

Electron Contribution to the Temperature Dependence of the Elastic Constants of Cubic Metals. I. Normal Metals*

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By direct calculation of the electron energy of a metal crystal as a function of elastic strain and temperature, it is shown that the elastic constants can exhibit a T^2 dependence at low temperatures. This temperature dependence arises from the displacement of the Fermi surface during strain and the simultaneous transfer of electrons across Brillouin zone boundaries. The results for face-centered cubic and body-centered cubic metals are obtained in terms of the energies of symmetry points in the Brillouin zone and the electron density of states and its first and second derivatives with respect to energy. The magnitude and algebraic sign of the temperature dependence are shown to depend critically on the shape of the Fermi surface and the electron density distribution. It is also shown that the form of the electron contribution to the temperature dependence of the elastic constants is directly analogous to that derived for the thermal variation of the paramagnetic susceptibility of metals at low temperatures.

1. INTRODUCTION

THE problem of the calculation of the elastic constants of solids has proceeded largely from the studies of Born and co-workers.¹ In this approach, a model of generalized forces between atoms is used to obtain interrelations between the atomic force constants at absolute zero and the macroscopic elastic constants. The temperature dependence of the elastic constants consequently arises from the variation of the lattice potential energy due to anharmonicity, or alternatively the temperature dependence of the elastic constants is described in terms of the phonon-phonon interactions due to the anharmonicity of the lattice vibrational frequencies.²

The Born approach, while a good approximation for insulators and perhaps semiconductors, is inadequate for metals. The total electron energy of a metal crystal arises from the interaction of the valence electrons with each other and with the ion-cores of the metal atoms. This interaction determines the phonon vibrational frequencies at absolute zero and, hence, the velocity of sound waves in the crystal.^{3,4} The elastic constants are obtained directly from the density of the metal and the sound velocities.⁴ An alternative approach has been to obtain the elastic constants by the direct calculation of the electron energy as a function of strain. This approach is discussed by Wigner and Seitz,⁵ Fuchs,⁶ Leigh,⁷ and others.^{8,9}

The thermal variation of the elastic constants of metals thus arises from the temperature dependence

of the electron energy due to the Fermi-Dirac distribution of electrons, and the temperature dependence of the lattice energy due to the anharmonicity of the crystal lattice vibrations.

Recent theoretical calculations by von Roos^{10,11} on the plasma theory of electron-phonon interactions in metals have shown that the electrons contribute to the temperature dependence of the renormalized longitudinal sound frequencies. Thus, the temperature dependence of ultrasonic sound velocities, and hence the elastic constants, may be expected to arise phenomenologically from the temperature dependence of the renormalized sound frequencies due to the electrons. Alers and Waldorf,¹² using a very sensitive ultrasonic technique, have found that in addition to a term in T^4 due to lattice anharmonicity, the elastic constants of vanadium and niobium exhibited a T^2 dependence at temperatures in the liquid-helium range. Alers¹³ further calculated that the estimated contributions from lattice anharmonicity were too small to be experimentally observed in the temperature range at which the T^2 dependence was found.

It is the purpose of this article to investigate the nature of the electron contribution to the temperature dependence of the elastic constants of cubic metals. It would perhaps be preferable to perform the calculations of the thermal variation on the basis of the plasma theory of electron-phonon interactions in order to preserve a logical progression of phenomenological effects. The limitations of a plasma theory and the present inability to treat shear distortions by this approach have directed our attention to calculating the electron energy of a metal crystal as a function of temperature and strain.⁵⁻⁹ As a result of these calculations we have found that the elastic constants can exhibit a T^2 dependence at low temperatures due to the electrons. The

* This work was initiated at the Union Carbide Research Institute, Tarrytown, New York, and completed at the American-Standard Research Division, New Brunswick, New Jersey.

¹ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954).

² E. A. Stern, *Phys. Rev.* **111**, 786 (1958).

³ J. Bardeen and D. Pines, *Phys. Rev.* **99**, 1140 (1955).

⁴ D. Bohm and T. Staver, *Phys. Rev.* **84**, 836 (1952).

⁵ E. P. Wigner and F. Seitz, *Phys. Rev.* **43**, 804 (1933).

⁶ K. Fuchs, *Proc. Roy. Soc. (London)* **A153**, 622 (1936).

⁷ R. S. Leigh, *Phil. Mag.* **42**, 139 (1951).

⁸ J. R. Reitz and C. S. Smith, *Phys. Rev.* **104**, 1253 (1956).

⁹ B. T. Bernstein, *J. Appl. Phys.* **33**, 143 (1962).

¹⁰ O. von Roos, *Phys. Rev.* **120**, 1641 (1960).

¹¹ O. von Roos, Jet Propulsion Laboratory Report, TR-32-106, 1961 (unpublished).

¹² G. A. Alers and D. L. Waldorf, *Phys. Rev. Letters* **6**, 677 (1961).

¹³ G. A. Alers (private communication).

magnitude and algebraic sign of the temperature dependence were found to depend critically on the shape of the Fermi surface and the electron density distribution. A model for the temperature dependence of the elastic shear constants of cubic metals is derived in Sec. 2. A derivation of the temperature dependence of the elastic bulk modulus for both isothermal and adiabatic strains is presented in Sec. 3. In Sec. 4 it is shown that the form of the temperature dependence of the elastic constants is directly analogous to that derived for the thermal variation of the paramagnetic susceptibility of metals at low temperatures. Finally, in Sec. 5, the results of the article are summarized and conclusions drawn.

