

# THE TEMPERATURE DEPENDENCE OF THE ELASTIC CONSTANTS OF A LATTICE

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## Summary

The temperature dependence of the elastic constants of a cubic lattice are calculated in the classical limit by means of a Bethe approximation. The expressions so derived are then applied to a simple model of some metals. The agreement between the derived and measured temperature dependence of the elastic constants of these metals is satisfactory.

## I. INTRODUCTION

In an earlier paper (Lloyd 1964, hereafter called I) the classical anharmonic contribution to the free energy of a lattice was evaluated using a Bethe approximation. This approximation may be viewed in either of two ways. Firstly, one can consider each atom in the lattice moving in an effective potential due to the other atoms. This effective potential is then determined in a self-consistent manner. Secondly, the approximation can be viewed as replacing the true lattice structure by a pseudo-lattice composed entirely of non-intersecting chains of atoms. In this respect the work is closely related to that of Barker (1961, 1962) and Lloyd and O'Dwyer (1963*a*, 1963*b*). The approximation is also entirely analogous to that of Bethe (1935), who studied the Ising model of ferromagnetism, with the exception that an atom has a continuum of possible positions while an Ising model spin may be only up or down. The pseudo-lattice of non-intersecting chains, which this approximation solves exactly, is known as a Bethe lattice. In I it was shown that this approximation was quite good when applied to a model which had been previously evaluated numerically by Maradudin, Flinn, and Coldwell-Horsfall (1961). Now the expression for the classical free energy, as derived in I, can be used to obtain the temperature dependence of the bulk modules of the solid in the high temperature limit. It cannot, however, be used to obtain the temperature dependence of the individual elastic constants  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$ . The reason for this is that the cubic lattice loses its symmetry under an arbitrary strain and this symmetry was implicitly assumed in the solution obtained in I. The purpose of the present paper is to derive the expressions for the temperature dependence of the elastic constants of a cubic lattice in the Bethe approximation.

The following work is also closely related to that of Born and his collaborators (Born 1939, 1943; Born and Bradburn 1943; Bradburn 1943; and Gow 1944), who have studied the equation of state of a lattice. To do so they introduced the "Born approximation" in which a lattice mode frequency squared,  $\omega^2$  is replaced by its average value  $\bar{\omega}^2$ . This approximation is equivalent to an Einstein approximation and as such it has been extended to lower temperatures by Henkel (1955)

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and Zucker (1958). The approximation has also been used by Leibfried and Hahn (1958), Ludwig (1958), and Leibfried and Ludwig (1961) to discuss the temperature dependence of the elastic constants. These authors use the Born approximation to evaluate the generalized Gruneisen constants of Davies and Parke (1959). Now the Born or Einstein approximation is the lattice dynamical analogue of the mean field approximation in the Ising model of ferromagnetism (cf. Domb 1960). By analogy with the Ising model the Bethe approximation is then the next logical approximation to investigate. However, while the Bethe approximation gives a significant improvement over the mean field approximation for the Ising model and a significant improvement over the Einstein approximation in evaluating the anharmonic correction to the specific heat, it is unlikely to cause much change in the calculated temperature dependence of the elastic constants. The adequacy of the Born approximation for this purpose has been discussed both by Bradburn (1943) and Leibfried and Ludwig (1961, Appendix, p. 439). The expressions derived below for the temperature dependence of the elastic constants may be used as a next higher approximation to test the accuracy of the Born approximation for a given model of the interatomic forces.

The expressions derived in the present paper are applied to a simple model of a metal. In particular they are applied to sodium, where the agreement with experiment is only marginal, and to the noble metals, copper and silver. Here the agreement with experiment is good.

## II. THE BETHE APPROXIMATION

The classical free energy of a pseudo-lattice of non-intersecting chains (the Bethe lattice or a Cayley tree characterized by the coordination number, cf. Domb 1960) with nearest neighbour forces, can be solved exactly. The reason for this is that as the chains do not intersect we can uniquely divide the atoms of the lattice into those to the left of a given nearest neighbour pair (1, 2), and those to the right; then any configurational integral taken over an atom to the left of atom 1 will lead to a contribution which is a function of the coordinates of atom 1 and not of both atom 1 and atom 2. If then  $U(\mathbf{q}_1, \mathbf{q}_2)$  is the nearest neighbour potential,  $\Psi(\mathbf{q}_1)$  is the contribution to the potential on atom 1 due to taking the configurational integral over all chains which join atom 1 through a given nearest neighbour bond, and  $\Sigma'\Psi(\mathbf{q}_1)$  is the potential on atom 1 due to taking the configurational integral over all atoms to the left of atom 1, we have

$$e^{-2\beta F}\rho_2(\mathbf{q}_1, \mathbf{q}_2) = \exp\{-\beta[\Sigma'\Psi(\mathbf{q}_1) + U(\mathbf{q}_1, \mathbf{q}_2) + \Sigma'\Psi(\mathbf{q}_2)]\}. \quad (2.1)$$

Here  $F$  is the configurational free energy per particle,  $\beta = 1/kT$  is the inverse temperature and  $\rho_2(\mathbf{q}_1, \mathbf{q}_2)$  is the probability distribution function of the nearest neighbour pair of atoms (1, 2). Similarly, if we now only consider one atom we obtain

$$e^{-\beta F}\rho_1(\mathbf{q}_1) = \exp\{-\beta\Sigma\Psi(\mathbf{q}_1)\}, \quad (2.2)$$

where  $\rho_1(\mathbf{q}_1)$  is the probability distribution function for one atom.  $\Sigma\Psi(\mathbf{q}_1)$  is the potential induced on atom 1 in the manner described above for two atoms. The lack of a prime on the summation denotes that the contribution from the chains

which join atom 1 through atom 2 are to be included in the summation. Due to the relation

$$\int \rho_2(\mathbf{q}_1, \mathbf{q}_2) d^3q_2 = \rho_1(\mathbf{q}_1), \quad (2.3)$$

this leads to an integral equation from which both  $\Psi(\mathbf{q}_1)$  and the free energy may be found.

