LATTICE VIBRATION AND THERMAL EXPANSION
OF MONOVALENT METALS[*].

By

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Introduction

Grüneisen[1] has first derived an expression of the coefficient α of thermal expansion, $i.e.$,

$$\alpha = \gamma \chi C_V / V, \tag{1}$$

where C_V is the heat capacity at constant volume, V the volume, χ the compressibility, and

$$\gamma \equiv -d \log \omega / d \log V \qquad \begin{array}{l}(\omega : \text{ circular frequency} \\ \text{of lattice vibration})\end{array} \tag{2}$$

assumed according to Grüneisen to be same for all modes of vibration of the metal. The constant γ is correlated with $d \log \chi / d \log V$, provided that the Poisson's ratio is independent of volume, as

$$\gamma = -\frac{1}{6} + \frac{1}{2} \frac{d \log \chi}{d \log V}, \tag{3}$$

as derived by Slater[2], or

$$\gamma = -\frac{1}{2} + \frac{1}{2} \frac{d \log \chi}{d \log V}, \tag{3a}$$

as corrected by Dugdale and MacDonald[3], so that $\gamma = 0$ for a crystal with harmonic potentials between adjacent atoms. The γ derived according to (3) or (3a) from the observed change of compressibility with pressure agrees approximately with that from the observed α, χ and C_V by (1), although the Poisson's ratio depends more or less on atomic volume, or the assumption of Grüneisen on γ is not exactly valid, as shown below.

The frequency of long wave-length is given as

$$M\omega(\mathbf{q})^2 = N^{-1}c_q|\mathbf{q}|^2,$$

where M is the mass of a metal atom, N the number of atoms per unit volume, $\mathbf{q}$ the wave number vector and c_q is the elastic constant[*] appropriate to the wave number vector $\mathbf{q}$ and the polarization vector $\mathbf{e}_q$, e.g., $\dfrac{1}{2}(c_{11}-c_{12})$ and c_{44} for the transversal modes propagating in the direction $(1,1,0)$[**]. We have from (2)[***],

$$\gamma_{t_1} = -(1/2)\,d\log(c_{11}-c_{12}/2\mathrm{N})/d\log V + 1/3 = 0.05$$

or

$$\gamma_{t_2} = -(1/2)\,d\log(c_{44}/N)/d\log V + 1/3 = 0.66$$

for Na respectively, by making use of the expressions of c_{44} and $1/2(c_{11}-c_{12})$, valid at any lattice constant, as derived by FUCHS[4].

Eq. (1) is exact, however, if we replace γ by the mean γ_M of $\gamma_q \equiv -d\log\omega(\mathbf{q})/d\log V$ with weights

$$(\hbar\omega/\kappa T)^2 \exp(\hbar\omega/\kappa T)\left\{\exp(\hbar\omega/\kappa T)-1\right\}^{-2},$$

where $\hbar$ is the PLANCK constant divided by 2π, and κ the BOLTZMANN constant. The γ_M is not a constant now, but depends on temperature. Actually, recent experiments by RUBIN, ALTMAN and JOHNSTON[5], BIJL and PULLAN[6][****], and SIMMONS and BALLUFFI[7] on the thermal expansion coefficient at low temperatures show that the γ of Cu, Al or Fe as determined by (1) decreases with decrease of temperature below $0.3\,\Theta$ (Θ: the DEBYE temperature). BARRON[8] has investigated the variation of γ_M with temperature according to the lattice dynamics. He carried out calculations for a cubic close packed lattice assuming central forces between nearest neighbours, and found that the theoretical γ_M obtained behaved qualitatively similarly to the γ determined experimentally by (1).

The anharmonicity of potentials of interatomic forces plays an essential rôle in the thermal expansion since γ, and consequently α, vanishes identically, if the potentials are harmonic, as discussed by BORN and BRODY[9], WALLER[10], DAMKÖHLER[11], and DUGDALE and MACDONALD[12]. Thus, one of the main

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[*] The c_q is the elastic constant in VOIGT's notation.

[**] It is necessary in order to designate a normal vibration to give $\mathbf{e}_q$ and $\mathbf{q}$, but we will not write $\mathbf{e}_q$ explicitly for the sake of simplicity.

[***] FUCHS assumed that the contributions from valence electrons to shear moduli is negligible. His aussumption is, however, not rigorous as will be seen in this paper (cf. also ref. (13)).

[****] Systematic error is present in the experiments by BIJL and PULLAN (ref. 6), as concluded by SIMMONS and BALLUFFI (ref. 7).

problems in the theory of thermal expansion is to determine the potentials between atoms in a metal, inclusive of anharmonic terms. However, it appears too difficult to give the correct potentials explicitly, since they are in general of long range and non-central forces.

The potential between atoms in a metal is given, on the other hand, as the sum of the COULOMB repulsive potential v_C between metal ions, the inter-action potential v_E induced by valence electrons, and the exchange repulsion potential v_R between atom cores. It is more general and straightforward, as investigated by the present author previously[13], to compute the respective contri-butions from v_C, v_E and v_R to the adiabatic potential of the normal mode at a given lattice constant, which includes automatically the contributions from the anharmonic terms in question as developed below §1. The calculated values of the appropriate mean γ_M of alkali metals (§2) and copper (§3) are found to be in good agreement with observed values. The temperature de-pendency of γ is also worked out, in good agreement with existing experimental results or predictively for unobserved values.

§ 1. Dispersion relation of normal vibration

We start with the Hamiltonian for a monovalent metal,

$$
\begin{aligned}
\mathscr{H} = (1/2\,m) \sum_i \mathbf{p}_i^2 &+ (1/2) \sum_{i \neq j} e^2/|\mathbf{r}_i - \mathbf{r}_j| + \sum_{i,l} v_I(\mathbf{r}_i - \mathbf{R}_l) \\
&+ (1/2) \sum_{l \neq l'} e^2/|\mathbf{R}_l - \mathbf{R}_{l'}| + (1/2) \sum_{l \neq l'} v_R(\mathbf{R}_l - \mathbf{R}_{l'}) + \sum_l (M/2) \dot{\mathbf{R}}_l^2 \,,
\end{aligned} \tag{4}
$$

where the first term is the kinetic energy of valence electrons $i, j, \cdots$, the second term the COULOMB repulsion potential between them, the third term the potential of electrons in the field of metal ions, the fourth or the fifth term the COULOMB or the exchange repulsion potential between ion-cores $l, l' \cdots$, respectively, and the last one the kinetic energy of the ions; $\mathbf{p}_i$ or $\mathbf{r}_i$ is the momentum or the coordinate vector of the i-th electron, m or M the mass of an electron or an ion, and $\mathbf{R}_l$ or $\dot{R}_l$ the coordidate or velocity vector of the l-th ion.

