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case certainly not so.¹⁾ The correct deviations of density in the solid are much smaller and have another dependence of temperature than that which DEBYE used.

In connection with what we found above in point 4, at last it remains to be said that especially the use of *statical* deviations of density instead of the *dynamic* ones is a great mistake. In some simple cases we have been able to demonstrate that also in three dimensions the latter do not produce any scattering. Our conclusion therefore is that the molecular theory of the heat-resistance still remains entirely open.

Physics. — “*Contributions to the kinetic theory of solids. III. The equation of state of the isotropic solid.*” By Prof. L. S. ORNSTEIN and Dr. F. ZERNIKE. (Communicated by Prof. H. A. LORENTZ.)

(Communicated in the meeting of June 24, 1916.)

In this contribution we shall use the method we developed in our first contribution for the determination of the expansion in order to deduce the equation of state, i.e. the connection between the strain and the stress in its dependence on the temperature. In contribution I we have treated only the simple case that the strains are zero, and have determined the stress resulting from heating (thermal pressure). A quite analogous deduction can be used in order to find the stresses of a solid, which has been deformed at the absolute zero (equation of state). The only difference with the former case lies in the fact, that by this strain the solid generally departs from exact isotropy. Hence a more ample calculation is necessary in the case of shearing.

Further we shall mention the terms which present themselves if we take into account the remark of the note on p. 1293.

Finally we shall show how the equation of state is also to be found with the aid of thermodynamic relations from the specific heat of solid bodies, which may be calculated from the formulae given by BORN. This method, for the present only mentioned in principle, is more analogous to that of DEBYE-EVERDINGEN than to our first deduction, which is purely dynamical.

1. Now we will calculate the force necessary to give the solid

¹⁾ See EPSTEIN, Physik. Zeitschr. XV.

body a homogeneous expansion at a given temperature, so that $e_1 = e_2 = e_3 = e$, $e_4 = e_5 = e_6 = 0$. This force consists of two parts. In the first place one may give the required expansion to the solid body at the absolute zero and thereupon supply at constant volume the energy necessary to give the solid body the required temperature. Therefore the thermal pressure as calculated in our first contribution has to be added to the elastic tension at the absolute zero.

Now in order to calculate the first part we use the expression for the energy

$$\epsilon = AI_1^2 + BI_2 + CI_1^3 + DI_1I_2 + EI_1^3 \dots \dots \dots (1)$$

It is immediately clear that the invariants have the following values

$$I_1 = 3e \quad , \quad I_2 = 3e^2 \quad , \quad I_3 = e^3.$$

so that the energy takes the form:

$$\epsilon = (9A + 3B)e^2 + (27C + 9D + E)e^3$$

For the tension at the absolute zero we find consequently

$$S_0 = \frac{d\epsilon}{d3e} = (6A + 2B)e + (27C + 9D + E)e^2.$$

For the thermal pressure (S_{th}) we found in Contribution I the expression

$$S_{th} = \frac{9C + 2D}{6A} \epsilon_l + \frac{3D + E}{6B} \epsilon_{tr} \dots \dots \dots (2)$$

Now A , B , C , and D are constants which are relative to the non-deformed substance. In our case however we must replace these constants by their values in the strained condition when calculating the thermal pressure. But as the solid in that condition remains isotropic, the given formula still holds. We will neglect the variation of C and D with e as this variation is determined by terms of higher order in the energy, which were neglected by us. The average energy of the longitudinal and the transversal vibrations may change also. When we have to do with so high a temperature that the theorem of equipartition is true, that change is zero as the number of degrees of freedom does not change by the expansion. For lower temperatures where the quantum-theory must be taken into consideration, the change of ϵ_l and ϵ_{tr} has to be taken into account.