2. ELECTRON CONTRIBUTION TO THE ELASTIC SHEAR CONSTANTS AT LOW TEMPERATURES

A. The Elastic Shear Constants

In this section, we consider the two elastic shear constants of cubic crystals, C and C' . The shear constant $C=C_{44}$ may be represented by volume conserving strains which change the crystal symmetry by extension in the $\langle 111 \rangle$ direction accompanied by that contraction in the perpendicular plane necessary to keep the volume constant. The shear constant $C'=\frac{1}{2}(C_{11}-C_{12})$ represents volume conserving strains which change the crystal symmetry by extension in the $\langle 001 \rangle$ direction accompanied by that contraction in the perpendicular plane necessary for volume conservation during shear. The shear constants C and C' correspond to strains which do not change the volume of a crystal during deformation, and, hence, are not dependent on whether the deformation is isothermal or adiabatic.

The internal energy of the electrons in a metal at low temperatures is given by the relation¹⁴

$$U(T) = U(0) + NV(T)^{\frac{1}{6}} (\pi kT)^2 g(\beta_0). \quad (1)$$

In Eq. (1), $U(0)$ is the internal energy at absolute zero, N is Avogadro's number, k is the Boltzmann constant, and V is the atomic volume. The parameter $g(\beta_0)$ is the total number of electron states per unit energy per unit volume, evaluated at the Fermi level β_0 at absolute zero. The spin factor of 2 is included in the expression for $g(\beta_0)$. The result of Eq. (1) is independent of any assumed model for the energy dependence of the density of states.¹⁴ It is for this reason that we have expressed the internal energy in the form given by Eq. (1) rather than assuming spheroidal energy surfaces and applying the Fermi-Dirac integral¹⁴ to obtain the temperature dependence. Since the adiabatic elastic shear constants are second derivatives of the internal energy with respect to strain, at constant entropy, the absence of volume change during shear considerably simplifies the differentiation of Eq. (1). If we let M represent C or C' and X an arbitrary strain parameter corresponding

to C or C' , the temperature dependence of the elastic shear constants is expressed directly as second derivatives of the total density of states at the Fermi level with respect to strain. This is given by the relation:

$$M(T) = M(0) \frac{V(0)}{V(T)} - \frac{1}{6} N (\pi kT)^2 \left(\frac{d^2 g(\beta_0)}{dX^2} \right)_0, \quad (2)$$

where the subscript zero indicates that the derivative is evaluated at zero strain.

B. Shear Distortion and the Electron Distribution

The calculations in this section and in Sec. 3 are considered for the case in which the deformation takes place slowly with respect to the electron relaxation time. As a consequence, the electron-phonon scattering processes have time to keep the electrons in equilibrium on the Fermi surface during strain. When a metal is sheared at constant volume the distortion of the lattice in real space causes a distortion of the Brillouin zone in reciprocal space. For those metals for which the Fermi surface is presumed to be a sphere lying wholly within the first Brillouin zone, the effect on the Fermi surface of movements of the bounding planes of the zone is small. As a consequence, the corresponding contribution to the elastic shear constants is negligible.⁷ For other metals the distortion of Brillouin zone boundaries, particularly in the case of electron overlap across or contact with zone boundaries, has an appreciable effect.⁷⁻⁹

The Brillouin zones for the body-centered cubic and face-centered cubic lattices, with points of symmetry designated, are shown in Figs. 1 and 2, respectively. During shear there is a shift of the electron energy surfaces near the Fermi surface, accompanied by electron transfer from certain positions on the Brillouin zone to others, in order that the electrons can occupy states of lower energy and maintain an equilibrium configura-

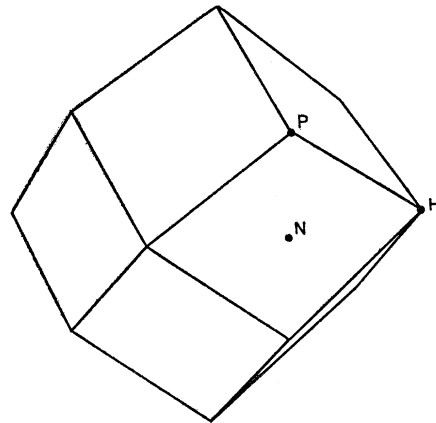


FIG. 1. Brillouin zone for the body-centered cubic lattice with points of symmetry shown.

¹⁴ R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, London, England, 1936), 2nd ed.

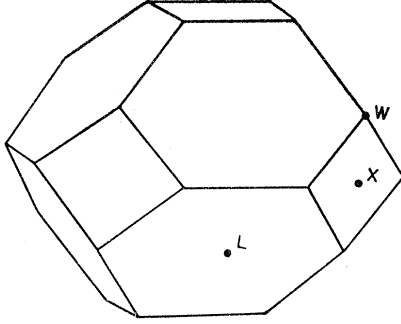


FIG. 2. Brillouin zone for the face-centered cubic lattice with points of symmetry shown.

tion. In addition, the curvature of the energy surfaces may change in order that the gradient of the energy vanishes at a point of symmetry in the sheared state. This corresponds to a change in the electron effective mass during shear.