Expression (4) reduces to the Hamiltonian $\mathscr{H}_0$ of a perfect crystal without any deformation, when each ion is at rest on the equilibrium lattice point $\mathbf{R}_l^0$. The displacement vector $\mathbf{u}_l = \mathbf{R}_l - \mathbf{R}_l^0$ of the l-th ion from its equilibrium position $\mathbf{R}_l^0$ may be expressed in terms of normal coordinates a_q and a_q^* as

$$
\mathbf{u}_l = \sum_{q, e_q}' N^{-1/2} \mathbf{e}_q \left\{ a_q \exp(i\mathbf{q}\mathbf{R}_l^0) + a_q^* \exp(-i\mathbf{q}\mathbf{R}_l^0) \right\} , \tag{5}
$$

where N is the number of ions per unit volume, $\mathbf{q}$ the wave number vector, and $\mathbf{e}_q$ the unit vector in the direction of polarization of lattice wave, taken in

the same sense as $\mathbf{e}_{-q}$, so that $a_q = a^*_{-q}$. The summation $\sum'$ is taken over either $+\mathbf{q}$ or $-\mathbf{q}$ on account that $a_q = a^*_{-q}$ by definition. It is convenient to express a_q or a^*_q and its conjugate momentum p_q or p^*_q by the creation and destruction operators α_q and α^*_q as

$$a_q = -(\hbar/2\omega_q M)^{1/2} (\alpha_q + \alpha^*_{-q}) ,$$
$$p_q = i (\hbar\omega_q M/2)^{1/2} (\alpha^*_q - \alpha_{-q}) , \tag{6}$$

where ω_q is the circular frequency of a normal vibration of wave number vector $\mathbf{q}$, as will be determined below. The commutation relations of α_q's are

$$\alpha_q \alpha_{q'} - \alpha_{q'} \alpha_q = \alpha^*_q \alpha^*_{q'} - \alpha^*_{q'} \alpha^*_q = 0$$
$$\alpha_q \alpha^*_{q'} - \alpha^*_{q'} \alpha_q = \delta_{qq'} , \tag{7}$$

and $\alpha^*_q \alpha_q = N_q$ is the number of the phonons designated by $\mathbf{q}$.

The Hamiltonian (4) may be expanded into a power series of a_q and a^*_q. The zeroth order term is the Hamiltonian $\mathcal{H}_0$ of a perfect crystal without any deformation. The first order coefficient of a_q, which arises from the third term of (4), is given as

$$v'_i = -N^{1/2} \sum_l \left\{ \exp(i\mathbf{q}\mathbf{R}^0_l) \mathbf{e}_q \cdot \operatorname{grad} v_1(\mathbf{r} - \mathbf{R}^0_l) \right\} , \tag{8}$$

and that of a^*_q by the complex conjugate of the above expression. The COULOMB repulsion potential between electrons given by the second term of (4) contributes also to the first order term of a_q or a^*_q in the one-electron HARTREE-FOCK wave equation derived from (4), since electrons redistribute to shield the perturbing ionic field v'_i given by (8) plus its complex conjugate v'^*_i. The explicit expression has been previously derived by the self-consistent field method, taking the exchange and correlation effects into account.

The terms of the second order coefficients of $a^*_q a_q$ arising from the third, fourth and fifth term of (4) are readily derived. It is not necessary to derive the coefficients of $a_q a_q$ or $a^*_q a^*_q$ explicitly, since they contribute nothing to the second order energy of the metal, up to which we are going to deal with.

The perturbed wave functions and hence the crystal energy are now worked out by extending HARTREE-FOCK method to take the effects, on the self-consistent shielding field, of the correlation as well as the exchange interactions between electrons into account[13][14]. The energy expression of a monovalent metal is thus derived from (4); it consists, as shown below, of the energy of the perfect crystal (zeroth order), the energy of lattice vibrations (2nd order) and electron-phonon interaction energy which arises from the non-adiabatic terms.

The adiabatic potential of lattice vibration of wave number $\mathbf{q}$ is given as

$$(E_I + E_{II} + E_C + E_R) , \tag{9}$$

where

$$E_{\mathrm{I}} = Ne^2(4\pi/3),\tag{9 a}$$

$$E_{\mathrm{II}} = \sum_{kh}\Big[f(\mathbf{k})\big\{1-f(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\big\}v_{ih}v_{ph}^*\big\{E(\mathbf{k})-E(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\big\}^{-1}$$

$$+f(\mathbf{k})\big\{1-f(\mathbf{k}-\mathbf{q}-\mathbf{K}_h)\big\}v_{ih}^*v_{ph}\big\{E(\mathbf{k})-E(\mathbf{k}-\mathbf{q}-\mathbf{K}_h)\big\}^{-1}\Big]$$

$$= \sum_{kh}\big\{f(\mathbf{k})-f(\mathbf{k}-\mathbf{q}-\mathbf{K}_h)\big\}v_{ih}^*v_{ph}\big\{E(\mathbf{k})-E(\mathbf{k}-\mathbf{q}-\mathbf{K}_h)\big\}^{-1}\tag{9 b}$$

and E_C or E_R is the contribution to the coefficient of $a_q^*a_q$ from the fourth or fifth term of (4) respectively. In (9b), $f(\mathbf{k})$ is the probability that a state $\mathbf{k}$ is occupied, $\mathbf{K}_h$ a vector of reciprocal lattice space, $E(\mathbf{k})$ the energy of an electron of wave number vector $\mathbf{k}$, which involves the exchange and correlation energies with other electrons, and v_{ih} or v_{ih}^* is the matrix element of the perturbation of ionic field v_i', *i.e.*,

$$v_{ih} = \int \phi^*(\mathbf{k}+\mathbf{q}+\mathbf{K}_h, \mathbf{r})v_i'\phi(\mathbf{k}, \mathbf{r})d\mathbf{r},\tag{10 a}$$

or

$$v_{ih}^* = \int \phi^*(\mathbf{k}, \mathbf{r})v_i'^*\phi(\mathbf{k}+\mathbf{q}+\mathbf{K}_h, \mathbf{r})d\mathbf{r}$$

$$= \int \phi^*(\mathbf{k}-\mathbf{q}-\mathbf{K}_h, \mathbf{r})v_i'^*\phi(\mathbf{k}, \mathbf{r})d\mathbf{r},\tag{10 b}$$

where $\phi(\mathbf{k}\pm\mathbf{q}\pm\mathbf{K}_h, \mathbf{r})$ or $\phi(\mathbf{k}, \mathbf{r})$ is the non-perturbed wave function of an electron of wave number vector $\mathbf{k}\pm\mathbf{q}\pm\mathbf{K}_h$ or $\mathbf{k}$, and the star signifies its complex conjugate. The v_{ph} in (9b) is the effective matrix element of the perturbation of the shielded ionic field by valence electrons, given as

$$v_{ph} = \frac{v_{ih}}{1+\{8\pi e^2/|\mathbf{q}+\mathbf{K}_h|^2-2B(\mathbf{q}+\mathbf{K}_h)\pi e^2/k_F^2\}\cdot\sum_h\{E(\mathbf{k}\pm\mathbf{q}\pm\mathbf{K}_h)-E(\mathbf{k})\}^{-1}}$$

for

$$8\pi e^2/|\mathbf{q}+\mathbf{K}_h|^2 > 2B(\mathbf{q}+\mathbf{K}_h)\pi e^2/k_F^2,\tag{11 a}$$

or as

$$v_{ph} = v_{ih} \qquad \text{for} \quad 8\pi e^2/|\mathbf{q}+\mathbf{K}_h|^2 \leq 2B(\mathbf{q}+\mathbf{K}_h)\pi e^2/k_F^2,\tag{11 b}$$

where k_F is the wave number of an electron on the Fermi surface, and $B(\mathbf{q}+\mathbf{K}_h)$ is approximately constant near unity as estimated previously[13][14], which allows for the effect of the exchange and correlation interactions between electrons.

The latter interactions taken into account in terms of $B(\mathbf{q}+\mathbf{K}_h)$ diminish the denominator of (11a) to increase the absolute value of the effective matrix elements. This effect may be interpreted physically as follows. The charge density of electrons is redistributed by crystal deformation, to shield the perturbing ionic field as mentioned above. Electrons tend, however, to keep apart

from each other by exchange and correlation interactions to reduce the shielding effect as given by the second term in the denominator of (11a).