That the exact solution of the pseudo-lattice can be found leads to an approximation for a real lattice by first replacing the interparticle potential by an approximate nearest neighbour potential and then finding the exact solution of the pseudo-lattice. This has been used to evaluate the anharmonic contributions to the specific heat in I.

In order to find the elastic constants we need to know the free energy to the second order in strain. Owing to surface effects, the static deformation method can lead to difficulties in the evaluation of the elastic constants (cf. Born and Huang 1956), but this is not so for central forces and we shall limit ourselves to this case.

Putting the interparticle potential as  $U_\alpha + \delta U_\alpha$ , where  $\alpha$  labels the nearest neighbour pair of atoms, and the configurational free energy as  $F_0 + \delta F$ , where  $\delta U_\alpha$  and  $\delta F$  are the strain-dependent parts, we have

$$\exp -\beta N(F_0 + \delta F) = \int \dots \int \left\{ \exp -\beta \sum_\alpha (U_\alpha + \delta U_\alpha) \right\} d^{3N}q.$$

Expanding this equation gives

$$\delta F = \frac{1}{N} \sum_\alpha \langle \delta U_\alpha \rangle - \frac{1}{2} \beta \frac{1}{N} \sum_\alpha \sum_\gamma \left\{ \langle \delta U_\alpha \delta U_\gamma \rangle - \langle \delta U_\alpha \rangle \langle \delta U_\gamma \rangle \right\}, \quad (2.4)$$

where the expectation  $\langle \dots \rangle$  is over the "unperturbed" distribution  $\sum_\alpha U_\alpha$ . The expectation  $\langle \delta U_\alpha \rangle$  is then

$$\langle \delta U_\alpha \rangle = \iint \delta U_\alpha(\mathbf{q}_1, \mathbf{q}_2) \rho_2(\mathbf{q}_1, \mathbf{q}_2) d^3q_1 d^3q_2 \quad (2.5)$$

and  $\rho_2(\mathbf{q}_1, \mathbf{q}_2)$  is known from the solution of the unperturbed case.

By use of the approximation explained above, terms of the form

$$T_\alpha = \sum_\gamma \left\{ \langle \delta U_\alpha \delta U_\gamma \rangle - \langle \delta U_\alpha \rangle \langle \delta U_\gamma \rangle \right\}, \quad (2.6)$$

which occur in (2.4), may also be evaluated. It may be noted that this expression is not of the order  $N$  even though it involves a summation over all nearest neighbour pairs  $\gamma$ . The reason for this is that unless the pair  $\alpha$  is close to the pair  $\gamma$  then

$$\langle \delta U_\alpha \delta U_\gamma \rangle = \langle \delta U_\alpha \rangle \langle \delta U_\gamma \rangle$$

and no contribution is given to the summation.

For the Bethe lattice the term  $T_\alpha$  may be reduced to the solution of an integral equation. To do so we write

$$T_\alpha = \sum \langle (\delta U_\alpha - \langle \delta U_\alpha \rangle) (\delta U_\gamma - \langle \delta U_\gamma \rangle) \rangle. \quad (2.7)$$

Again, if the atoms of the pseudo-lattice are divided into those to the left of the pair  $\alpha$  and those to the right of the pair  $\alpha$ , then we may write

$$T_\alpha = \langle (\delta U_\alpha - \langle \delta U_\alpha \rangle) (\Sigma' \Phi(\mathbf{q}_1) + \delta U_\alpha - \langle \delta U_\alpha \rangle + \Sigma' \Phi(\mathbf{q}_2)) \rangle. \quad (2.8)$$

Here  $\Sigma' \Phi(\mathbf{q}_1)$  is the contribution of all members of the summation over  $\gamma$  which have  $\gamma$  to the left of the pair  $\alpha$ , and are on chains which join atom 1 through differing nearest neighbours. This expectation may be then taken as in (2.5). If we consider the detailed process of taking the configurational integral and the summation we see that  $\Phi(\mathbf{q}_1)$  satisfies the integral equation

$$\int \{ \Sigma' \Phi(\mathbf{q}_1) + \delta U_{\gamma}(\mathbf{q}_1, \mathbf{q}_2) - \langle \delta U_{\gamma} \rangle \} \rho_2(\mathbf{q}_1, \mathbf{q}_2) d^3q_1 = \Phi(\mathbf{q}_2) \rho_1(\mathbf{q}_2). \quad (2.9)$$

The elastic constants may then be found by

- (i) forming the change in the potential energy on strain,  $\delta U_\alpha$ ;
- (ii) calculating the free energy to second order in strain by means of (2.4), which is in turn evaluated using (2.5), (2.8), and (2.9);
- (iii) differentiating the free energy with respect to the strain components in order to obtain the elastic constants.