We now make the assumption, as a first approximation, that during shear the energy at each overlap or hole symmetry point moves rigidly with the Brillouin zone boundary and that the electron effective mass is not a function of strain.^{7,8} Let us now consider the case where electron overlap across zone boundaries or contact with zone boundaries is present. We define by $g_i(\mu)$ the contribution to the total density of states at the Fermi level, $g(\beta_0)$, from those overlap or hole states with energy E_{ij} , i refers to the symmetry point of the zone and j refers to the number of equivalent pairs in the sheared state. We thus obtain the relations

$$\left(\frac{dg_i(\mu)}{dX}\right)_0 = \left(\frac{dg_i(\mu)}{d\mu}\right)_0 \left(\frac{d\mu}{dX}\right)_0 \quad (3)$$

and

$$\left(\frac{d^2g_i(\mu)}{dX^2}\right)_0 = \left(\frac{d^2g_i(\mu)}{d\mu^2}\right)_0 \left(\frac{d\mu}{dX}\right)_0^2 + \left(\frac{dg_i(\mu)}{d\mu}\right)_0 \left(\frac{d^2\mu}{dX^2}\right)_0, \quad (4)$$

where X represents a shear strain parameter corresponding to C or C' . We must now evaluate the first and second derivatives of the energies E_{ij} and β_0 in order to use Eq. (4) to solve for the second derivative of the total density of states at the Fermi level with respect to strain, as given in Eq. (2) and, hence, obtain the temperature dependence of C and C' .

C. Strain Dependence of the Electron Energies

In order to evaluate the strain dependence of the E_{ij} and β_0 we must consider how the reciprocal lattice, and hence the Brillouin zone, changes as the metal undergoes shear. The strain energy, per unit volume, of a cubic lattice is given in terms of the three independent elastic constants, C_{11} , C_{12} , and C_{44} , by the

equation

$$W = W_0 + \frac{1}{2}C_{11}(e_x^2 + e_y^2 + e_z^2) + C_{12}(e_x e_y + e_y e_z + e_z e_x) + \frac{1}{2}C_{44}(\gamma_1^2 + \gamma_2^2 + \gamma_3^2), \quad (5)$$

where e_x, e_y, e_z are the diagonal components of the strain tensor and the γ 's are the off-diagonal terms representing changes in angles between the principal axes of the crystal. For convenience in calculating contributions to the strain energy of the solid under the appropriate shear, it is expedient to write the lattice vectors in terms of a strain parameter $X = \xi, \eta$.

For the body-centered cubic lattice, the direct and reciprocal lattice vectors for the shear corresponding to C may be written in terms of a strain parameter η as

$$\begin{aligned} a_1 &= \frac{1}{2}a(1/B)(-\eta^{-1}, 1, 1), \\ a_2 &= \frac{1}{2}a(1/B)(1, -1, \eta^{-1}), \\ a_3 &= \frac{1}{2}a(1/B)(1, 1, -\eta^{-1}), \\ b_1 &= (\pi/a)(1/B^2)(\eta^{-2} - 1, 1 + \eta^{-1}, 1 + \eta^{-1}), \\ b_2 &= (\pi/a)(1/B^2)(1 + \eta^{-1}, \eta^{-2} - 1, 1 + \eta^{-1}), \\ b_3 &= (\pi/a)(1/B^2)(1 + \eta^{-1}, 1 + \eta^{-1}, \eta^{-2} - 1), \end{aligned}$$

with $B = \frac{1}{4}(3\eta^{-1} - \eta^{-3} + 2)$. The shear constant C is then given by

$$C = \frac{1}{3}(d^2W/d\eta^2)_0, \quad (7)$$

where at zero strain $\eta = 1$. For C' , the direct and reciprocal lattice vectors for the body-centered cubic lattice are written in terms of a strain parameter ξ as

$$\begin{aligned} a_1 &= \frac{1}{2}a\xi^{1/3}(-1, 1, \xi^{-1}), \\ a_2 &= \frac{1}{2}a\xi^{1/3}(1, -1, \xi^{-1}), \\ a_3 &= \frac{1}{2}a\xi^{1/3}(1, 1, -\xi^{-1}), \\ b_1 &= \frac{1}{2}a(2\pi/a)\xi^{1/3}(0, 1, \xi), \\ b_2 &= (2\pi/a)\xi^{-1/3}(1, 0, \xi), \\ b_3 &= (2\pi/a)\xi^{-1/3}(1, 1, 0). \end{aligned} \quad (8)$$

The shear constant C' is then given by

$$C' = \frac{3}{4}(d^2W/d\xi^2)_0, \quad (9)$$

where at zero strain $\xi = 1$.

The direct and reciprocal lattice vectors for the face-centered cubic lattice for shears corresponding to C and C' will not be tabulated here as they have already been given by Leigh.⁷

The reciprocal lattice vectors in the sheared state are used to determine $(dE_{ij}/dX)_0$ and $(d^2E_{ij}/dX^2)_0$ for C and C' for both the body-centered cubic and face-centered cubic lattices. Thus, one obtains

$$\left(\frac{dE_{ij}}{dX}\right)_0 = \left(\frac{dE_{ij}}{dK_{ij}}\right)_0 \left(\frac{dK_{ij}}{dX}\right)_0 \quad (10)$$

and

$$\left(\frac{d^2E_{ij}}{dX^2}\right)_0 = \left(\frac{d^2E_{ij}}{dK_{ij}^2}\right)_0 \left(\frac{dK_{ij}}{dX}\right)_0^2 + \left(\frac{dE_{ij}}{dK_{ij}}\right)_0 \left(\frac{d^2K_{ij}}{dX^2}\right)_0, \quad (11)$$

where K_{ij} is a reciprocal lattice vector from the origin of the Brillouin zone to the point of symmetry. For both the body-centered cubic and face-centered cubic lattices, it was found that

$$\sum_{ij}(dK_{ij}/dX)_0=0 \quad (12)$$

for all i . The vanishing of the sum of $(dK_{ij}/dX)_0$ for all i follows from the symmetry of the shear distortion for C and C' . As a consequence of Eq. (12) it is found that

$$\sum_{ij}(dE_{ij}/dX)_0=0. \quad (13)$$

In addition, from symmetry arguments,¹⁵

$$(d\beta/dX)_0=0. \quad (14)$$

Thus, it is found that

$$\sum_i(dg_i(\mu)/dX)_0=0 \quad (15)$$

and that there is no change to first order in the total density of states at the Fermi level.