These interactions affect, on the other hand, the effective matrix elements through the approximate relation

$$\sum \left\{ E(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)-E(\mathbf{k}) \right\}^{-1} = D/D_0 \sum \left\{ E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)-E_0(\mathbf{k}) \right\}^{-1}, \quad (12)$$

where $E_0(\mathbf{k})$ is the HARTREE energy of $\mathbf{k}$-electron, and D or D_0 is the density of states in the presence or absence of the exchange and correlation energies.

BARDEEN and PINES[15] have recently investigated the rôle of the exchange and correlation interactions between electrons by extending the BOHM-PINES collective description method and concluded that their effects on the adiabatic potential (9) and on the effective matrix element (11) are negligible, in deviation from the present conclusion. It has been shown, however, in favour of the present theory that the compressibilities, the electric conductivities and the DEBYE temperatures of alkali metals derived from (9) and (11) are respectively in good agreement with experimental values as well as with those from WIGNER-SEITZ theory in the case of compressibilities, whereas the neglect of the exchange and correlation effects leads to the values of compressibilities and conductivities twice as large as the experimental values and to those of the DEBYE temperatures larger than the observations by 25%.

Expression (9) is in general a quadratic form of e_{qx}, e_{qy} and e_{qz}, so that the normal modes as well as the vibrational frequencies ω_q are determined by transforming it to their principal axes (see §2). The Hamiltonian of lattice vibrations is now given as

$$\sum_q \left\{ \frac{1}{2M} p_q^* p_q + \frac{1}{2} M \omega_q^2 a_q^* a_q \right\} = \frac{1}{2} \sum_q \left\{ \alpha_q^* \alpha_q + \alpha_q^* \alpha_q \right\} \hbar \omega_q$$
$$= \sum_q \left\{ \alpha_q^* \alpha_q + \frac{1}{2} \right\} \hbar \omega_q . \qquad (13)$$

It should be remarked that the frequencies thus derived without any reference to the equilibrium lattice constant are exact at any lattice constant and in consequence the same is the case with $\gamma_q = -d \log \omega_q / d \log V$ derived from them.

The electron-phonon interaction energy arising from the non-adiabatic terms is given as[14],

$$-\frac{1}{2} \sum_q \sum_{kh} f(\mathbf{k}) f(\mathbf{k}-\mathbf{q}-\mathbf{K}_h) \hbar^2 v_{ph}^* v_{ph} \Big/ \left\{ (E(\mathbf{k})-E(\mathbf{k}-\mathbf{q}-\mathbf{K}_h))^2 - (\hbar \omega_q)^2 \right\} ,$$

which represents alternatively the electron-electron interaction via lattice vibrations. Its order of magnitude is a few cal/mol and is important only for such

phenomena at extremely low temperatures as superconductivity.

The contributions to the entropy of the crystal from the distribution of valence electrons may be neglected except at extremely low temperatures and those from the non-adiabatic energy as well, as mentioned above, hence the free energy F of the crystal is given by the usual expression as

$$F = E_C + \kappa T \sum_q \log \left\{ 1 - \exp(-\hbar \omega_q / \kappa T) \right\} , \tag{15}$$

where E_C is the cohesion energy at absolute zero inclusive af the zero-point energy. Differentiating (15) with respect to the volume, we have

$$-P = \partial F / \partial V = \partial E_C / \partial V + (1/V) \sum_q \overline{N}_q \hbar \omega_q (d \log \omega_q / d \log V) \tag{16}$$

remembering $\overline{N}_q = \{ \exp(\hbar \omega_q / \kappa T) - 1 \}^{-1}$. Hence we have

$$(\partial P / \partial T)_V = (1/V) \gamma_M C_V ,$$

or, referring to the relations $(\partial P / \partial T)_V = -(\partial V / \partial T)_p / (\partial V / \partial P)_T$, $\alpha = (1/V)(\partial V / \partial T)_p$ and $\chi = -(1/V)(\partial V / \partial P)_T$,

$$\alpha = \gamma_M \chi C_V / V , \tag{17}$$

where γ_M is the mean of γ_q's, defined by

$$\gamma_M = \frac{\sum_q \gamma_q (\hbar \omega_q / \kappa T)^2 \exp(\hbar \omega_q / \kappa T) \{ \exp(\hbar \omega_q / \kappa T) - 1 \}^{-2}}{\sum_q (\hbar \omega_q / \kappa T)^2 \exp(\hbar \omega_q / \kappa T) \{ \exp(\hbar \omega_q / \kappa T) - 1 \}^{-2}} , \tag{18}$$

At high temperatures γ_M is simply the arithmetical mean of γ_q's, as readily be seen from the above equation, but at low temperatures γ_q of lower frequency increasingly preponderates, so that γ_M depends on temperature in general.

§2. Evaluation of Grüneisen constants of alkali metals

The expression (9) of the adiabatic potential of lattice vibration of wave number vector $\mathbf{q}$ is a quadratic form of e_{qx}, e_{qy}, and e_{qz}, as mentioned in the preceding section, *i.e.*,

$$E_I + E_{II} + E_C + E_R = \sum_{(xy)} [xy] e_{qx} e_{qy} , \tag{19}$$

where $[xy] \equiv [xy]^E + [xy]^C + [xy]^R$,

$$E_I + E_{II} = \sum [xy]^E e_{qx} e_{qy} , \tag{19 E}$$

$$E_C = \sum [xy]^C e_{qx} e_{qy} , \tag{19 C}$$

and

$$E_R = \sum [xy]^R e_{qx} e_{qy} .\tag{19 R}$$

With approximations

$$\phi(\mathbf{k}, \mathbf{r}) = U_0(\mathbf{r}) \exp\{i\mathbf{k}\mathbf{r}\}, \qquad |U_0(r_s)|^2 \approx 1 ,\tag{20}$$

and its HARTREE energy

$$E_0(\mathbf{k}) = E_0 + (\hbar^2/2\mathrm{m}) k^2 ,\tag{21}$$

we have from (10)

$$v_{ih} = iN^{1/2} \cos(e_q, \mathbf{q} + \mathbf{K}_h) \frac{4\pi e^2}{|\mathbf{q} + \mathbf{K}_h|^2} G(t) ,\tag{22}$$

where r_s is the radius of a sphere of atomic volume,

$$G(t) = \left\{ 1 + (V(r_s) - E_0) \frac{3\pi}{e^2 k_F} t^2 \right\} g(2k_F r_s t) ,\tag{22 a}$$