### III. EXPANSION OF THE POTENTIAL

Let  $\phi(r)$  be the central nearest neighbour potential for the pair of atoms of interest. We shall expand  $\phi(r)$  about  $\mathbf{r} = a\mathbf{p}$ , where  $a$  is the equilibrium nearest neighbour distance and  $\mathbf{p}$  a unit vector from atom 1 to atom 2. When the atoms are displaced and the lattice is strained we have

$$\mathbf{r} = a\mathbf{p} + a\mathbf{e} \cdot \mathbf{p} + \Delta\mathbf{q}, \quad (3.1)$$

where  $\mathbf{e}$  is the strain tensor and  $\Delta\mathbf{q} = \mathbf{q}_2 - \mathbf{q}_1$  is the displacement of the atoms from the strained equilibrium positions. This then gives

$$r^2 = a^2 + 2a^2\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p} + 2a\mathbf{p} \cdot \Delta\mathbf{q} + a^2\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{e} \cdot \mathbf{p} + 2a\Delta\mathbf{q} \cdot \mathbf{e} \cdot \mathbf{p} + \Delta\mathbf{q} \cdot \Delta\mathbf{q}. \quad (3.2)$$

The potential may now be expanded about  $\phi(a)$ . Only terms that are even in  $\mathbf{p}$  have been retained, as when the summation over all pairs of atoms is taken terms which are of odd order in  $\mathbf{p}$  will vanish. The result of the expansion to the necessary order (to give all terms which contribute to the elastic constants a term linear in temperature) is

$$\begin{aligned} \phi(r) = & \phi(a) + K_1 a \mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p} \\ & + \left\{ \frac{1}{2} K_1 a \mathbf{p} \cdot \mathbf{e} \cdot \mathbf{e} \cdot \mathbf{p} + \frac{1}{2} K_2 a^2 (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})^2 \right\} \\ & + \left\{ \frac{1}{2} K_2 a^2 (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p}) (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{e} \cdot \mathbf{p}) + \frac{1}{6} K_3 a^3 (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})^3 \right\} \\ & + \left\{ \frac{1}{2} a^{-1} K_1 (\Delta\mathbf{q} \cdot \Delta\mathbf{q}) + \frac{1}{2} K_2 (\mathbf{p} \cdot \Delta\mathbf{q})^2 \right\} \\ & + \left\{ \frac{1}{2} K_2 (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p}) (\Delta\mathbf{q} \cdot \Delta\mathbf{q}) + K_2 (\mathbf{p} \cdot \Delta\mathbf{q}) (\Delta\mathbf{q} \cdot \mathbf{e} \cdot \mathbf{p}) + \frac{1}{2} K_3 a (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p}) (\mathbf{p} \cdot \Delta\mathbf{q})^2 \right\} \\ & + \left\{ \frac{1}{4} K_2 (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{e} \cdot \mathbf{p}) (\Delta\mathbf{q} \cdot \Delta\mathbf{q}) + \frac{1}{2} K_2 \mathbf{p} (\Delta\mathbf{q} \cdot \mathbf{e} \cdot \mathbf{p})^2 \right\} \\ & + \left\{ \frac{1}{4} K_3 a (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})^2 (\Delta\mathbf{q} \cdot \Delta\mathbf{q}) + \frac{1}{4} K_3 a (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{e} \cdot \mathbf{p}) (\mathbf{p} \cdot \Delta\mathbf{q})^2 \right. \\ & \left. + K_3 a (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p}) (\mathbf{p} \cdot \Delta\mathbf{q}) (\Delta\mathbf{q} \cdot \mathbf{e} \cdot \mathbf{p}) + \frac{1}{4} K_4 a^2 (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})^2 (\mathbf{p} \cdot \Delta\mathbf{q})^2 \right\}, \end{aligned} \quad (3.3)$$

where

$$\begin{aligned} K_1 &= \phi^I(a) \\ K_2 &= \phi^{II}(a) - a^{-1}\phi^I(a) \\ K_3 &= \phi^{III}(a) - 3a^{-1}\phi^{II}(a) + 3a^{-2}\phi^I(a) \\ K_4 &= \phi^{IV}(a) - 6a^{-1}\phi^{III}(a) + 15a^{-2}\phi^{II}(a) - 15a^{-3}\phi^I(a). \end{aligned}$$

These terms give the following contributions to the free energy.

1.  $\phi(a)$  is a constant term, independent of both strain and temperature. This gives a contribution to the dissociation energy of the lattice.
2.  $K_1 a \mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p}$  forms part of a contribution which must vanish if “ $a$ ” is the equilibrium distance. This is the equilibrium distance at  $T = 0$  classically, and in practice is the “linearly extrapolated to zero” distance (cf. Leibfried and Ludwig 1961).
3.  $\{\frac{1}{2}K_1 a \mathbf{p} \cdot \mathbf{e} \cdot \mathbf{e} \cdot \mathbf{p} + \frac{1}{2}K_2 a^2 (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})^2\}$  forms part of the contribution to the temperature independent part of the elastic constants.
4.  $\{\frac{1}{2}K_2 a^2 (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})(\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{e} \cdot \mathbf{p}) + \frac{1}{8}K_3 a^3 (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})^3\}$  forms part of the contribution to the third-order, temperature-independent elastic constants.
5.  $\{\frac{1}{2}a^{-1}K_1(\Delta \mathbf{q} \cdot \Delta \mathbf{q}) + \frac{1}{2}K_2(\mathbf{p} \cdot \Delta \mathbf{q})^2\}$  is the strain-independent harmonic term which gives rise to the unperturbed probability distribution. This part has been treated in I and gives rise to the distribution

$$\rho_2(\mathbf{q}_1, \mathbf{q}_2) = N \exp\{-\frac{1}{2}\beta[\mathbf{q}_1 \cdot \mathbf{A} \cdot \mathbf{q}_1 - 2\mathbf{q}_1 \cdot \boldsymbol{\alpha} \cdot \mathbf{q}_2 + \mathbf{q}_2 \cdot \mathbf{A} \cdot \mathbf{q}_2]\}, \quad (3.4)$$

where the tensor  $\mathbf{A}$  is given by

$$\mathbf{A} = A_1 \mathbf{p} \mathbf{p} + A_2 (\mathbf{I} - \mathbf{p} \mathbf{p}),$$

and

$$\boldsymbol{\alpha} = \alpha_1 \mathbf{p} \mathbf{p} + \alpha_2 (\mathbf{I} - \mathbf{p} \mathbf{p}). \quad (3.5)$$

Explicit expressions for  $A_1$  and  $A_2$  are given in I.

