves of  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$  and particularly the zero points on them, we see that the curves of  $c_{12}$  and  $c_{44}$ , for  $\epsilon=0$ , practically coincide. The  $c_{11}$  curves lie lower and are flatter; this, as we have said already, is a consequence of the fact that the body-centered lattice is not the densest packing.

We have now to consider whether the order of magnitude is right. This depends on the values of  $\Theta$  and  $p_0$ .

We introduce in (40)

$$m = \frac{n}{2} = 6, \quad \gamma = 4, \quad V_0 = N\gamma a_0^3 = \frac{N\gamma r_0^3}{3\sqrt{3}}, \quad M = \mu N;$$

then we get the dissociation energy  $u$  for a pair of particles in the form

$$D = Nu = R\Theta = \frac{\pi^2}{6\sqrt[3]{16}} \nu_0^2 M \left( \frac{V_0}{N} \right)^{\frac{1}{3}}. \quad (47)$$

If we express this in kcal, we find with  $R=2$  cal.

$$\Theta = D \cdot 500^\circ, \quad p_0 = \frac{D}{V_0} \cdot 41,400 \text{ atmos.} \quad (48)$$

For  $D=5$ ,  $V_0=20$  e.g. we have  $\Theta=2500^\circ$ ,

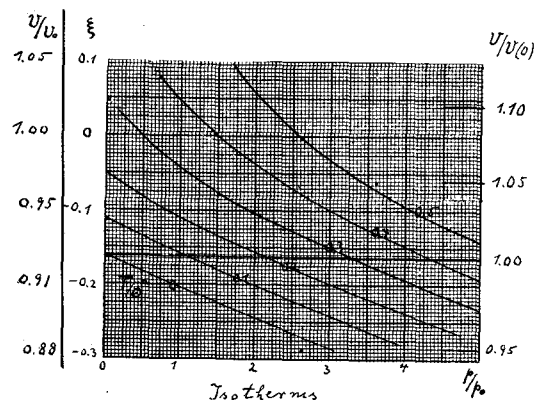


FIG. 2.

$p_0 = 10,000$  atmos. Our scale therefore covers the domain of high pressures investigated by Bridgman.

Figure 7 gives the melting point  $T_m$  as some numerical fraction of  $\Theta$  for each value of  $p$ , say

$$T_m = \alpha \Theta. \quad (49)$$

Introducing this in (47) and solving with respect to  $\nu_0$  we get

$$\begin{aligned} \nu_0 &= CR^{\frac{1}{2}} N^{\frac{1}{2}} (T_m/M)^{\frac{1}{2}} V_0^{-\frac{1}{2}} \\ &= C \times 0.77 \times 10^{12} (T_m/MV_0^{\frac{1}{2}})^{\frac{1}{2}}; \end{aligned} \quad (50)$$

if we take for  $\alpha$  the value from Fig. 7 which corresponds to  $p=0$ ,  $\alpha=0.35$ , we obtain

$$C = \frac{1}{\pi} \left( \frac{6 \cdot 4^{\frac{1}{2}}}{\alpha} \right)^{\frac{1}{2}} = 2.10. \quad (51)$$

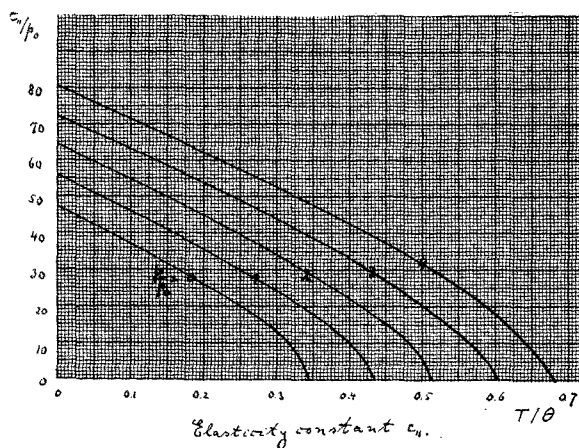


FIG. 3.

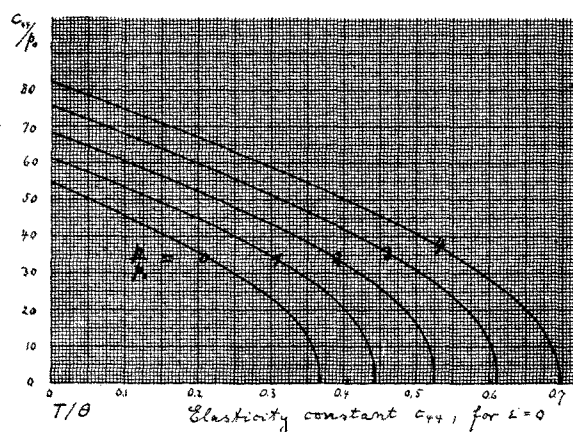


FIG. 5.