$g(x) = 3(\sin x - x \cos x)/x^3$, $V(r_s)$ the HARTREE potential at r_s so that $V(r_s) \approx 0$, and $t = |\mathbf{q} + \mathbf{K}_h|/2k_F$. The summation in the denominator of (11) is given, on the other hand, as

$$\sum \left\{ E(\mathbf{k} + \mathbf{q} + \mathbf{K}_h) - E(\mathbf{k}) \right\}^{-1} = \frac{D}{D_0} \sum \left\{ E_0(\mathbf{k} + \mathbf{q} + \mathbf{K}_h) - E_0(k) \right\}^{-1}$$
$$= \frac{D}{D_0} \frac{3N}{4\zeta_0} f(t) .\tag{23}$$

with $f(t) = \dfrac{1}{2} + \dfrac{(1-t^2)}{4t} \log \left| \dfrac{1+t}{1-t} \right|$ and $\zeta_0 = (\hbar^2/2m) k_F^2$. The $[xy]^E$ is now given from (9), (11), (19 E), (22) and (23), as

$$[xy]^E = Ne^2 \left\{ -\frac{4\pi}{3} \delta_{xy} + 4\pi \sum_h \frac{(\bar{q}_x + h_x)(\bar{q}_y + h_y)}{|\bar{q} + h|^2} \right\} G(t)^2 F(t)^{-1} f(t) ,\tag{24}$$

where $\bar{\mathbf{q}} \equiv (\bar{q}_x, \bar{q}_y, \bar{q}_z)(= (r_0/\pi)\mathbf{q})$ and $\mathbf{h} \equiv (h_x, h_y, h_z)(= (r_0/\pi)\mathbf{K}_h)$, r_0 being the half of the lattice constant[*], and

$$F(t) = \frac{D_0}{D} \frac{\pi \hbar^2 k_F}{me^2} t^2 + (1 - Bt^2) f(t) .\tag{25}$$

The $[xy]^C$ is readily formulated as

$$[xy]^C = \sum_l \left\{ v_c(R_l^0 - R_{l=0}^0) \right\} \exp\left\{ i\mathbf{q}(\mathbf{R}_l^0 - \mathbf{R}_{l=0}^0) \right\} ,\tag{26}$$

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[*] $(h_x + h_y + h_z)$ is even for *b.c.c.* crystal, and h_x, h_y, h_z are all odd or all even for *f.c.c.* crystal.

where $v_C(R_l^0 - R_{l=0}^0) = e^2/|R_l^0 - R_{l=0}^0|$ for $l \neq 0$, $v_C(R_l^0 - R_{l=0}^0)$ for $l = 0$ being defined by

$$\lim_{q \to 0} \{[xy]^F + [xy]^C\} = 0 ,\tag{27}$$

and the subscripts xy of $\{v_C(\mathbf{R})\}_{xy}$ signify the partial differential coefficient $\partial^2 v_C(\mathbf{R})/\partial X \partial Y$ (X, Y and Z are components of $\mathbf{R}$). We have, by applying the method of EWALD[16], from (26)

$$[xy]^C = Ne^2 \left[-G_{xy} + H_{xy} + \begin{cases} \dfrac{16}{3\sqrt{\pi}} \varepsilon^3 \delta_{xy} & \text{for } (b.c.c.) \\[2mm] \dfrac{8}{3\sqrt{\pi}} \varepsilon^3 \delta_{xy} & \text{for } (f.c.c.) \end{cases} \right] ,\tag{28}$$

where

$$G_{xy} = 4\pi \sum_h \frac{(\bar{q}_x + h_x)(\bar{q}_y + h_y)}{|\bar{\mathbf{q}} + \mathbf{h}|^2} \exp\left\{ -\frac{\pi^2}{4\varepsilon^2} (\bar{\mathbf{q}} + \mathbf{h})^2 \right\}$$

and

$$H_{xy} = \begin{Bmatrix} 4 \\ 2 \end{Bmatrix} \times \sum_{l \neq 0}' \left[-f(l)\delta_{xy} + g(l)\frac{l_x l_y}{l^2} \right] \cos \pi(\bar{\mathbf{q}}, \mathbf{l}) \quad \begin{cases} \text{for } b.c.c. \\ \text{for } f.c.c. \end{cases}$$

with

$$f(l) = \frac{2}{\sqrt{\pi}} \varepsilon \frac{e^{-\varepsilon^2 l^2}}{l} + \frac{\varphi(\varepsilon l)}{l^3} ,$$

$$g(l) = \frac{4}{\sqrt{\pi}} \varepsilon^3 e^{-\varepsilon^2 l^2} + \frac{6}{\sqrt{\pi}} \varepsilon \frac{e^{-\varepsilon^2 l^2}}{l} + \frac{3\varphi(\varepsilon l)}{l^3} ,$$

$$\varphi(\varepsilon l) = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\varepsilon l} e^{-\xi^2} d\xi .$$

$$R_l^0 = r_0(l_x, l_y, l_z) ,$$

$$l = (l_x^2 + l_y^2 + l_z^2)^{1/2} ,$$

and ε is a constant, which should be chosen so as to make the both series $\sum_h$ and $\sum_{l \neq 0}'$ rapidly convergent.

The exchange repulsion potential between two ions is given, according to BORN and MAYER, as

$$v_R(\mathbf{R}) = A \exp\{(2r_B - R)/\rho\} ,$$

where $A = 1.25 \cdot 10^{-12}$ erg, $\rho = 0.345 \cdot 10^{-8}$ cm and r_B is given in units of 10^{-8} cm as

Na	K	Rb	Cs
0.875	1.185	1.320	1.455

The $[xy]^R$ is expressed as

$$[xy]^R = \sum_l \left\{ v_R(\mathbf{R}_l^0 - \mathbf{R}_{l=0}^0) \right\}_{xy} \cdot \exp \left\{ i\mathbf{q}(\mathbf{R}_l^0 - \mathbf{R}_{l=0}^0) \right\}$$

$$= \frac{A}{\rho} \sum_{l\neq 0}{}' \exp \left\{ (2r_B - r_0 l)/\rho \right\} \left\{ -\frac{1}{r_0 l} \delta_{xy} + \left(\frac{1}{\rho} + \frac{1}{r_0 l} \right) \frac{l_x l_y}{l^2} \right\} \quad (29)$$

$$\times \left\{ \exp(i\pi\bar{\mathbf{q}}\mathbf{l}) - 1 \right\} ,$$

$v_R(\mathbf{R}_l - \mathbf{R}_{l=0})$ for $l = 0$ being defined by

$$\lim_{q \to 0} [xy]^R = 0 .$$

The equation for the normal mode $\mathbf{e}_q$ is now given as

$$[xx]e_{qx} + [xy]e_{qy} + [xz]e_{qz} = -M\omega_q^2 e_{qx} ,$$
$$[xy]e_{qx} + [yy]e_{qy} + [yz]e_{qz} = -M\omega_q^2 e_{qy} , \quad (30)$$
$$[xz]e_{qx} + [yz]e_{qy} + [zz]e_{qz} = -M\omega_q^2 e_{qz} ,$$

where the circular frequency ω_q is given by the secular equation

$$\begin{vmatrix} [xx] + M\omega_q^2 & [xy] & [xz] \\ [xy] & [yy] + M\omega_q^2 & [yz] \\ [xz] & [yz] & [zz] + M\omega_q^2 \end{vmatrix} = 0 . \quad (31)$$

For vibrations propagating in the $(1, 0, 0)$, $(1, 1, 0)$ or $(1, 1, 1)$ direction, the modes as well as the frequencies are given readily as

(i)　$\mathbf{q} = \pi/r_0(\bar{q}, 0, 0)$:

　　L (longitudinal) :　$\mathbf{e}_q = (1, 0, 0)$,　　$M\omega_q^2 = -[xx]$,　　　　$(32\,L)$

　　T_1' (transversal) :　$\mathbf{e}_q = (0, 1, 0)$,　　$M\omega_q^2 = -[yy]$,　　　　$(32\,T_1)$

　　T_2 (transversal) :　$\mathbf{e}_q = (0, 0, 1)$,　　$M\omega_q^2 = -[zz]$,　　　　$(32\,T_2)$

　　　　　　　　$(T_1$ and T_2 degenerated$)$

(ii)　$\mathbf{q} = \pi/r_0(\bar{q}, \bar{q}, 0)$:

　　L :　$\mathbf{e}_q = (1/\sqrt{2}, 1/\sqrt{2}, 0)$　　$M\omega_q^2 = -\{[xx] + [xy]\}$,　　$(33\,L)$

　　T_1 :　$\mathbf{e}_q = (1/\sqrt{2}, -1/\sqrt{2}, 0)$,　$M\omega_q^2 = -\{[xx] - [xy]\}$,　　$(33\,T_1)$

　　T_2 :　$\mathbf{e}_q = (0, 0, 1)$,　　　　　$M\omega_q^2 = -[zz]$.　　　　　　$(33\,T_2)$

(iii)　$\mathbf{q} = \pi/r_0(\bar{q}, \bar{q}, \bar{q})$:

$$L : \quad \mathbf{e}_q = (1/\sqrt{3},\ 1/\sqrt{3},\ 1/\sqrt{3}),\quad M\omega_q^2 = -\{[xx]+2[xy]\}, \quad (34\ L)$$

$$T_1: \quad \mathbf{e}_q = (1/\sqrt{2},\ -1/\sqrt{2},\ 0),\quad M\omega_q^2 = -\{[xx]-[xy]\}, \quad (34\ T_1)$$

$$T_2: \quad \mathbf{e}_q = (1/\sqrt{6},\ 1/\sqrt{6},\ -2/\sqrt{6}),\ M\omega_q^2 = -\{[xx]-[xy]\}. \quad (34\ T_2)$$

$$(T_1 \text{ and } T_2 \text{ degenerated})$$

The validity of these equations at the equilibrium lattice constant has been previously examined in details[13], and applied to the calculations of the frequency *versus* wave number vector relations for monovalent metals. These formulae are also rigorous at any lattice constant, since they are derived without any reference to the equilibrium lattice constant, provided the approximations of (20) and (21), as well as the approximation of (12) and the approximate value of $B(\mathbf{q}+\mathbf{K}_h)$, are valid.

As an example, we compare the compressibility[13] derived from $(32\,L)$ and $(33\,T_1)$ for $|\mathbf{q}|\leqslant 1$ with the one in the WIGNER-SEITZ theory of a perfect crystal. The reciprocal of compressibility $1/\chi = c_{11}-(2/3)\,(c_{11}-c_{12})$ is given in the present formulation as*)

$$\frac{1}{\chi} = N\left[-2(V(r_s)-E_0)+\frac{2}{3}\zeta_0+\frac{0.20e^2}{r_s}-\frac{0.204e^2}{r_s}\right.$$
$$\left.-\left\{(B-1)\frac{0.204e^2}{r_s}+\frac{2}{3}\zeta_0\left(1-\frac{D_0}{D}\right)\right\}\right]. \quad (35)$$

On the other hand, the cohesion energy E_C per electron of perfect crystal is expressed, according to the WIGNER-SEITZ theory, as

$$E_C = E_0(r_s)+\frac{3}{5}\zeta_0-\frac{0.60e^2}{r_s}-\frac{0.458e^2}{r_s}-\left\{C_0+C_1\log\left(\frac{r_s}{a_H}\right)+C_2\left(\frac{r_s}{a_H}\right)\right\}\frac{e^2}{2a_H},$$

where the first term is the HARTREE energy of an electron $k=0$ given by (21), the second the FERMI energy, the third term corrects for the doubly reckoned COULOMB energy in the first term, the fourth the exchange energy, and the last term is the correlation energy[17], C_0, C_1 and C_2 being constants and a_H the BOHR radius. We have from the above expression,

$$\frac{1}{\kappa} = \frac{1}{12\pi r_s}\left\{\frac{d^2 E_C}{dr_s^2}-\frac{2}{r_s}\frac{dE_C}{dr_s}\right\}$$
$$= N\left[-2(V(r_s)-E_0)+\frac{2}{3}\zeta_0+\frac{0.20e^2}{r_s}-\frac{0.204e^2}{r_s}\right. \quad (36)$$
$$\left.+\left\{\frac{1}{3}C_1+\frac{2}{9}C_2\left(\frac{r_s}{a_H}\right)\right\}\frac{e^2}{2a_H}\right],$$

---

*) The contributions of exchange repultions between ion-cores are neglected for the sake of simplicity.

making use of the relation[14a]

$$\frac{dE_0}{dr_s} = \frac{3}{r_s}\left\{(V(r_s)-E_0)-\frac{0.20\,e^2}{r_s}\right\}.$$

Eqs. (35) and (36) are identical except the last terms, which are approximately numerically equal with each other for $B=1.25$ on the base of $C_1=0.0313$ and $C_2=0.0005$[17], indicating that the dispersion relations (31), (32), (34) and (35) are valid at any lattice constant.

Now, we are ready to evaluate $\gamma_q=-d\log\omega_q/d\log V$ for the modes of waves propagating along the three principal axes from (32), (33) and (34). The γ_q for the longitudinal mode of $(1,0,0)$ direction is given, for example, from $(32L)$, (24), (28) and (29) as

$$\begin{aligned}
\gamma_q &\equiv -d\log\omega_q/d\log V = -\frac{1}{2}\frac{d\log(-[xx])}{d\log V}, \\
&= \frac{-1}{2[xx]}\left\{\frac{d[xx]^E}{d\log V}+\frac{d[xx]^C}{d\log V}+\frac{d[xx]^R}{d\log V}\right\}, \\
&= \frac{1}{2}\frac{[xx]^E+[xx]^C}{[xx]}-\frac{1}{6[xx]}\frac{d[xx]^R}{d\log r_0} \\
&\quad -\frac{4\pi Ne^2}{6[xx]}\sum_h\frac{(\bar{q}_x+h_x)^2}{|\bar{\mathbf{q}}+\mathbf{h}|^2}\,G(t)^2F(t)^{-1}f(t)\left\{\frac{2d\log G(t)}{d\log r_s}-\frac{d\log F(t)}{d\log r_s}\right\},
\end{aligned}$$
(37)

where

$$\begin{aligned}
\frac{d[xx]^R}{d\log r_0} &= \frac{A}{\rho}\sum_{l\neq0}{}'\exp\left\{(2r_B-r_0l)/\rho\right\}\left[\frac{1}{\rho}+\frac{1}{r_0l}\right. \\
&\quad \left.-\left\{\frac{r_0l}{\rho^2}+\frac{1}{\rho}+\frac{1}{r_0l}\right\}\frac{l_x^2}{l^2}\right]\left\{\exp(i\pi\bar{\mathbf{q}}\mathbf{l})-1\right\},
\end{aligned}$$
(37 a)

$$\frac{d\log G(t)}{d\log r_s} = \left\{\frac{1.8\pi}{r_sk_F}-2(V(r_s)-E_0)\frac{3\pi}{e^2k_F}\right\}t^2g(t)G(t)^{-1},$$
(37 b)

$$\frac{d\log F(t)}{d\log r_s} = -\left[\left\{\left(\frac{D_0}{D}\right)-\frac{r_sd}{dr_s}\left(\frac{D_0}{D}\right)\right\}\frac{2\pi\zeta_0}{e^2k_F}+\frac{r_sdB}{dr_s}f(t)\right]t^2F(t)^{-1}$$
(37 c)

with reference to the relations

$$\frac{d\log k_F}{d\log r_s} = -1,$$

$$\frac{d\log\zeta_0}{d\log r_0} = -2,$$

$$\frac{r_s dE_0}{dr_s} = 3 \left\{ (V(r_s) - E_0) - \frac{0.20\,e^2}{r_s} \right\} ,$$

and

$$\frac{dN}{d\log V} = -N ,$$

We have, furthermore,

$$r_s \frac{d}{dr_s} \left(\frac{D_0}{D} \right) = \frac{(r_s/a_H)}{d_0} \left\{ d_1 + 2d_2(r_s/a_H) - 1 - \log (r_s/a_H) \right\} ,$$

using the relation according to Pines[17]

$$\frac{D_0}{D} = 1 + \frac{(r_s/a_H)}{d_0} \left\{ d_1 + d_2(r_s/a_H) - \log(r_s/a_H) \right\} , \qquad (37\,\text{d})$$

where d_0, d_1, and d_2 are constants.