The variation of A and B with e can be found in the following manner. The strain can be represented by

¹⁾ Conf. for the notations Contribution I,

$$e_1 = e + e'_1, \quad e_2 = e + e'_2, \quad e_3 = e + e'_3, \quad e_4 = e'_4, \quad e_5 = e'_5, \quad e_6 = e'_6.$$

We introduce this into the expression for the energy and determine the part of the second degree with respect to the quantities e' . As e'_1 etc. represent the deformations from the strained condition (e), the coefficients of the invariants I_1^2 and I_2 will give the new values of A and B . We find

$$\begin{aligned} A' &= A + (9C + 2D)e \\ B' &= B + (3D + E)e. \end{aligned}$$

Now when we introduce these values for A' and B' into the expression for the thermal pressure and when we add to it the elastic tension at the absolute zero, we find for the total tension in the case of equipartition

$$\begin{aligned} S = & (6A + 2B)e + (27C + 9D + E)e^2 + \left(\frac{9C + 2D}{18A} + \frac{3D + E}{9B} \right) \epsilon - \\ & - \left(\frac{(9C + 2D)^2}{18A^2} + \frac{(3D + E)^2}{9B^2} \right) \epsilon e. \end{aligned} \quad (3)$$

In this ϵ is the total energy which is proportional to T . Thus the equation of state for changes in which the solid body remains isotropic has been found.

To find the modulus of compression we determine $\frac{dS}{d3e}$; for this we find

$$m = \frac{6A + 2B}{3} + \frac{54C + 18D + 2E}{3} e - \left(\frac{(9C + 2D)^2}{54A^2} + \frac{(3D + E)^2}{27B^2} \right) \epsilon \quad (4)$$

The factor e now still depends on the temperature; to find this factor we can apply (3), where the last term may be neglected as we will confine ourselves to a linear expression in ϵ . The e can then be found by considering the expansion at zero pressure. When we put in (3) $S = 0$ we find

$$\begin{aligned} e &= \frac{\left(\frac{9C + 2D}{18A} + \frac{3D + E}{9B} \right) \epsilon}{6A + 2B} \\ m &= \frac{6A + 2B}{3} - \left\{ \frac{27C + 9D + E}{9A + 3B} \left(\frac{9C + 2D}{18A} + \frac{3D + E}{9B} \right) + \right. \\ & \quad \left. + \frac{(9C + 2D)^2}{54A^2} + \frac{(3D + E)^2}{27B^2} \right\} \epsilon \end{aligned} \quad (5)$$

Easily the form of the equation of state can be indicated in the case that the quantum-theory is introduced. We will confine ourselves to the case of the temperatures being so low that the upper

limit of the integral in the expression (196), which is given by BORN for the energy does not come into account. Then we have to take into consideration for the thermal pressure in formula (2) not only the variation of A and B with e , but also that of the longitudinal and the transversal energy.

By application of the formulae which BORN has given in § 21, we find after a simple calculation as equation of state

$$S = (6A + 2B)e^2 + (27C + 9D + E)e^3 - e \left\{ \frac{5(9C + 2D)^2}{6A^2} \epsilon_l + \frac{5(3D + E)^2}{6B^2} \epsilon_{tr} \right\} \quad (6)$$

into which may be introduced the values for the energy of the longitudinal and the transversal vibration. From this the modulus of compression can afterwards be calculated. We find thus

$$m = \frac{6A + 2B}{3} - \frac{5(9C + 2D)^2}{18A^2} \epsilon_l - \frac{5(3D + E)^2}{18B^2} \epsilon_{tr} - \left. \begin{aligned} & - \frac{(27C + 9D + E)}{9A + 3B} \left\{ \frac{9C + 2D}{3A} \epsilon_l + \frac{3D + E}{3B} \epsilon_{tr} \right\} \end{aligned} \right\} \quad (7)$$

2. Now we can try to deduce the shearing stresses and their dependence on temperature in a way analogous to the one that has been used for the thermal pressure. For this purpose we can determine the space-time average of the force $\frac{\partial \epsilon}{\partial e_4}$.

We have

$$X_4 = \frac{\partial \epsilon}{\partial e_4} = -\frac{1}{2} B e_4 + \frac{1}{2} E (e_1 e_2 - e_1 e_4) - \frac{1}{2} D (e_1 e_4 + e_2 e_4 + e_3 e_4).$$

Now we have to determine the mean force when the solid body has a given strain $e_4 = e$ in the initial condition. Thus, if we call again $e'_1 \dots e'_6$ the deformations from the strained condition, we get

$$X_4 = -\frac{1}{2} B (e + e'_4) + \frac{1}{2} E (e'_1 e'_2 - e'_1 (e + e'_4)) - \frac{1}{2} D (e'_1 + e'_2 + e'_3) (e + e'_4).$$