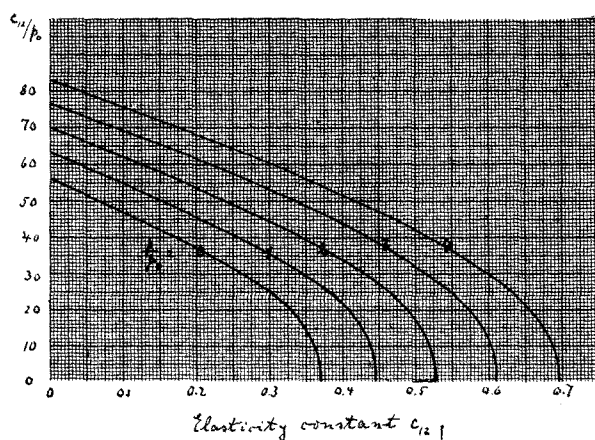


FIG. 4.

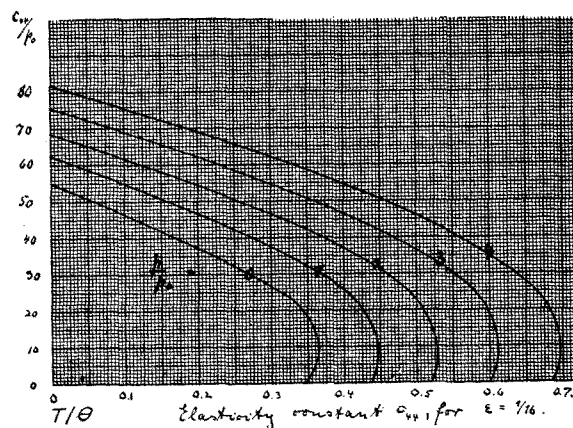


FIG. 6.

The expression (50) is Lindemann's well-known formula with a definite numerical constant. Lindemann's empirical value is  $C=2.75$ ; it is derived from those frequencies which allow the representation of specific heat with the help of Einstein's formula. Our  $\nu_0$  cannot be directly considered as a vibration of the lattice.

One can calculate the Debye frequency

$$\nu_D = c_m (3N/4\pi V)^{\frac{1}{3}}, \quad (52)$$

where  $c_m$  is a mean velocity of sound, from the theoretical expressions of  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$ ; but as the Debye formula of specific heat is valid only for deep temperatures, this calculation has nothing to do with our theory which is concerned with high temperatures (and pressures). I shall only show that  $\nu_D$  differs from  $\nu_0$  only by a numerical factor. As  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$  are proportional to  $p_0$  we

have

$$\rho c_m^2 = \beta p_0, \quad (53)$$

where  $\rho$  is the density and  $\beta$  a numerical factor. Now  $\rho = M/V$  which we can replace by  $M/V_0$  (since, according to Fig. 1,  $V/V_0 = 0.93$  for  $T=0$ ). Then we have with the help of (47)

$$c_m^2 = \beta V_0 p_0 / M = \beta R \Theta / M = (\pi^2 \beta / 6 \sqrt[3]{16}) \nu_0^2 (V_0 / N)^{\frac{2}{3}},$$

hence

$$\nu_D = 0.50 \beta^{\frac{1}{2}} \cdot \nu_0. \quad (54)$$

All numerical values calculated in this paper are valid only for lattices of the body-centered cubic type and for the assumed law of force with  $m=n/2=6$ ; for substances of this kind a "law of corresponding states" holds with respect to  $p$  and  $T$  if these are expressed as multiples of  $p_0$  and  $\Theta$ . I shall illustrate this by a remark about the latent heat of melting which, as we have said, cannot be calculated from the theory, since the change of volume depends on the properties of the liquid state. But if  $\Delta V$  is given we can apply the Clausius-Clapeyron formula

$$Q = T(dp/dT)\Delta V$$

and take  $dp/dT$  from Fig. 7. We find

$$\begin{aligned} dp/dT &= 11.1 p_0 / \Theta = 11.1 R / V_0, \\ Q &= 11.1 (\Delta V / V_0) R T_m = 32. \end{aligned} \quad (55)$$

The latent heat is proportional to the melting temperature and to  $\Delta V/V$  with a numerical

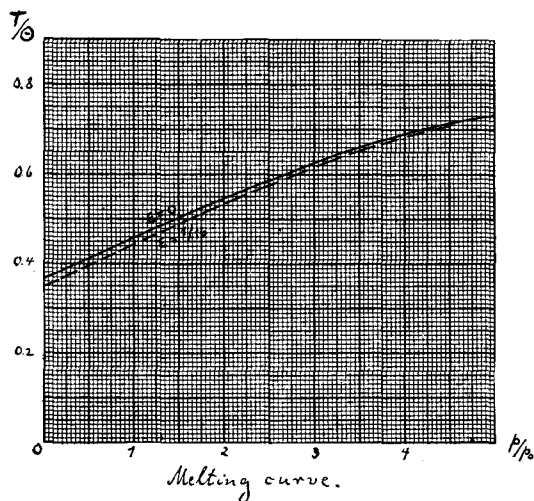


FIG. 7.