The $r_s dB/dr_s$ is estimated by putting the last term of (35) equal to the last one of (36), $i, e.$,

$$B = 1 - \frac{r_s}{0.204\,e^2} \left\{ \frac{2}{3} \zeta_0 \left(1 - \frac{D_0}{D}\right) + \left(\frac{1}{3}C_1 + \frac{2}{9}C_2 \frac{r_s}{a_H}\right) \frac{e^2}{2a_H} \right\} , \quad (37\,\text{e})$$

hence

$$r_s \frac{dB}{dr_s} = -\frac{r_s}{0.204\,e^2} \left\{ \frac{2}{3} \zeta_0 \left(1 - \frac{D_0}{D}\right) + \left(\frac{1}{3}C_1 + \frac{4}{9}C_2 \frac{r_s}{a_H}\right) \frac{e^2}{2a_H} \right\} .$$

The estimated values are given on the base of $d_0 = 12.07$, $d_1 = 1.47$, $d_2 = 0.0625$, $C_1 = 0.0313$ and $C_2 = 0.0005$[17] as below :

	Na	K	Rb	Cs
$r_s \dfrac{d}{dr_s} \left(\dfrac{D_0}{D} \right)$	0.13	0.20	0.25	0.29
$r_s \dfrac{dB}{dr_s}$	−0.28	−0.16	−0.17	−0.17

The contributions from these terms to γ_q are only a few percent of the resultant values.

The numerical results for γ_q of longitudinal and transversal modes in the three principal axes are given in Figs. 1, 2, 3 and Table A I in Appendix for Na and K, and in Figs, 4, 5 and 6 for Rb and Cs[*]. The second, third and

---

[*] The singular behavior of γ_q at $|q| \approx 0.1\,\pi/r_0$ of the T_1-branch of the transversal wave propagating in the direction (110) is due to the contribution from valence electrons (see the column (III) of (T_1) of (ii) in Table A I in Appendix).
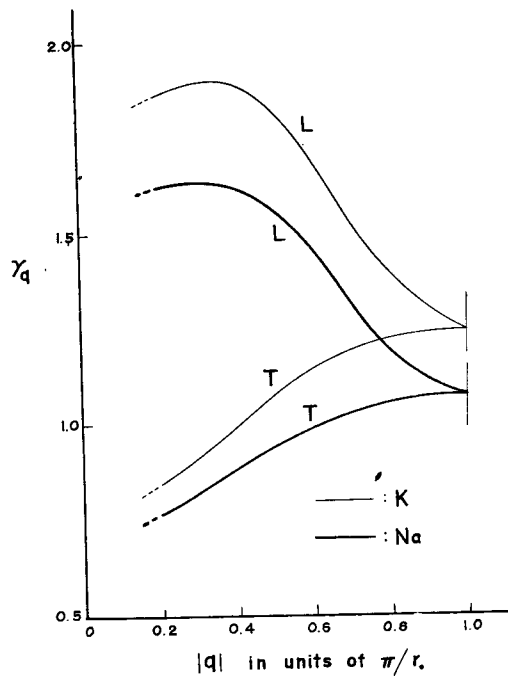
Fig. 1. The γ_q *versus* wave number vector $q = \pi/r_0$ $(\bar{q},\ 0,\ 0)$ for Na and K.
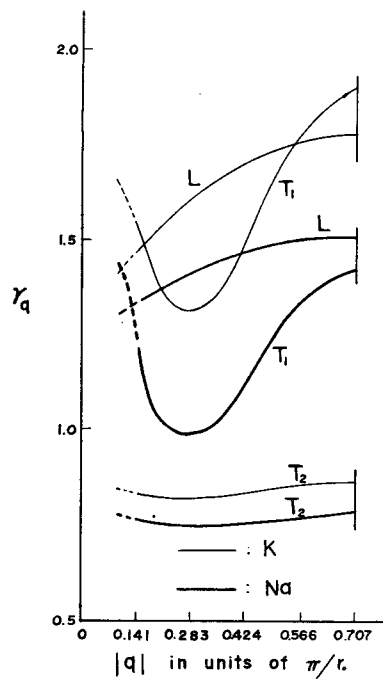
Fig. 2. The γ_q *versus* wave number vector $q = \pi/r_0$ $(\bar{q},\ \bar{q},\ 0)$ for Na and K.
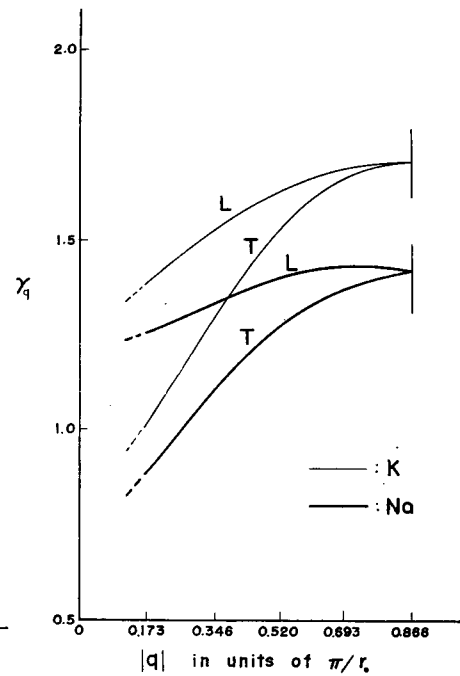
Fig. 3. The γ_q *versus* wave number vector $q = \pi/r_0$ $(\bar{q},\ \bar{q},\ \bar{q})$ for Na and K.
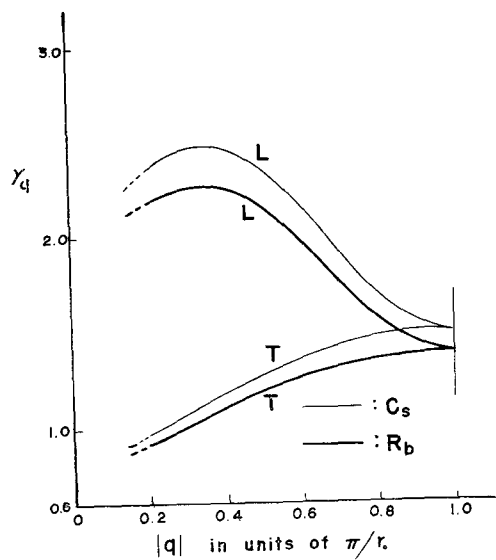
Fig. 4. The r_q *versus* wave number vector $q = \pi/r_0 \ (q, \ 0, \ 0)$ for Rb and Cs.
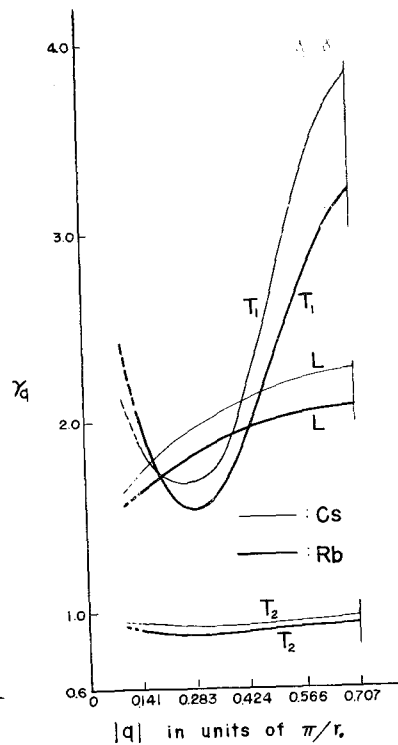
Fig. 5. The r_q *versus* wave number vector $q = \pi/r_0 \ (q, \ \bar{q}, \ 0)$ for Rb and Cs.
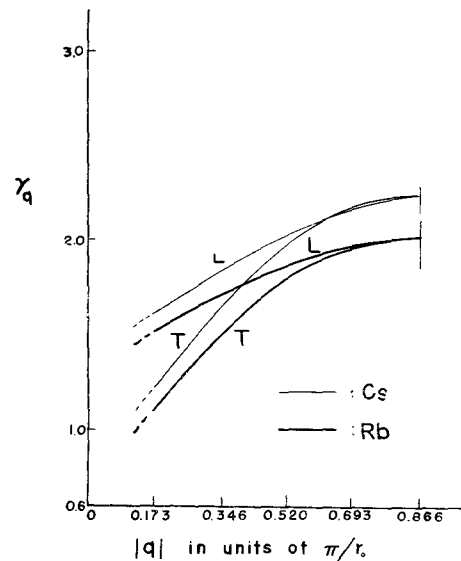
Fig. 6. The r_q *versus* wave number vector $q = \pi/r_0 \ (\bar{q}, \ \bar{q}, \ \bar{q})$ for Rb and Cs.