Now we have to find the space-time-average of this force. It should be taken into consideration that $\overline{e'_1} = \overline{e'_2} = \overline{e'_3} = \overline{e'_4} = 0$, whence

$$\overline{X_4} = -\frac{1}{2} B e + \frac{1}{2} E (\overline{e'_1 e'_2} - \overline{e'_1 e'_4}) - \frac{1}{2} D (\overline{e'_1 e'_4} + \overline{e'_2 e'_4} + \overline{e'_3 e'_4}) \quad (8)$$

The mean values $\overline{e'_1}, \overline{e'_2}, \dots$ etc. which vanish in the case the body remains isotropic will now, by the existence of the initial shearing $e_4 = e$, have values deviating from zero in consequence of the fact that the body presently behaves like a rhombic crystal. Thus far the calculation corresponds with that of the thermal pressure. The force calculated is indeed the force required to keep a certain deformation given at the absolute zero unchanged when the tempe-

perature is increased. But, whereas mean forces occurring at the thermal pressure could be deducted at once from the energy, this time this is not the case, and thus here it will be necessary to calculate the mean values e'_1, e'_4 separately.

This calculation of which here only the general course will be indicated, is performed a little more easily for another case, i.e. for the case that the given deformation at the absolute zero is

$$e_1 = e_1, e_2 = e_2, e_3 = e_3, e_4 = e_4 = e_5 = 0.$$

Then only tensions X_x, Y_y and Z_z occur and the mean values

$$\overline{e_1'^2}, \overline{e_1'e_2'}, \overline{e_2'^2}, \overline{e_1'e_3'}, \overline{e_3'^2}, \overline{e_2'e_3'}$$

will have to be determined.

These mean values can be found by considering the progressive waves in the rhombic crystal into which the body has changed by the deformation.

The total change can be characterized as follows. First the energy in the isotropic body is divided equally in all directions over the waves of the same frequency; for the crystal this is not the case.

In the second place in the isotropic substance there are longitudinal and transversal waves; with the crystal the direction of the displacement is no longer so simple. Now e_1, e_2 and e_3 are small quantities, the change is therefore for both cases small; e.g. from the longitudinal wave arises a wave the elongation of which has a small inclination with respect to the wave-normal. As the effects are so small we are able to determine the influence on the averages separately. Indeed we may in calculating the influence of the new division of energy overlook the "declivity" of the waves, hence we may substitute the direction in the isotropic case for that of the vector of displacement. When we examine however the influence of the "declivity", we can take into account the division of the energy for an isotropic body, i.e. the homogeneous distribution over the directions.

As has been said above, we do not intend to reproduce here the calculation, but are going to show only how the elastic constants of the rhombic crystal are expressed in the magnitudes e_1, e_2, e_3 .

We introduce the notation of VOIGT so that $c_{11}, c_{12}, c_{13}, c_{22}, c_{23}, c_{33}, c_{44}, c_{45}, c_{66}$ are the constants of the rhombic crystal, i.e. the coefficients of $e_1'^2, e_1'e_2$, etc. in the energy. When the strain at the absolute zero is represented by $e_1, e_2, e_3, 0, 0, 0$, and the arbitrary strain which is superposed on it by $e'_1, e'_2, e'_3, e'_4, e'_5, e'_6$, then the terms with C, D and E give quadratic parts in e'_1 , etc. viz.

$$\left. \begin{aligned} & 3C(e_1 + e_2 + e_3)I_1'^2 + D(e_1 + e_2 + e_3)I_2' + \\ & + DI_1'(e_1'(e_2 + e_3) + e_2'(e_1 + e_3) + e_3'(e_1 + e_2)) \\ & E[e_1'e_2'e_3 + e_2'e_3'e_1 + e_1'e_3'e_2 - e_4'^2e_1 - e_5'^2e_2 - e_6'^2e_3] \end{aligned} \right\} \quad (9)$$

These parts should be added to $AI_1'^2 + BI_2'$, therefore the coefficient of $e_1'^2$ increases by

$$3C(e_1 + e_2 + e_3) + D(e_2 + e_3)$$

that of $e_1'e_2'$ by

$$(6C + 2D)(e_1 + e_2 + e_3) + (D + E)e_3$$

that of $e_4'^2$ by

$$- \frac{1}{4}D(e_1 + e_2 + e_3) - Ee_1$$

from which the other follow by cyclic change. In order to introduce the notation of VOIGT also for the isotropic body one should remember that $c_{12} = c_{11} - c_{44}$, whereas $A = \frac{1}{2}c_{11}$, $B = -2c_{44}$. From this therefore the constants for the rhombic crystal are at once to be written down. From the elastic differential equation afterwards the determinant equation for the velocity of transmission in its dependence upon the direction is deduced, and also the frequency of the normal vibrations can be determined. The further, more detailed calculation will finally for the mean values in question, except the terms which appear also in the isotropic case, yield values which linearly depend on e_1 , e_2 and e_3 .