In order to evaluate the second derivative of the Fermi level, β_0 , with respect to strain, we make use of the relation for the number of overlap electrons or holes per unit volume, n_{ij} , in the sheared state. This relation is given by

$$n_{ij}=\pm \int_0^{\beta_0-E_{ij}} g_i(\alpha)d\alpha, \quad (16)$$

where $\alpha=E-E_{ij}$, the plus refers to overlap electrons, and the minus to holes. Since the total number of overlap electrons minus the total number of holes is a constant, independent of the state of strain of the crystal, differentiation of Eq. (16) with respect to X

and summation over all ij gives the relations

$$\sum_{ij}\left(\frac{dn_{ij}}{dX}\right)_0=\sum_i g_i(\mu)\left(\frac{d\beta_0}{dX}\right)_0-\sum_{ij} g_i(\mu)\left(\frac{dE_{ij}}{dX}\right)_0=0 \quad (17)$$

and

$$\begin{aligned} \sum_{ij}\left(\frac{d^2n_{ij}}{dX^2}\right)_0 &= \sum_i g_i(\mu)\left(\frac{d^2\beta_0}{dX^2}\right)_0 - \sum_{ij} g_i(\mu)\left(\frac{d^2E_{ij}}{dX^2}\right)_0 \\ &+ \sum_{ij}\left(\frac{dg_i(\mu)}{d\mu}\right)_0\left(\frac{dE_{ij}}{dX}\right)_0=0. \end{aligned} \quad (18)$$

From Eq. (18) one obtains

$$\begin{aligned} \left(\frac{d^2\beta_0}{dX^2}\right)_0 &= \frac{1}{\sum_i g_i(\mu)}\left[\sum_i g_i(\mu)\left(\frac{d^2E_{ij}}{dX^2}\right)_0\right. \\ &\left.- \sum_{ij}\left(\frac{dg_i(\mu)}{d\mu}\right)_0\left(\frac{dE_{ij}}{dX}\right)_0\right]. \end{aligned} \quad (19)$$

D. Temperature Dependence of C and C'

We can now evaluate the sum of the $[d^2g_i(\mu)/dX^2]_0$ of Eq. (4) by means of Eqs. (10)–(19). In order to simplify the discussion to be given in Sec. 4, we will assume that the first and second derivatives of E_{ij} are proportional to E_{ij} , the constant of proportionality being determined uniquely by the geometry of the Brillouin zone. The expressions for the temperature dependence of the elastic shear constants of the body-centered cubic lattice may now be expressed in terms of the energies of the symmetry points shown in Fig. 1, as follows:

$$\begin{aligned} C(T) &= C(0)\frac{V(0)}{V(T)} - \frac{N(\pi kT)^2}{18}\left\{\frac{\sum_i 2E_i g_i(\mu')}{\sum_i g_i(\mu')}\sum_i\left(\frac{dg_i(\mu')}{d\mu'}\right)_0\right. \\ &\left.- \sum_i 2E_i\left(\frac{dg_i(\mu)}{d\mu}\right)_0 + E^2_N\left[\left(\frac{d^2g_N(\mu')}{d\mu_N'^2}\right)_0 - \frac{1}{\sum_i g_i(\mu)}\left(\frac{dg_N(\mu')}{d\mu_N'}\right)_0\sum_i\left(\frac{dg_i(\mu')}{d\mu'}\right)_0\right]\right. \\ &\left.+ \frac{4}{3}E^2_P\left[\left(\frac{d^2g_P(\mu')}{d\mu_P'^2}\right)_0 - \frac{1}{\sum_i g_i(\mu)}\left(\frac{dg_P(\mu')}{d\mu_P'}\right)_0\sum_i\left(\frac{dg_i(\mu')}{d\mu'}\right)_0\right]\right\} \end{aligned} \quad (20)$$

and

$$\begin{aligned} C'(T) &= C'(0)\frac{V(0)}{V(T)} - \frac{N(\pi kT)^2}{18}\left\{\frac{\sum_i 2E_i g_i(\mu')}{\sum_i g_i(\mu')}\sum_i\left(\frac{dg_i(\mu')}{d\mu'}\right)_0\right. \\ &\left.- \sum_i 2E_i\left(\frac{dg_i(\mu')}{d\mu'}\right)_0 + \frac{1}{2}E^2_N\left[\left(\frac{d^2g_N(\mu')}{d\mu_N'^2}\right)_0 - \frac{1}{\sum_i g_i(\mu')}\left(\frac{dg_N(\mu')}{d\mu_N'}\right)_0\sum_i\left(\frac{dg_i(\mu')}{d\mu'}\right)_0\right]\right. \\ &\left.+ 2E^2_H\left[\left(\frac{d^2g_H(\mu')}{d\mu_H'^2}\right)_0 - \frac{1}{\sum_i g_i(\mu)}\left(\frac{dg_H(\mu')}{d\mu_H'}\right)_0\sum_i\left(\frac{dg_i(\mu')}{d\mu'}\right)_0\right]\right\}, \end{aligned} \quad (21)$$

where now $\mu'= \beta_0 - E_i$.

¹⁵ A. B. Pippard, Proc. Roy. Soc. (London) A257, 165 (1960).