fourth columns of Table A I in Appendix show the contributions from the first, second and third terms on the fifth member of (37) respectively for $(1, 0, 0)$ and coresponding terms for $(1, 1, 0)$ and $(1, 1, 1)$.

The γ_M at high temperatures $T \geqslant \Theta$ is estimated by (18), assuming that its weight in q-space is proportional to $|q|^2$, and taking into account that the proportion of the weight of $(1, 0, 0)$, $(1, 1, 0)$ and $(1, 1, 1)$ directions is $6 : 12 : 8$. The theoretical results are given in Table I in comparison with the experimental

TABLE I. γ at $T > \Theta$

	Na	K	Rb	Cs
r_s (in atomic units)	3.96	4.87	5.18	5.57
ζ_0 (eV)	3.17	2.10	1.86	1.61
B $(q = 0)$	1.25	1.21	1.18	1.18
D/D_0	0.90	0.935	0.945	0.965
$V(r_s) - E_0$ (eV)	0.08	− 0.02	0.03	0.00
γ (theoretical)	1.24	1.46	1.76	1.93
γ derived from (3)	1.19	1.30	0.90	1.14
γ derived from (3a)	0.86	0.97	0.57	0.81
γ (experimental)[*]	1.25	1.34	1.48	1.29
γ (experimental)[**]	1.37	1.41	1.86	1.60

[*] Given by GRÜNEISEN (see ref. (18)).
[**] Revised value by GILVARRY (see ref. (18)).
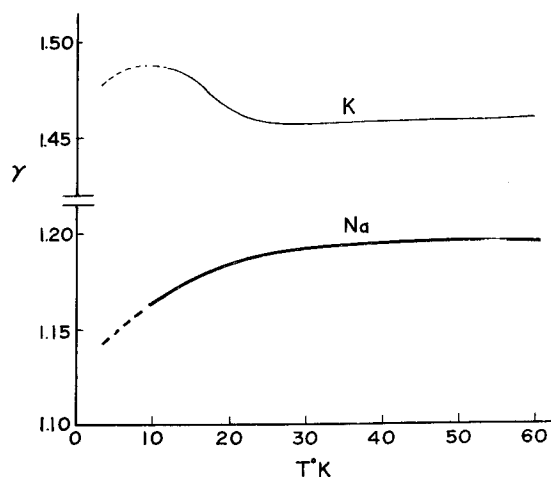
Fig. 7. Crüneisdn $\gamma = \alpha V / \varkappa C_V$ *versus* temperature for Na and K (theoretical).

values as well as those given by (3) or (3a). The $\gamma(T)$ as a function of T is predictively calculated for Na and K according to (18), as shown in Fig. 7. The γ_M of Na decreases at low temperatures, while that of K has a maximum at $T \approx 10°K$, because of the T_1-branch propagating in the $(1, 1, 0)$ direction with low frequencies and large γ_q.

§ 3. Normal vibrations and Grüneisen constant of Cu

The electronic structure of Cu has been investigated theoretically by a number of authors[19][20][21]. Extending the quantum defect method, KAMBE[19] obtained 0.988 for the reciprocal of the ratio of the effective electron mass to the free electron mass, and $|U_0(r_s)|^2 = 1.01$. HOWARTH[20], by applying the argumented plane wave method, and FUKUCHI[21], by applying the orthogonalized plane wave method, concluded that the effective mass is almost equal to the free electron mass, except for electrons of energies near the Fermi surface. These conclusions of KAMBE, HOWARTH and FUKUCHI indicate that the approximations of (20) and (21) are close enough to apply the formulae given in the preceding section directly to the evaluation of normal vibrations and γ_q's of Cu.

The theoretical values of E_0 are not, however, coincident with each other as $E_0 = -2.7$ eV obtained by KAMBE[19] and $E_0 = -4.2$ eV by FUKUCHI[21]. The former value gives too small a cohesion energy of Cu, while the latter too large one. In the present paper, we have carried out calculations for three values of E_0 inbetween these values, *i.e.*, (a) $E_0 = -3.33$ eV, (b) $E_0 = -3.70$ eV and (c) $E_0 = -4.07$ eV. We have $D/D_0 = 0.875$ and $B = 1.37$ respectively from (37 d) and (37 e) for the present calculation.

Correction terms $2.90 \cdot 10^{-4} \, r_s^4 (q_x^4 + q_y^4 + q_z^4) - 2.06 \cdot 10^{-4} \, r_s^4 |\mathbf{q}|^4$ is added to $g(2k_F r_s t)$ in the expression (22) of v_{ih}, so as to satisfy the condition $v_{ih} = v_{ph} = 0$ for $\mathbf{K}_h = (\pi/r_0)(1, 1, 1)$ and $\mathbf{K}_h = (\pi/r_0)(2, 0, 0)$[*].

BORN-MAYER type $\bar{A} \, exy(-R/\rho)$ of exchange repulsion potential between a pair of ion-cores is assumed, and the two constants $\bar{A}$ and ρ are so adjusted as to give the observed frequencies of the longitudinal and transversal modes of $q_m = (\pi/r_0)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ observed by JACOBSEN[22][**].

The values of $\bar{A}$ and ρ thus determined assuming $V(r_s) = 0$ are[***]:

(a) $E_0 = -3.33$ eV ;

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[*] Any such correction term were not required in the case of alkali metals of *b.c.c.* structure and very small value of $V(r_s) - E_0$, since then $v_{ih} \approx 0$ already for $|\mathbf{q} + \mathbf{K}_h| > \mathbf{K}_h$, $\mathbf{K}_h = (\pi/r_0) \times (1, 1, 0)$ without any correction terms.