6.  $\{\frac{1}{2}K_2(\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})(\Delta \mathbf{q} \cdot \Delta \mathbf{q}) + K_2(\mathbf{p} \cdot \Delta \mathbf{q})(\Delta \mathbf{q} \cdot \mathbf{e} \cdot \mathbf{p}) + \frac{1}{2}K_3 a (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})(\mathbf{p} \cdot \Delta \mathbf{q})^2\}$ . This term contributes to the free energy in two ways. When substituted in (2.7) to first order it gives a contribution to the free energy proportional to  $T$  and to  $(e_{11} + e_{22} + e_{33})$ . This term then gives the thermal expansion. The result is identical with that obtained in I. When this term is substituted in (2.7) to the second order, we obtain a contribution to the elastic constants which is proportional to temperature. As this contribution depends on the third-order differential of the potential squared, we shall denote it by  $c^{(3,3)}$ .
7. The last part of the expansion (3.3) need only be substituted in (2.7) to first order to obtain a contribution to the elastic constants which is proportional to temperature. As this depends on the fourth-order differential of the potential we shall denote this contribution by  $c^{(4)}$ .

#### IV. EVALUATION OF $c^{(4)}$

In order to evaluate the fourth-order part of the elastic constants we form the first-order contribution to the free energy (2.7)

$$\delta F = \frac{1}{N} \sum_{\alpha} \langle \delta \phi_{\alpha} \rangle,$$

with

$$\begin{aligned} \delta\phi_\alpha = & \frac{1}{2}K_2(\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{e} \cdot \mathbf{p})(\Delta\mathbf{q} \cdot \Delta\mathbf{q}) + \frac{1}{2}K_2(\Delta\mathbf{q} \cdot \mathbf{e} \cdot \mathbf{p})^2 + \frac{1}{4}K_3a(\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})^2(\Delta\mathbf{q} \cdot \Delta\mathbf{q}) \\ & + K_3a(\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})(\mathbf{p} \cdot \Delta\mathbf{q})(\Delta\mathbf{q} \cdot \mathbf{e} \cdot \mathbf{p}) + \frac{1}{4}K_4a^2(\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})^2(\mathbf{p} \cdot \Delta\mathbf{q})^2. \end{aligned} \quad (4.1)$$

As all atoms are equivalent (2.7) may be altered to

$$\delta F = \frac{1}{2} \sum_{\mathbf{p}} \langle \delta\phi_\alpha \rangle.$$

Using the distribution (3.4), (3.5) the expectation may be taken to give

$$\begin{aligned} \delta F = & \frac{1}{2} \sum_{\mathbf{p}} \left\{ \frac{2}{\beta} \frac{1}{A_1 + \alpha_1} \left[ \left( \frac{1}{4}K_3a + \frac{1}{4}K_2 \right) (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{e} \cdot \mathbf{p}) + \left( \frac{1}{4}K_4a^2 + \frac{5}{4}K_3a + \frac{1}{2}K_2 \right) (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})^2 \right] \right. \\ & \left. + \frac{2}{\beta} \frac{1}{A_2 + \alpha_2} \left[ K_2(\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{e} \cdot \mathbf{p}) + \left( \frac{1}{2}K_3a - \frac{1}{2}K_2 \right) (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})^2 \right] \right\}. \end{aligned} \quad (4.2)$$

The summation over  $\mathbf{p}$  may now be taken. We use the formula

$$\left. \begin{aligned} \sum_{\mathbf{p}} p_i p_i &= q\epsilon_0, \\ \sum_{\mathbf{p}} p_i p_i p_i p_i &= q\epsilon_1, \\ \sum_{\mathbf{p}} p_i p_i p_i p_i p_i &= q\epsilon_2. \end{aligned} \right\} \quad (4.3)$$

Here  $q$  is the coordination number and we have for a face-centred cubic (f.c.c.) lattice

$$q = 12, \quad \epsilon_0 = \frac{1}{3}, \quad \epsilon_1 = \frac{1}{6}, \quad \epsilon_2 = \frac{1}{12}, \quad (4.4)$$

while for a body-centred cubic (b.c.c.) lattice we have

$$q = 8, \quad \epsilon_0 = \frac{1}{3}, \quad \epsilon_1 = \frac{1}{9}, \quad \epsilon_2 = \frac{1}{9}. \quad (4.5)$$

The summation is then equated to

$$\delta F = \frac{1}{2} V_A \{ c_{11}^{(4)}(e_{11}^2 + e_{22}^2 + e_{33}^2) + 2c_{12}^{(4)}(e_{22}e_{33} + e_{11}e_{33} + e_{11}e_{22}) + 4c_{44}^{(4)}(e_{23}^2 + e_{13}^2 + e_{12}^2) \}, \quad (4.6)$$

where  $V_A$  is the volume of one atom.