Similarly the expressions for the temperature dependence of C and C' for the face-centered cubic lattice may now be expressed in terms of the energies of the symmetry points shown in Fig. 2, as follows:

$$C = C(0) \frac{V(0)}{V(T)} - \frac{N(\pi kT)^2}{18} \left\{ 2E_L \left[\frac{g_L(\mu)}{\sum_i' g_i(\mu)} \sum_i \left(\frac{dg_i(\mu)}{d\mu} \right)_0 - \left(\frac{dg_L(\mu)}{d\mu_L} \right)_0 \right] \right. \\ \left. + 2E_X \left[\frac{g_X(\mu)}{\sum_i g_i(\mu)} \sum_i \left(\frac{dg_i(\mu)}{d\mu} \right)_0 - \left(\frac{dg_X(\mu)}{d\mu_X} \right)_0 \right] + \frac{14}{5} E_W \left[\frac{g_W(\mu)}{\sum_i g_i(\mu)} \sum_i \left(\frac{dg_i(\mu)}{d\mu} \right)_0 - \left(\frac{dg_W(\mu)}{d\mu_W} \right)_0 \right] \right. \\ \left. + \frac{4}{3} E^2_L \left[\left(\frac{d^2 g_L(\mu)}{d\mu^2} \right)_0 - \frac{1}{\sum_i g_i(\mu)} \left(\frac{dg_L(\mu)}{d\mu_L} \right)_0 \sum_i \left(\frac{dg_i(\mu)}{d\mu} \right)_0 \right] \right\} \quad (22)$$

and

$$C' = C'(0) \frac{V(0)}{V(T)} - \frac{N(\pi kT)^2}{18} \left\{ 2E_L \left[\frac{g_L(\mu)}{\sum_i g_i(\mu)} \left(\frac{dg_L(\mu)}{d\mu} \right)_0 - \left(\frac{dg_i(\mu)}{d\mu_i} \right)_0 \right] + 2E_X \left[\frac{g_X(\mu)}{\sum_i g_i(\mu)} \sum_i \left(\frac{dg_i(\mu)}{d\mu} \right)_0 - \left(\frac{dg_X(\mu)}{d\mu_X} \right)_0 \right] \right. \\ \left. + \frac{22}{5} E_W \left[\frac{g_W(\mu)}{\sum_i g_i(\mu)} \sum_i \left(\frac{dg_i(\mu)}{d\mu} \right)_0 - \left(\frac{dg_W(\mu)}{d\mu_W} \right)_0 \right] + 2E^2_X \left[\left(\frac{d^2 g_X(\mu)}{d\mu^2} \right)_0 - \frac{1}{\sum_i g_i(\mu)} \left(\frac{dg_X(\mu)}{d\mu_X} \right)_0 \sum_i \left(\frac{dg_i(\mu)}{d\mu} \right)_0 \right] \right. \\ \left. + \frac{2}{25} E^2_W \left[\left(\frac{d^2 g_W(\mu)}{d\mu^2} \right)_0 - \frac{1}{\sum_i g_i(\mu)} \left(\frac{dg_W(\mu)}{d\mu_W} \right)_0 \sum_i \left(\frac{dg_i(\mu)}{d\mu} \right)_0 \right] \right\}, \quad (23)$$

where again $\mu' = \beta_0 - E_i$.

3. ELECTRON CONTRIBUTION TO THE ELASTIC BULK MODULUS AT LOW TEMPERATURES

A. The Elastic Bulk Modulus

In this section we consider the elastic bulk modulus of cubic crystals, $B = \frac{1}{3}(C_{11} + 2C_{12})$. The bulk modulus corresponds to dilatational strains which leave the crystal symmetry unchanged. The isothermal bulk modulus is obtained by differentiation of the Helmholtz free energy, A , of a solid with respect to volume at constant temperature. The electron contribution to the Helmholtz free energy at low temperatures is given by¹⁴

$$A(T) = U(0) - NV(T) \frac{1}{6} (\pi kT)^2 g(\beta_0), \quad (24)$$

where the notation is the same as that used in Eq. (1). The isothermal bulk modulus is given by

$$B_T = V(\partial^2 A / \partial V^2)_T. \quad (25)$$

The adiabatic bulk modulus, B_S , can be obtained by differentiation of Eq. (1) and is given by

$$B_S = V(\partial^2 U / \partial V^2)_S. \quad (26)$$

B. Dilatational Distortion and the Electron Distribution

Contrary to the situation discussed in Sec. 2, dilatational distortion gives rise to an electron contribution to the elastic bulk modulus and its temperature dependence even for those metals for which the Fermi surface is presumed to be a sphere lying wholly within the first

Brillouin zone. This arises from the volume change accompanying dilatation with corresponding first-order changes in the total density of states and the Fermi level, as well as second-order effects. We will consider in this section the situations in which the Fermi surface is a sphere lying within the first Brillouin zone as well as the case of electron overlap across zone boundaries or contact with zone boundaries.

We proceed in a manner similar to that used in Sec. 2, obtaining the relations analogous to Eqs. (3) and (4):

$$\left(\frac{dg_i(\mu')}{dV} \right)_0 = \left(\frac{dg_i(\mu')}{d\mu'} \right)_0 \left(\frac{d\mu'}{dV} \right)_0 \quad (27)$$

and

$$\left(\frac{d^2 g_i(\mu)}{dV^2} \right)_0 = \left(\frac{d^2 g_i(\mu')}{d\mu'^2} \right)_0 \left(\frac{d\mu^2}{dV} \right)_0 + \left(\frac{dg_i(\mu')}{d\mu'} \right)_0 \left(\frac{d^2 \mu'}{dV^2} \right)_0, \quad (28)$$