3. In a note to our contribution (I) already we have pointed to the fact that the ordinary formula which was used there for the tension was not exact. In the following manner the accurate form for finite deformations is found.

The elastic energy ε can also in that case be represented by the already often used formula (I), provided only that the correct signification is assigned to the quantities e_1, \dots, e_6 . Let us now represent the differential quotients $\frac{\partial u}{\partial x}, \frac{\partial u}{\partial y}$ etc. by a_{11}, a_{12} etc., then we must take¹⁾

$$\left. \begin{aligned} e_1 &= a_{11} + \frac{1}{2}(a_{11}^2 + a_{21}^2 + a_{31}^2) \\ e_4 &= a_{22} + a_{32} + a_{12}a_{13} + a_{22}a_{23} + a_{32}a_{33} \end{aligned} \right\} \dots \quad (11)$$

From the energy ε it will be possible to find the tension N_x by means of a virtual elongation σ in the x -direction. This now has to be composed with the known deformation, which is determined by the magnitudes a_{11} etc. Hence a_{11} , a_{12} and a_{13} change and further also all magnitudes e . For the new values we find

¹⁾ Vide e.g. LOVE.

$$\begin{aligned} e_1' &= e_1 + (1 + a_{11})^2 d \\ e_2' &= e_2 + a_{12}^2 d \\ e_4' &= e_4 + 2a_{12}a_{13} d \\ e_5' &= e_5 + a_{13} (1 + 2a_{11}) d \end{aligned}$$

From these values the variation of the energy may be found. Apparently now also the terms AI_1^2 and BI_2 give parts which are quadratic in the quantities e (or a) and which therefore on the average do not drop off. After using the symmetry of the expression it is possible to put down the result as follows

$$\frac{2}{3} A \overline{I_1^2} + \frac{2}{3} B \overline{I_2}.$$

However, another correction of the same nature will still be required. Above it was taken as a matter of course that the averages of first powers of $e_1 \dots e_6$ will be zero. Properly taken this is the case with the quantities $\sigma_{11} = \frac{\partial u}{\partial x}$. On the other hand one finds from the relations (11)

$$\bar{e}_1 = \frac{1}{2} (\overline{e_1^2} + \frac{1}{2} \overline{e_4^2}).$$

This value should be taken into account if we take the mean value of the principal term of the tension Λ_x

$$2AI_1 + B(e_2 + e_3)$$

therefore a correction is found to an amount of

$$(A + \frac{1}{2} B) (\overline{I_1^2} - 2 \overline{I_2}).$$

Consequently on the whole, to the thermal pressure we found before,

$$\frac{5A+B}{3} \overline{I_1^2},$$

has to be added.

It will be permitted to neglect this term when the coefficients C and D are large with respect to A and B .

Of course it would be likewise possible to indicate the corresponding terms at the farther calculations of the equation of state which we have mentioned in this contribution. To indicate the principle it seemed to us to be sufficient to treat only the thermal pressure in this way. Further we must point out that if once these terms are neglected it will have no sense to make any difference between the density before and after the strain, when we calculate the energy for a unit of volume, or to take into account other differences of the same kind. VAN EVERDINGEN has not always considered this (l.c. pg. 22—23); in consequence of this there occur terms in his results that are of the same order as the other neglected terms.