When this is done the final result is

$$\begin{aligned} c_{11}^{(4)} = & \frac{q}{V_A \beta} \left\{ \frac{\frac{1}{2}\epsilon_0}{A_1 + \alpha_1} (K_3a + K_2) + \frac{\frac{1}{2}\epsilon_1}{A_1 + \alpha_1} (K_4a^2 + 5K_3a + 2K_2) \right. \\ & \left. + \frac{2\epsilon_0}{A_2 + \alpha_2} K_2 + \frac{\epsilon_1}{A_2 + \alpha_2} (K_3a - K_2) \right\}, \end{aligned} \quad (4.7)$$

$$c_{12}^{(4)} = \frac{q}{V_A \beta} \left\{ \frac{\frac{1}{2}\epsilon_2}{A_1 + \alpha_1} (K_4a^2 + 5K_3a + 2K_2) + \frac{\epsilon_2}{A_2 + \alpha_2} (K_3a - K_2) \right\}, \quad (4.8)$$

$$c_{44}^{(4)} = \frac{q}{V_A \beta} \left\{ \frac{\frac{1}{2}\epsilon_0}{A_1 + \alpha_1} (K_3 a + K_2) + \frac{\frac{1}{2}\epsilon_2}{A_1 + \alpha_1} (K_4 a^2 + 5K_3 a + 2K_2) + \frac{\epsilon_0}{A_2 + \alpha_2} K_2 + \frac{\epsilon_2}{A_2 + \alpha_2} (K_3 a - K_2) \right\}. \quad (4.9)$$

### V. EVALUATION OF $c^{(3,3)}$

The evaluation of the cubic squared contributions are not as straightforward as the evaluation of  $c^{(4)}$ . In order to find (2.7) we have

$$\delta F = -\frac{1}{2}\beta \frac{1}{N} \sum_{\alpha} \sum_{\gamma} \left\{ \langle \delta\phi_{\alpha} \delta\phi_{\gamma} \rangle - \langle \delta\phi_{\alpha} \rangle \langle \delta\phi_{\gamma} \rangle \right\},$$

with

$$\delta\phi_{\alpha} = \frac{1}{2}K_2(\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})(\Delta\mathbf{q} \cdot \Delta\mathbf{q}) + K_2(\mathbf{p} \cdot \Delta\mathbf{q})(\Delta\mathbf{q} \cdot \mathbf{e} \cdot \mathbf{p}) + \frac{1}{2}K_3 a(\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})(\mathbf{p} \cdot \Delta\mathbf{q})^2. \quad (5.1)$$

We must first solve the integral equation (2.5) and reduce (2.3) to (2.4). Equation (2.3) is closely related to (2.7) if  $\theta_{\alpha} = \delta\phi_{\alpha}$ ,  $\phi_0 = \delta\phi_{\gamma}$ . By selecting one atom and nearest neighbour direction  $\mathbf{p}$  for  $\gamma$  and calling this "0" we have

$$\delta F = -\frac{1}{4}\beta \sum_{\mathbf{p}} \left\{ \sum_{\alpha} (\langle \delta\phi_{\alpha} \delta\phi_0 \rangle - \langle \delta\phi_{\alpha} \rangle \langle \delta\phi_0 \rangle) \right\}, \quad (5.2)$$

or

$$\delta F = -\frac{1}{4}\beta \sum_{\mathbf{p}} \left\{ [\Sigma' \Phi(\mathbf{q}_1) + \delta\phi_0(\mathbf{q}_1, \mathbf{q}_2) - \langle \delta\phi \rangle + \Sigma' \Phi(\mathbf{q}_2)] [\delta\phi_0(\mathbf{q}_1, \mathbf{q}_2) - \langle \delta\phi_0 \rangle] \right\}. \quad (5.3)$$

$\Phi(\mathbf{q})$  satisfies the integral equation

$$\int [\Sigma' \Phi(\mathbf{q}_1) + \delta\phi(\mathbf{q}_1, \mathbf{q}_2) - \langle \delta\phi \rangle] \rho_2(\mathbf{q}_1, \mathbf{q}_2) d^3 q_1 = \Phi(\mathbf{q}_2) \rho_1(\mathbf{q}_2). \quad (5.4)$$

The integral equation (5.4) may be solved with  $\Phi(\mathbf{q})$  as the sum of a harmonic function and a constant. It may be noted that the constant is irrelevant to the determination of  $\delta F$  and will be ignored. A solution for the harmonic part of  $\Phi(\mathbf{q})$  may be found by substituting

$$\begin{aligned} \Phi(\mathbf{q}) = & \{k_0 |e| \mathbf{q} \cdot \mathbf{q} + k_1 \mathbf{q} \cdot \mathbf{e} \cdot \mathbf{q} + k_2 \mathbf{q} \cdot \hat{\mathbf{z}} \cdot \mathbf{q} \\ & + k_3 |e| (\mathbf{p} \cdot \mathbf{q})^2 + 2k_4 (\mathbf{p} \cdot \mathbf{q})(\mathbf{q} \cdot \mathbf{e} \cdot \mathbf{p}) \\ & + 2k_5 (\mathbf{p} \cdot \mathbf{q})(\mathbf{q} \cdot \hat{\mathbf{z}} \cdot \mathbf{p}) + k_6 (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})(\mathbf{q} \cdot \mathbf{q}) \\ & + k_7 (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})(\mathbf{p} \cdot \mathbf{q})^2 + k_8 (\mathbf{p} \cdot \hat{\mathbf{z}} \cdot \mathbf{p})(\mathbf{p} \cdot \mathbf{q})^2 \}. \end{aligned} \quad (5.5)$$

Here

$$|e| = e_{11} + e_{22} + e_{33}$$

and  $\hat{\mathbf{z}}$  is the diagonal part of the strain tensor  $\mathbf{e}$ , that is,

$$\hat{\mathbf{z}} = \begin{bmatrix} e_{11} & 0 & 0 \\ 0 & e_{22} & 0 \\ 0 & 0 & e_{33} \end{bmatrix}.$$

This is a tensor under the restricted group of rotations corresponding to cubic lattice symmetry.