where for the case of electron overlap across zone boundaries or contact with zone boundaries, $\mu' = \beta_0 - E_i$ and i refers to the symmetry point of the zone. For the case of a spherical Fermi surface, $\mu' = \beta_0$ and i has no significance. In order to evaluate the first and second derivatives of the Fermi level, β_0 , with respect to volume we make use of analogous relations to Eq. (16) to find for the case of electron overlap

$$\left(\frac{d\beta_0}{dV} \right)_0 = \frac{1}{\sum_i g_i(\mu')} \left[\sum_i g_i(\mu') \left(\frac{dE_i}{dV} \right)_0 - \frac{1}{V^2} \sum_i n_i \right] \quad (29)$$

and

$$\begin{aligned} \left(\frac{d^2\beta_0}{dV^2}\right)_0 &= \frac{1}{\sum_i g_i(\mu')} \left[\left(\frac{d\beta_0}{dV}\right)_0 \sum_i \left(\frac{dg_i(\mu')}{d\mu'}\right)_0^2 \right. \\ &\quad \times \left(\frac{d\beta_0}{dV}\right)_0 \sum_i \left(\frac{dg_i(\mu')}{d\mu'}\right)_0 \left(\frac{dE_i}{dV}\right)_0 \\ &\quad \left. + \sum_i \left(\frac{dg_i(\mu')}{d\mu'}\right)_0 \left(\frac{dE_i}{dV}\right)_0^2 + \frac{2}{V^3} \sum_i n_i \right], \quad (30) \end{aligned}$$

where n_i are the number of electrons or holes related to symmetry points of type i . For the case of a spherical Fermi surface:

$$\left(\frac{d\beta_0}{dV}\right)_0 = \frac{n}{V^2} \frac{1}{g(\beta_0)} \quad (31)$$

and

$$\left(\frac{d^2\beta_0}{dV^2}\right)_0 = \frac{2n}{V^3} \frac{1}{g(\beta_0)} - \frac{n}{V^4} \frac{1}{[g(\beta_0)]^3} \left(\frac{dg(\beta_0)}{d\beta_0}\right)_0, \quad (32)$$

where n is the total number of electrons in the Fermi sphere.

C. The Isothermal Bulk Modulus

The temperature dependence of the isothermal bulk modulus due to the electrons is obtained from Eqs. (24) and (25) as

$$\begin{aligned} B_T &= B(0) \frac{V(T)}{V(0)} - NV(T) \frac{1}{3} (\pi k T)^2 \\ &\quad \times \left[\left(\frac{dg(\beta_0)}{dV(0)}\right)_0 + \frac{1}{2} V(T) \left(\frac{d^2g(\beta_0)}{dV(0)^2}\right)_0 \right], \quad (33) \end{aligned}$$

where $B(0)$ is the bulk modulus at absolute zero. For the simple case of a spherical Fermi surface we obtain, using Eqs. (27), (28), (31), and (32),

$$\begin{aligned} B_T &= B(0) \frac{V(T)}{V(0)} - \frac{N}{V(T)^2} \left(\frac{n}{[g(\beta_0)]}\right)^2 \\ &\quad \times \frac{1}{3} (\pi k T)^2 \left[\left(\frac{d^2g(\beta_0)}{d\beta_0^2}\right)_0 - \frac{1}{g(\beta_0)} \left(\frac{dg(\beta_0)}{d\beta_0}\right)_0^2 \right]. \quad (34) \end{aligned}$$

The temperature dependence of B_T for the case of electron overlap may be obtained by suitable substitution of Eqs. (27)–(30) into Eq. (33).

D. The Adiabatic Bulk Modulus

The derivation of the temperature dependence of the adiabatic bulk modulus, B_S , due to the electrons is somewhat more complicated than the straightforward method for the isothermal bulk modulus. This arises from the variation of temperature with volume at con-

stant entropy. The equation for the electron entropy, S , is given by¹⁴

$$S = NV(T) T \frac{1}{3} (\pi k)^2 g(\beta_0). \quad (35)$$

By differentiation of Eq. (1), we obtain

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_S &= \frac{\partial U(0)}{\partial V} + \frac{1}{3} N (\pi k T)^2 \\ &\quad \times \left[g(\beta_0) + V \left(\frac{dg(\beta_0)}{dV}\right)_0 + \frac{2}{T} g(\beta_0) \left(\frac{\partial T}{\partial V}\right)_S \right]. \quad (36) \end{aligned}$$

Differentiation of Eq. (35) gives the relation

$$\left(\frac{\partial T}{\partial V}\right)_S = -T \left\{ \frac{1}{V} + \frac{1}{g(\beta_0)} \left(\frac{dg(\beta_0)}{dV}\right)_0 \right\}. \quad (37)$$

Successive differentiation of Eq. (36), using the result of Eq. (37), yields the electron contribution to the temperature dependence of the adiabatic bulk modulus as

$$\begin{aligned} B_S &= B(0) \frac{V(T)}{V(0)} + NV \frac{1}{3} (\pi k T)^2 \left[\frac{1}{V(T)} g(\beta_0) + \left(\frac{dg(\beta_0)}{dV(0)}\right)_0 \right. \\ &\quad \left. + \frac{V(T)}{g(\beta_0)} \left(\frac{dg(\beta_0)}{dV}\right)_0^2 - \frac{1}{2} V(T) \left(\frac{d^2g(\beta_0)}{dV^2(0)}\right)_0 \right]. \quad (38) \end{aligned}$$

For the simple case of a spherical Fermi surface we obtain, using Eqs. (27), (28), (31), and (32),

$$\begin{aligned} B_S &= B(0) \frac{V(T)}{V(0)} + \frac{1}{3} N (\pi k T)^2 \left\{ g(\beta_0) - \frac{2n}{V(T)} \right. \\ &\quad \times \frac{1}{g(\beta_0)} \left(\frac{dg(\beta_0)}{d\beta_0}\right)_0 - \frac{1}{2} \left(\frac{n}{V(T)g(\beta_0)}\right)^2 \\ &\quad \left. \times \left[\left(\frac{d^2g(\beta_0)}{d\beta_0^2}\right)_0 - \frac{3}{g(\beta_0)} \left(\frac{dg(\beta_0)}{d\beta_0}\right)_0^2 \right] \right\}. \quad (39) \end{aligned}$$

The temperature dependence of B_S for the case of electron overlap may be obtained by suitable substitution of Eqs. (27)–(30) into Eq. (38).