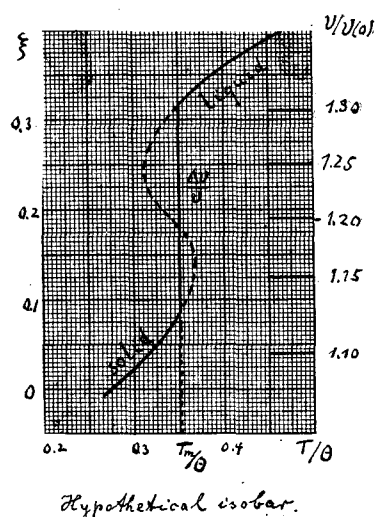


FIG. 8.

factor depending only on the lattice type and the exponent  $m$ .

I wish to make a final, quite hypothetical remark; it concerns the dotted parts of the expansion curves of Fig. 1. They represent completely unstable states of the lattice; but it can be expected that a more perfect theory which takes account of the disordered state of the liquid (as the theory of Lennard-Jones) will modify this part of the curves in the way indicated in Fig. 8. The ordinate of the melting point would intersect the curve in three points; the middle one would not represent a stable state, but the highest intersection point would correspond to the liquid in equilibrium with the solid. The liquid state would be represented by the continuation of the curve, exactly as in van der Waals theory of condensation. The existence of a critical point between liquid and solid seems therefore not impossible.

I expect that the method explained in this paper, properly improved, will be capable of accounting for the properties of strength, sliding and breaking of crystals. We have only to treat another stress component in the same way as we have here done with the pressure; we have to calculate the limit of stability with increasing temperature for a finite stress  $X_x$  (breaking) or  $X_y$  (sliding). This kind of problem is of special interest in connection with Bridgman's experimental investigations on breaking strength.

Bridgman has also discovered numerous allotropic transformations under high pressure; it will be interesting to see whether these can be accounted for by comparing the free energy of different lattices.

Metals need a special treatment as the forces arising from the free electrons are not central.

The extension of the theory to higher and deeper temperatures (anharmonic vibrations

giving terms with  $T^2$ , quantum effects terms with  $1/T$ ) will also be considered.

A complete account of the calculations will be published in collaboration with Dr. R. Schlapp. I have to thank him and Dr. K. Fuchs for valuable assistance in discussing the problems and checking the calculations, and Dr. E. W. Kellermann for computing the numerical table.

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## The Equation of State of Frozen Neon, Argon, Krypton, and Xenon\*

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The interaction between two rare gas atoms is assumed to have the form  $-Ar^{-6} + AB(\exp^{-r/\rho})$ . The values of  $A$  and  $B$  are found from the lattice distances and the heats of sublimation of frozen neon, argon, krypton and xenon for  $\rho = 0.2091\text{\AA}$  and  $\rho = 0.345\text{\AA}$ . The equations of state of the solids are then calculated, including the Debye  $\theta$ 's and the breakdown points, which occur a few degrees below the melting points. For krypton, the expansion coefficient and the specific heat are calculated, but are found too high at higher temperatures.

**B**Y means of the crystal lattice theory and thermodynamics, it is possible to determine theoretically the structure and properties of matter from the potential energy of molecular interaction. The potential energy of interaction between pairs of particles may be divided into a repulsive and an attractive part. According to the quantum theory, the former has the form  $be^{-r/\rho}$  for helium and neon. For other atoms or ions, there is good reason to assume the same form, but the value of the constants  $b$  and  $\rho$  is unknown; and even for helium and neon, it is not certain how far the necessary mathematical approximations have affected the calculated values. The Coulomb energy of attraction between ionic charges, which is proportional to  $-e^2/r$ , had first to be considered alone for ionic crystals, to which the theory was first applied. It turned out, however, that the van der Waals attraction, of the form  $-A_1r^{-6} - A_2r^{-8}$ , had also to be taken into account. Here again approximation formulae were available for the  $A$ 's, but different methods of approximation gave differ-

ent values. It seemed therefore advisable to take from the theory only the form of the energy expression and to leave the constants  $A$ ,  $b$ ,  $\rho$ , etc., to be determined from experiment.

Since the van der Waals attraction plays a minor role in the determination of lattice distance and lattice energy,  $A$  cannot be determined from the experimental data on these quantities. On the other hand, the van der Waals energy is extremely important for the calculation of the elastic properties. If a large number of suitably selected properties of the solid were known with great accuracy, it would be possible to determine the coefficients of the potential energy function from the measurements, but even then the calculations would be very complex.

One can hope that the situation is simpler for the rare gases. In the absence of charges,  $-Ar^{-6}$  is the first term in the potential energy of attraction and one may assume as a first approximation this single type of attraction (the van der Waals attraction due to dipole-dipole interaction) and a single type of repulsion (that due to overlap of electron clouds). If the equilibrium distance between two atoms and the depth of

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