The summation over the nearest neighbour directions, excluding the direction  $\mathbf{p}$ , gives

$$\begin{aligned} \Sigma' \Phi(\mathbf{q}) = & \{l_0|e|\mathbf{q} \cdot \mathbf{q} + l_1\mathbf{q} \cdot \mathbf{e} \cdot \mathbf{q} + l_2\mathbf{q} \cdot \hat{\mathbf{e}} \cdot \mathbf{q} \\ & - k_3|e|(\mathbf{p} \cdot \mathbf{q})^2 - 2k_4(\mathbf{p} \cdot \mathbf{q})(\mathbf{q} \cdot \mathbf{e} \cdot \mathbf{p}) \\ & - 2k_5(\mathbf{p} \cdot \mathbf{q})(\mathbf{q} \cdot \hat{\mathbf{e}} \cdot \mathbf{p}) - k_6(\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})(\mathbf{q} \cdot \mathbf{q}) \\ & - k_7(\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})(\mathbf{p} \cdot \mathbf{q})^2 - k_8(\mathbf{p} \cdot \hat{\mathbf{e}} \cdot \mathbf{p})(\mathbf{p} \cdot \mathbf{q})^2\}, \end{aligned} \quad (5.6)$$

where

$$l_0 = (q-1)k_0 + q\epsilon_0k_3 + q\epsilon_0k_6 + q\epsilon_2k_7 + q\epsilon_2k_8, \quad (5.7)$$

$$l_1 = (q-1)k_1 + 2q\epsilon_0k_4 + 2q\epsilon_2k_7, \quad (5.8)$$

$$l_2 = (q-1)k_2 + 2q\epsilon_0k_5 + q(\epsilon_1 - 3\epsilon_2)k_7 + q(\epsilon_1 - \epsilon_2)k_8. \quad (5.9)$$

Substituting equations (5.6) and (5.1) into the integral equation (5.4), and using the distribution (3.4), gives nine algebraic equations for the nine unknowns  $k_0 \dots k_8$ . When these are solved we obtain

$$k_6 = \frac{1}{2}(1-r_2)^2(1+r_2^2)^{-1}K_2, \quad (5.10)$$

and

$$\begin{aligned} l_1 \left\{ 1 - (q-1)r_2^2 - q\epsilon_0 \frac{2(r_1-r_2)r_2}{1+r_1r_2} - q\epsilon_2 \frac{2(r_1-r_2)^2}{1+r_1^2} \cdot \frac{(1-r_1r_2)}{1+r_1r_2} \right\} \\ = q\epsilon_2(K_3a + 3K_2) \frac{(1-r_1)^2}{1+r_1^2} + qK_2 \left\{ (\epsilon_0 - 2\epsilon_2) \frac{(1-r_1)(1-r_2)}{1+r_1r_2} - \epsilon_2 \frac{(1-r_2)^2}{1+r_2^2} \right\}. \end{aligned} \quad (5.11)$$

(In order to avoid confusion the denominator has not been transferred to the right-hand side.)

$$k_4 = \frac{(r_1-r_2)r_2}{1+r_1r_2}l_1 + \frac{(1-r_1)(1-r_2)}{1+r_1r_2} \frac{1}{2}K_2, \quad (5.12)$$

$$k_7 = \frac{(r_1-r_2)^2}{1+r_1^2} \cdot \frac{(1-r_1r_2)}{1+r_1r_2}l_1 + \frac{1}{2} \frac{(1-r_1)^2}{1+r_1^2} (K_3a + 3K_2) - K_2 \left\{ \frac{1}{2} \frac{(1-r_2)^2}{1+r_2^2} + \frac{(1-r_1)(1-r_2)}{1+r_1r_2} \right\}, \quad (5.13)$$

$$l_2 \left\{ 1 - (q-1)r_2^2 - q\epsilon_0 \frac{2(r_1-r_2)r_2}{1+r_1r_2} - q(\epsilon_1 - \epsilon_2) \frac{(r_1-r_2)^2}{1+r_1^2} \cdot \frac{(1-r_1r_2)}{1+r_1r_2} \right\} = q(\epsilon_1 - 3\epsilon_2)k_7, \quad (5.14)$$

$$k_5 = \frac{(r_1-r_2)r_2}{1+r_1r_2}l_2, \quad (5.15)$$

$$k_8 = \frac{(r_1-r_2)^2}{1+r_1^2} \frac{(1-r_1r_2)}{1+r_1r_2}l_2, \quad (5.16)$$

$$l_0 \left\{ 1 - (q-1)r_2^2 - q\epsilon_0 \frac{r_1^2 - r_2^2}{1+r_1^2} \right\} = q\epsilon_0k_6 + q\epsilon_2k_7 + q\epsilon_2k_8, \quad (5.17)$$

$$k_3 = \frac{r_1^2 - r_2^2}{1 + r_1^2}, \quad (5.18)$$

where

$$r_1 = a_1/A_1, \quad r_2 = a_2/A_2. \quad (5.19)$$

These equations solve the integral equation. Now we substitute  $\Sigma'\Phi$  (equation 5.6) into the equation (5.3) for  $\delta F$ , take the expectation and the summation over  $\mathbf{p}$ , and then separate into the elastic constants, as was done for  $c^{(4)}$ . The result is

$$\begin{aligned} c_{11}^{(3,3)} = & -\frac{q}{V_A\beta} \left\{ \frac{K_3 a + 3K_2}{(A_1 + a_1)^2} \times \right. \\ & [\epsilon_0(l_0 - k_3) + \epsilon_1(K_3 a + 3K_2 + l_1 + l_2 - 2k_4 - 2k_5 - k_6 - k_7 - k_8)] \\ & + \frac{2K_2}{(A_1 + a_1)(A_2 + a_2)} [(\epsilon_0 - \epsilon_1)(K_2 + l_1 + l_2 - k_4 - k_5)] \\ & \left. + \frac{K_2}{(A_2 + a_2)^2} [\epsilon_0(2l_0 + l_1 + l_2) + \epsilon_1(2K_2 - l_1 - l_2 - 2k_6)] \right\}, \quad (5.20) \end{aligned}$$