4. RELATION TO THE PARAMAGNETIC SUSCEPTIBILITY AND THE FERMI SURFACE

A. Temperature Dependence of the Paramagnetic Susceptibility

The temperature dependence of the paramagnetic susceptibility, χ , of metals at low temperatures has been derived by Stoner¹⁶ as

$$\chi = \chi(0) + \frac{1}{15} (\pi k T)^2 \mu \left[\frac{d^2g(\beta_0)}{d\beta_0^2} - \frac{1}{g(\beta_0)} \left(\frac{dg(\beta_0)}{d\beta_0}\right)_0^2 \right]. \quad (40)$$

¹⁶ E. C. Stoner, Proc. Roy. Soc. (London) A154, 656 (1936).

In Eq. (40), $\chi(0)$ is the paramagnetic susceptibility at absolute zero, μ is the Bohr magneton, and the other terms are identical to those used in Eq. (1). Attention is now called to the striking similarity of Eq. (40) to Eqs. (20)–(23), (34), and (39). The term in square brackets in Eq. (40) is identical to the equivalent term in Eq. (34), and with the exception of numerical factors, to that in Eq. (39). In addition, the dominant terms of Eqs. (20)–(23) are those arising from electron transfer during shear distortion and are represented by the square of the energy of a point of symmetry. This term is modified by a factor equivalent to the term in square brackets of Eq. (40).

On the basis of the above discussion, it is seen that the sign and magnitude of the electron contribution to the temperature dependence of the elastic constants, similar to the paramagnetic susceptibility, is determined by the first and second derivatives of the electronic density of states with energy, evaluated at the Fermi level. The temperature dependence of the elastic constants may exhibit positive or negative coefficients dependent upon whether the Fermi level is at a minimum or maximum of the electron density of states, respectively. Kriesmann and Callen¹⁷ have interpreted the positive temperature coefficient of the paramagnetic susceptibility of chromium on the basis of the Fermi level lying near a minimum of the theoretical density of states curve.

With the exception of the case of a spherical Fermi surface, one would not expect an exact correlation between the paramagnetic susceptibility, which is a second-rank tensor property, and the elastic constants, which are fourth-rank tensor properties. This is obvious from an investigation of the relations for C , C' , B_T , and B_S for the case in which contact with zone boundaries or electron overlap across zone boundaries is present. In this case it is seen that the shape of the Fermi surface may influence the sign and magnitude of the temperature dependence of the elastic constants.

B. Elements with Spherical Fermi Surfaces: Sodium

As an example of an element for which it is assumed that the Fermi surface is spherical we take the case of sodium. Since we assume a spherical Fermi surface, there is no contribution from the electrons to the temperature dependence of C and C' and the electrons contribute only to the temperature dependence of the elastic bulk modulus. We obtain $g(\beta_0)$ from electron specific heat data¹⁸ as 0.764 eV⁻¹ per atom and a value for β_0 of 3.5 eV from measurements of the soft x-ray emission spectra by Skinner.¹⁹ A value of $B(0)$ of 5.32×10^{10} dyn/cm² is obtained from the experimental

¹⁷ C. J. Kriesmann and H. B. Callen, Phys. Rev. **94**, 837 (1954).

¹⁸ J. G. Daunt, *Progress in Low Temperature Physics*, edited by C. J.orter (North-Holland Publishing Company, Amsterdam, 1955), Chap. XI.

¹⁹ H. W. B. Skinner, Trans. Roy. Soc. (London) **A239**, 95 (1940).

TABLE I. Electron contribution to the temperature dependence of the elastic constants of sodium, copper, aluminum, and vanadium.

Element	Modulus	Calculated	α (°K ⁻²) Experimental ^a
Na	B_T	-4.98×10^{-10}	...
	B_S	-9.94×10^{-9}	...
	C	0	...
Cu	C'	0	...
	B_T	-3.97×10^{-11}	...
	B_S	-4.84×10^{-10}	...
	C	-1.04×10^{-10}	...
Al	C'	0	...
	C	-6.15×10^{-9}	...
V	C'	-2.90×10^{-9}	...
	C	$\sim 10^{-8}$	1.03×10^{-6}
	C'	$\sim 10^{-6}$	0.46×10^{-6}

^a See Ref. 12.

measurements of Quimby and Siegel²⁰ at 80°K extrapolated by Stern² to absolute zero. A parabolic density of states versus energy distribution of the form

$$g(E) = \frac{1}{2} \pi^2 (2m/\hbar^2)^{3/2} E^{1/2} \quad (41)$$

is assumed in order to calculate the first and second derivatives of $g(E)$ with respect to E . The results were calculated in the form

$$M(T) = M(0)(1 - \alpha T^2), \quad (42)$$

where M represents an elastic constant. The results for sodium are tabulated in Table I.