4. Besides the dynamic way we developed above, there is another method in which the results of BORN's general theory about the specific heat as well as known thermodynamic relations are used. This method shows a certain conformity with the one used by DEBYE-v. EVERDINGEN, but enables us to put the problem more strictly, whereas it has in common with the method given above the advantage that it can introduce or not the theory of the quanta of energy and may be easily extended to the temperatures where the approximations of v. EVERDINGEN prevail no more. Moreover it can easily be extended to a theory of the equation of state of a crystal of any class of symmetry. Instead of using a characteristic temperature as v. EVERDINGEN does — who also introduces the incorrect approximation that there is only *one* characteristic temperature — the specific heat itself is used. Hence the approximation which v. EVERDINGEN introduces on p. 35 of his dissertation, the consequences of which it is impossible fully to survey, viz. the application of formulae which prevail for the isotropic body to a aeolotropic body, can be avoided.

Now the principle of our method is as follows. When the deformations e_1, e_2, e_3 are given to the body X_x may be represented (as is demonstrated in (2)) e.g. by

$$X_x = X_x^t + a e_1 + b (e_2 + e_3)$$

in which X_x^t is the thermal pressure for the isotropic body for $e_1 = e_2 = e_3 = 0$, and a and b are functions of temperature. On account of the isotropy in X_x the coefficient of e_2 has to be equal to that of e_3 ; Y_y and Z_z hence follow by cyclic interchange.

X_y etc., on account of the isotropy, are at the given deformation zero.

Now the specific heat can be calculated by application of the formulae of BORN to the rhombic crystal with the e 's given above. As we start from an isotropic body the development of the specific heat in terms of e_1, e_2, e_3 will only depend on the invariants. So we may put

$$C_v = C_{v0} + a I_1 + \beta I_1^2 + \gamma I_2 + \dots$$

in which C_v means the specific heat at constant e_1, e_2, e_3 , C_{v0} that for $e_1 = e_2 = e_3 = 0$.

Now we can apply the thermodynamic relation

$$\frac{\partial C_v}{\partial e_1} = T \frac{d^2 X_x}{dT^2}$$

This gives

$$a + 2\beta (e_1 + e_2 + e_3) + \gamma (e_2 + e_3) = T \left\{ \frac{d^2 X_x^t}{dT^2} + \frac{d^2 a}{dT^2} e_1 + \frac{d^2 b}{dT^2} (e_2 + e_3) \right\}$$

from which follows:

$$\alpha = T \frac{d^2 X_x}{dT^2}$$

$$2\beta = T \frac{d^2 a}{dT^2}$$

$$2\beta + \gamma = T \frac{d^2 b}{dT^2}$$

The functions of temperature $\alpha \beta \gamma$ can be calculated from the formulae of BORN so that X_x , a and b can be determined. In a more detailed communication we will communicate this calculation itself also.

Delft, June 1916.

Phys. Lab. of the T. H. S.

Physics. — “The influence of accidental deviations of density on the equation of state.” By Prof. L. S. ORNSTEIN and Dr. F. ZERNIKE. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of June 24, 1916).

In their article in the Encyclopädie der mathematischen Wissenschaften the following statement by Prof. KAMERLINGH ONNES and Dr. KEESOM is found:

“Da bei der Annäherung an den kritischen Punkt Liquid—Gas die von den BOLTZMANN-GIBBS'schen Prinzipien beherrschten Dichteunterschiede (Schwambildung Nr 48f), der bis ∞ ansteigenden Zusammendrückbarkeit der Substanz wegen, besonders hervortreten, ist zu erwarten, dass bei der Entwicklung der Zustandsgleichung für die Umgebung des kritischen Punktes nach jenen Prinzipien Glieder auftreten werden, die mit der grossen Zusammendrückbarkeit in der Nähe des kritischen Punktes zusammenhängen. Diese Glieder werden wahrscheinlich durch die Art der Abweichung der Zusammendrückbarkeit in dem kritischen Gebiet (∞ im kritischen Punkt und von diesem aus, soweit sie das realisierbare homogene Gebiet betrifft, allseitig schnell abfallend) für dasselbe eine besondere Bedeutung erlangen, während sie für benachbarte Gebiete nicht mehr in Betracht kommen. Während eine allmähliche Verschiebung oder Verzerrung, die sich durch das ganze Diagramm durchzieht, wie z. B. eine kontinuierliche Aenderung von a_w , b_w oder R_w , sich experimentell nicht besonders zeigen würde, werden die betreffende Glieder in der Zustandsgleichung in der Nähe des kritischen Punktes demgemäss zum Schluss führen können, dass die Eigenschaften in diesem Gebiet in beobacht-