$$\begin{aligned} c_{12}^{(3,3)} = & -\frac{q}{V_A\beta} \left\{ \frac{K_3 a + 3K_2}{(A_1 + a_1)^2} \times \right. \\ & [\epsilon_0(l_0 - k_3) + \epsilon_2(K_3 a + 3K_2 + l_1 + l_2 - 2k_4 - 2k_5 - k_6 - k_7 - k_8)] \\ & + \frac{2K_2}{(A_1 + a_1)(A_2 + a_2)} [(-\epsilon_2)(K_2 + l_1 + l_2 - k_4 - k_5)] \\ & \left. + \frac{K_2}{(A_2 + a_2)^2} [\epsilon_0(2l_0 + l_1 + l_2) + \epsilon_2(2K_2 - l_1 - l_2 - 2k_6)] \right\}, \quad (5.21) \end{aligned}$$

$$\begin{aligned} c_{44}^{(3,3)} = & -\frac{q}{V_A\beta} \left\{ \frac{K_3 a + 3K_2}{(A_1 + a_1)^2} [\epsilon_2(K_3 a + 3K_2 + l_1 - 2k_4 - k_6 - k_7)] \right. \\ & + \frac{2K_2}{(A_1 + a_1)(A_2 + a_2)} [(\frac{1}{2}\epsilon_0 - \epsilon_2)(K_2 + l_1 - k_4)] \\ & \left. + \frac{K_2}{(A_2 + a_2)^2} [\epsilon_2(2K_2 - l_1 - 2k_6)] \right\}. \quad (5.22) \end{aligned}$$

## VI. FURTHER CONTRIBUTIONS TO THE TEMPERATURE DEPENDENCE OF THE ELASTIC CONSTANTS

If we desired to calculate the temperature dependence of the isothermal elastic constants, measured under conditions in which the external hydrostatic pressure was adjusted to maintain a constant volume independent of temperature, then the result would be the sum of the two contributions already calculated. However, we desire to calculate the temperature dependence of the adiabatic elastic constants, measured under conditions of a fixed external pressure so that thermal expansion takes place. This gives rise to three further contributions.

The difference between the adiabatic and isothermal elastic constant will be denoted by  $c^{(D)}$  and for a cubic lattice we have

$$\left. \begin{aligned} c_{11}^{(D)} &= c_{12}^{(D)} = 3\gamma^2/\beta V_A, \\ c_{44}^{(D)} &= 0, \end{aligned} \right\} \quad (6.1)$$

where

$$\gamma = \alpha V_A(c_{11} + 2c_{12})/c_v$$

is the Gruneisen constant.

The effect of the thermal expansion can be broken into two parts. The first part is due to the volume expansion. This gives a contribution

$$c_{ij}^{(V)} = -3\alpha T c_{ij}^{(0)}, \quad (6.2)$$

where  $c_{ij}^{(0)}$  is the temperature-independent part of the elastic constants and  $\alpha$  is the linear thermal expansion.

The thermal expansion also causes the value of the harmonic constants at the equilibrium distance to alter. This gives a contribution

$$c_{ij,mn}^{(H)} = \frac{1}{V_A} \sum_{r,s} \frac{\partial^3 F}{\partial e_{ij} \partial e_{mn} \partial e_{rs}} \left\{ \alpha \delta_{rs} T \right\}. \quad (6.3)$$

The appropriate part of the free energy to use is

$$\delta F = \frac{1}{2} \sum_p \left\{ \frac{1}{2} K_2 a^2 (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})(\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{e} \cdot \mathbf{p}) + \frac{1}{6} K_3 a^3 (\mathbf{p} \cdot \mathbf{e} \cdot \mathbf{p})^3 \right\}. \quad (6.4)$$

In Voigt notation this gives the contribution

$$c_{11}^{(H)} = (qaTa^2/2V_A) \{ \epsilon_1 [K_3 a + 3K_2] + (\epsilon_0 - \epsilon_1) K_2 \}, \quad (6.5)$$

$$c_{12}^{(H)} = (qaTa^2/2V_A) \{ \epsilon_2 [K_3 a + 3K_2] - \epsilon_2 K_2 \}, \quad (6.6)$$

$$c_{44}^{(H)} = (qaTa^2/2V_A) \{ \epsilon_2 [K_3 a + 3K_2] + (\frac{1}{2}\epsilon_0 - \epsilon_2) K_2 \}. \quad (6.7)$$

The total contribution to the temperature-dependent part of the adiabatic elastic constant is then

$$c_{ij} = c_{ij}^{(4)} + c_{ij}^{(3,3)} + c_{ij}^{(D)} + c_{ij}^{(V)} + c_{ij}^{(H)}. \quad (6.8)$$

### VII. APPLICATION TO SOME METALS

In I an extension of a model due to Fuchs (1935) was used. In this model it is assumed that the conduction electrons give rise to a contribution to the free energy of the analytic form

$$F_e = F_1(V) + F_2(V)T^2 + 0(T^3). \quad (7.1)$$

This is the same analytic form as given for the one-electron model. It is also assumed that short-range restoring potentials exist between the individual ions of the lattice. A model very similar to this has been used by Horton (1961) in order to discuss the thermal expansion of copper. However, the model must be treated

as phenomenological, since Daniels and Smith (1958) have shown that it is impossible to predict the pressure dependence of the elastic constants using this model. The harmonic part of the short-range potentials is taken to be adequately represented by a central force between nearest and next nearest neighbours. This has been the basis of several studies of the vibration spectra of metals (cf. de Launay 1956). If  $\alpha_1$  is the harmonic constant for nearest neighbours and  $\alpha_3$  that for second nearest neighbours, then the electronic contribution to the elastic constants may be eliminated to give

$$\alpha_1 = \frac{3}{2}bc_{44}, \quad \alpha_3 = \frac{1}{2}b(c_{11}-c_{12}) \quad (7.2)$$

for a b.c.c. lattice. For a f.c.c. lattice we obtain

$$\alpha_1 = bc_{44}, \quad \alpha_3 = \frac{1}{4}b(c_{11}-c_{12}-c_{44}). \quad (7.3)$$

Here  $b$  is the cubic cell parameter.