C. Contact with Zone Boundaries: Copper

There has been extensive study of the Fermi surface of copper by galvanomagnetic and magnetoacoustic measurements.²¹ A model of the Fermi surface of copper is shown in Fig. 3. As seen from Fig. 3, the Fermi surface contacts the Brillouin zone boundary at the hexagonal faces of the Brillouin zone. Thus, there are no contributions to the total density of states at the Fermi level from symmetry points equivalent to points X and W of Fig. 2. Consequently, we may omit all terms in X and W in consideration of the elastic shear constants C and C' of Eqs. (22) and (23), respectively. Investigation of Eq. (23) shows that there is no contribution to the temperature dependence of C' from the conduction electrons. For the shear constant C there is a contribution to the temperature dependence arising from the term in E_L^2 in Eq. (22). We obtain $g(\beta_0)$ from electron specific heat data¹⁸ as 0.320 eV⁻¹ per atom and a value of β_0 of 6.8 eV from the x-ray emission spectra results of Skinner.²² A value of $C(0)$ of 8.17×10^{11} dyn/cm² is obtained from the experimental measurements of Overton and Gaffney.²³ In addition, we assume

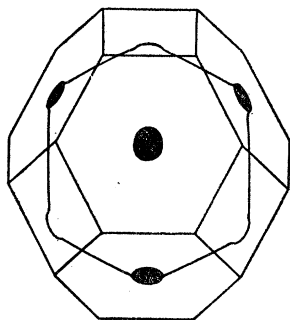
²⁰ S. L. Quimby and S. Siegel, Phys. Rev. **65**, 293 (1938).

²¹ D. Shoenberg, *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), pp. 74–83.

²² H. W. B. Skinner, Phil. Mag. (7) **45**, 1070 (1954).

²³ W. C. Overton, Jr., and J. Gaffney, Phys. Rev. **98**, 969 (1955).

FIG. 3. The Fermi surface of copper.



that E_L lies so close to β_0 that we may approximate E_L by assuming that $E_L \approx \beta_0$. In a manner analogous to that used for sodium, we estimate the temperature dependence of B_T and B_S using the available experimental data^{18,22} and the value of $B(0)$ of 14.1×10^{11} dyn/cm² obtained by Overton and Gaffney.²³ The results are tabulated in Table I.

D. Overlap Across Zone Boundaries: Aluminum

Theoretical calculation of the electronic contribution to the elastic shear constants of aluminum have been performed by Leigh.⁷ Leigh assumed electron overlap across the hexagonal and square faces of the Brillouin zone of Fig. 2 and the absence of holes at the corner points, W . On the basis of the number of approximations involved in the calculations of Leigh, it is quite difficult to place much confidence in the relative contributions to the elastic shear constants and to the Fermi surface obtained from this treatment.⁹ We, therefore, use the calculations of Leigh solely to obtain an estimate of the order of magnitude of the electron contribution to the temperature dependence of the elastic shear constants. The elastic constants, C and C' at 0°K are obtained from the work of Sutton,²⁴ as 3.09×10^{11} and 2.60×10^{11} dyn/cm², respectively; the other parameters in Eqs. (22) and (23) being obtained from the work of Leigh. The results of these calculations are tabulated in Table I.

E. Comparison with Experiment: Vanadium

Since no information is available at present about the Fermi surface of vanadium, it is quite difficult to calculate the electron contribution to the temperature dependence of the elastic constants. We can show, however, that the order of magnitude of the T^2 dependence of vanadium can be predicted on the basis of experimental evidence. A curve of the energy dependence of the electron density of states for bcc transition metals

has been obtained by Cheng *et al.*^{25,26} from measurements of the electron specific heat of transition metal alloys. From the results of Cheng and co-workers we estimate the slope and curvature of the electron density of states at the Fermi level as 7.7 and 33 eV⁻³ per atom, respectively. The density of states for vanadium at the Fermi level is also given by Cheng²⁶ as 3.908 eV⁻¹ per atom. We obtain β_0 once again from the experimental results of Skinner as 7.74 eV and for purposes of qualitative calculation assume E_N , E_H , and E_P are approximately equal to β_0 . The values of the elastic shear constants C and C' at absolute zero are obtained from the data of Alers and Waldorf,¹² as 4.60×10^{11} and 5.65×10^{11} dyn/cm², respectively.

5. SUMMARY AND CONCLUSIONS

It is shown that the electrons contribute a term in T^2 to the temperature dependence of the elastic constants of metals at low temperatures. The algebraic sign and order of magnitude of this temperature dependence are determined critically by the electron density distribution and the shape of the Fermi surface. Representative calculations are performed for sodium, copper, aluminum, and vanadium. In all these calculations it has been assumed that $V(T)$ is equal to $V(0)$ over the temperature range considered. This assumption seems justified by the results of White²⁷ which show that the thermal-expansion coefficient for vanadium and most other metals investigated is approximately 10^{-8} deg⁻¹ in the temperature range considered in this work.

The experimental measurements of Alers and Waldorf¹² have a sensitivity of one part in 10^7 . From the results of Table I it is doubtful that the T^2 dependence may be observed in copper, but possibly may be observed in sodium and aluminum. From the results for vanadium it is probable that the effect will be most pronounced for transition metals. It becomes clear that measurements such as those performed by Alers and Waldorf are valuable for checking the results of energy band calculations, or conversely, for providing information about the Fermi surface.

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²⁵ C. H. Cheng, C. T. Wei, and P. A. Beck, Phys. Rev. **120**, 426 (1960).

²⁶ C. H. Cheng, K. P. Gupta, E. C. van Reuth, and P. A. Beck, Phys. Rev. **126**, 2030 (1962).

²⁷ G. K. White, Cryogenics **2**, 292 (1962).

²⁴ P. M. Sutton, Phys. Rev. **91**, 816 (1953).