In order to study the effect of anharmonicity on the elastic constants we make some additional assumptions. We assume that the anharmonic part of the potential can be adequately represented by a central nearest neighbour force. In addition we assume that the ratio of the derivatives of the potential are the same as for a Morse potential, which is the potential often used for a diatomic molecule. This then gives

$$\left. \begin{aligned} \phi^{\text{II}}(a) &= \alpha_1, \\ \phi^{\text{III}}(a) &= -3(A/a)\alpha_1, \\ \phi^{\text{IV}}(a) &= 7(A/a)^2\alpha_1. \end{aligned} \right\} \quad (7.4)$$

The form of the electronic contribution as given by (7.1) affects neither the temperature dependence of the elastic constants nor the Gruneisen constant. The latter is given in I (for this model) as

$$\gamma = \frac{1}{3}q\{a_1A/2(A_1+a_1)-a_1/3A_2\}. \quad (7.5)$$

The Gruneisen constant will be fitted in order to obtain  $A$ . The temperature-independent part of the elastic constants will be used to determine  $\alpha_1$  and  $\alpha_3$ .

$$\alpha_2 = 0.$$

We have from I that

$$\begin{aligned} A_2 &= \frac{1}{3}q\eta + \frac{1}{3}q'\alpha_3, \\ A_1 &= A_2 - \eta + \alpha_1, \end{aligned} \quad (7.6)$$

where

$$\eta = \frac{1}{3}\alpha_1\{(1-3\alpha_3/\alpha_1)+[(1-3\alpha_3/\alpha_1)^2+30\alpha_3/\alpha_1]^{\frac{1}{2}}\}$$

for a b.c.c. lattice and

$$\eta = \frac{1}{3}\alpha_1\{(1-\alpha_3/\alpha_1)+[(1-\alpha_3/\alpha_1)^2+6\alpha_3/\alpha_1]^{\frac{1}{2}}\} \quad (7.7)$$

for a f.c.c. lattice.

With these assumptions the temperature dependence of the elastic constants of sodium and the noble metals, copper and gold, may be calculated. The elastic data

for these metals have been taken from Leibfried and Ludwig (1961), while the thermal expansion data have been taken from Collins and White (1964). The results have been set out in Table 1 in the form

$$c_{ij} = c_{ij}^{(0)}[1 - D_{ij}kT],$$

together with the experimental values, which were also taken from Leibfried and Ludwig.

TABLE 1  
TEMPERATURE DEPENDENCE OF THE ELASTIC CONSTANTS  
The calculated results are expressed as  $c_{ij} = c_{ij}^{(0)}[1 - D_{ij}kT]$ .  
The experimental values are taken from Leibfried and Ludwig  
(1961).

Metal	$D_{11}k$ ( $10^{-3}$ deg $^{-1}$ )	$D_{12}k$ ( $10^{-3}$ deg $^{-1}$ )	$D_{44}k$ ( $10^{-3}$ deg $^{-1}$ )
Sodium			
(calculated)	1.204	1.450	1.814
(measured)	0.69	0.65	1.26
Copper			
(calculated)	0.237	0.163	0.274
(measured)	0.24 (0.34)	0.15 (0.27)	0.38 (0.35)
Silver			
(calculated)	0.242	0.158	0.315
(measured)	0.24	0.16	0.40

It can be seen that all the results for sodium are too high. A specific breakdown of the contributions to  $D_{ij}k$  for sodium is

$$\begin{aligned} D_{11}^{(4)}k &= -0.232 \times 10^{-3} \text{ deg}^{-1}, \\ D_{11}^{(3,3)}k &= +0.800 \times 10^{-3} \text{ deg}^{-1}, \\ D_{11}^{(D)}k &= -0.171 \times 10^{-3} \text{ deg}^{-1}, \\ D_{11}^{(V)}k &= +0.205 \times 10^{-3} \text{ deg}^{-1}, \\ D_{11}^{(H)}k &= +0.602 \times 10^{-3} \text{ deg}^{-1}, \end{aligned}$$

while the other components,  $D_{12}$  and  $D_{44}$ , are in much the same ratio. The agreement in the case of sodium could be greatly improved by raising  $\phi^{IV}(a)$  above that predicted by the Morse potential. This would also tend to improve the agreement between the measured rate of change of specific heat with temperature and that predicted in I.

In the case of the noble metals, copper and silver, the agreement between the predicted results and the experimental results is seen to be quite good. Leibfried and Ludwig (1961) quote two sets of values for the elastic constants of copper but only the main set has been used here. The second set of values gives results quite

close to those obtained with the first set. They also quote two sets of values for the measured rate of change of the elastic constants of copper with temperature. As these differ quite strongly, both sets have been included in Table 1. A detailed breakdown of the individual contributions to  $D_{11}k$  in the case of silver is

$$\begin{aligned} D_{11}^{(A)}k &= -0.233 \times 10^{-3} \text{ deg}^{-1}, \\ D_{11}^{(B,3)}k &= +0.309 \times 10^{-3} \text{ deg}^{-1}, \\ D_{11}^{(D)}k &= -0.104 \times 10^{-3} \text{ deg}^{-1}, \\ D_{11}^{(V)}k &= +0.053 \times 10^{-3} \text{ deg}^{-1}, \\ D_{11}^{(H)}k &= +0.217 \times 10^{-3} \text{ deg}^{-1}. \end{aligned}$$

The ratio of these contributions is much the same for the other components of silver and for copper.

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