[**] According to JACOBSEN, the data for the $(1, 1, 1)$ direction is the most accurate (private communication).

[***] We have to replace $A \exp(-2r_B/\rho)$ in (29) and (37a) by $\bar{A}$ in this section.

$$\bar{A} = 0.123 \exp(\sqrt{2}\, r_0/\rho) \ \text{eV} \ \text{and} \ r_0/\rho = 7.730,$$

hence

$$v_R(R) = 0.123 \exp\left\{10.94(R_e - R)/R_e\right\} \ \text{eV},$$

where $R_e = \sqrt{2}\, r_0$ is the distance between nearest neighbours in the equilibrium configuration of the lattice.

(b) $E_0 = -3.70 \ \text{eV}$:

$$\bar{A} = 0.156 \exp(\sqrt{2}\, r_0/\rho) \ \text{eV} \ \text{and} \ r_0/\rho = 7.148,$$

hence

$$v_R(R) = 0.156 \exp\left\{10.12(R_e - R)/R_e\right\} \ \text{eV},$$

(c) $E_0 = -4.07 \ \text{eV}$:

$$\bar{A} = 0.192 \exp(\sqrt{2}\, r_0/\rho) \ \text{eV} \ \text{and} \ r_0/\rho = 6.717$$

hence

$$v_R(R) = 0.192 \exp\left\{9.46(R_e - R)/R_e\right\} \ \text{eV}.$$

The frequency *versus* wave vector relations are calculated for waves propagating in the (100), (110) and (111) directions. The results are tabulated in Table A II in Appendix and shown by solid curves in Figs, 8, 9 and 10 for the case of (b) in comparison with the experimental results of JACOBSEN[22] given by crosses there. The dispersion relations derived for the three sets of values (a), (b) and (c) coincide with each other within a few percent as seen from Table A II.

The elastic constants c_{11}, c_{44} and $c_{11} - c_{12}$ are estimated from the long wavelength limit of the above relations to be 14,0, 8.2 and 4.6 in units of 10^{11} dynes/cm², respectively. The electronic term E_{II} of (9) compensates *ca.* 80% or 20% of the contribution to c_{44} or $c_{11} - c_{12}$ respectively from the $E_I + E_C$ of (9). The value of c_{11} is somewhat small as compared with the experimental value of $17.0\ 10^{11}$ dynes/cm². The discrepancy might be attributed to the free electron approximations of (20) and (21) for electrons of energies lying near the FERMI surface, which contribute to longitudinal frequencies of long wave-length (as readily seen from (9a)) and consequently to the elastic constant c_{11}, since these electrons are expected according to the investigations by HOWARTH[20] and FUKUCHI[21] to deviate in behaviour from free electrons.

The Υ_q's are calculated similarly as in the case of alkali metals. The results are tabulated in Table A III and shown in Figs. 11, 12 and 13 for the case of (*b*). The $\Upsilon_M(T)$ calculated by (18) in given in Fig. 14, in comparison with the experimental results obtained by RUBIN, ALTMAN and JOHNSTON[5], and
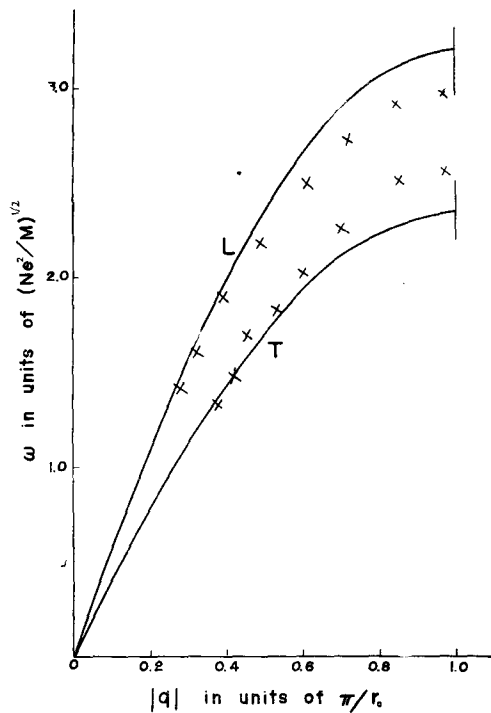
Fig. 8. Circular frequency ω *versus* wave number vector $\mathbf{q} = \pi/r_0\,(\bar{q}, 0, 0)$ for Cu in the case of (b) $E_0 = -3.7$ eV. Crosses are experimental values by JACOBSEN (ref. 22).
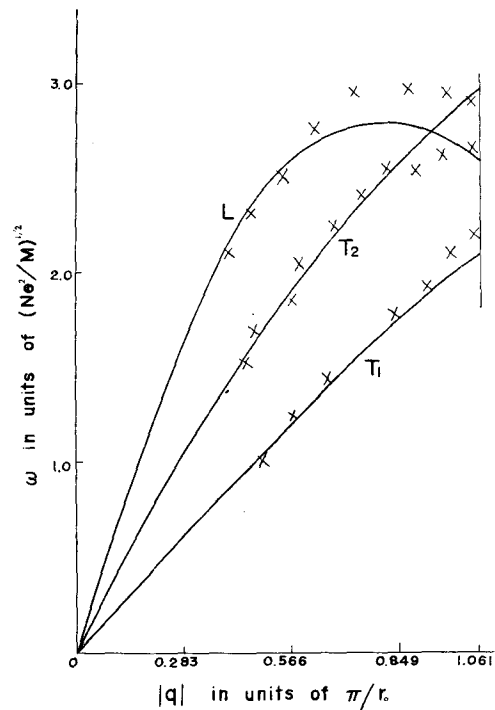
Fig. 9. Circular frequency ω *versus* wave number vector $\mathbf{q} = \pi/r_0\,(\bar{q}, \bar{q}, 0)$ for Cu in the case of (b) $E_0 = -3.7$ eV. Crosses are experimental values by JACOBSEN (ref. 22).
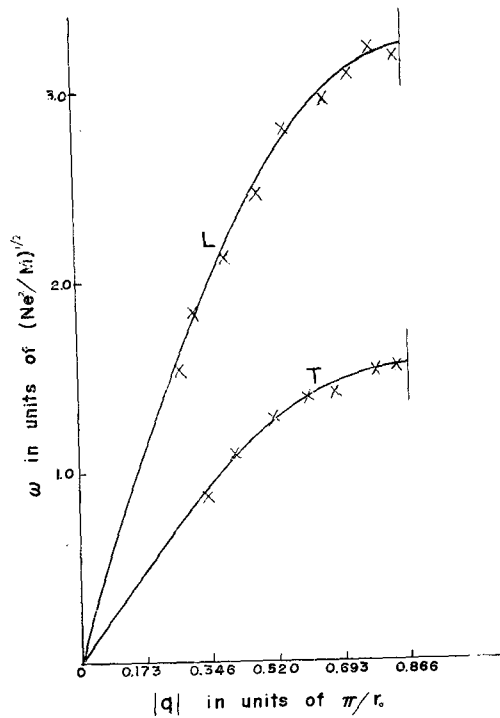
Fig. 10. Circular frequency ω *versus* wave number vector $\mathbf{q} = \pi/r_0\,(\bar{q}, \bar{q}, \bar{q})$ for Cu in the case of (b) $E_0 = -3.7$ eV. Crosses are experimental values by JACOBSEN (ref. 22).
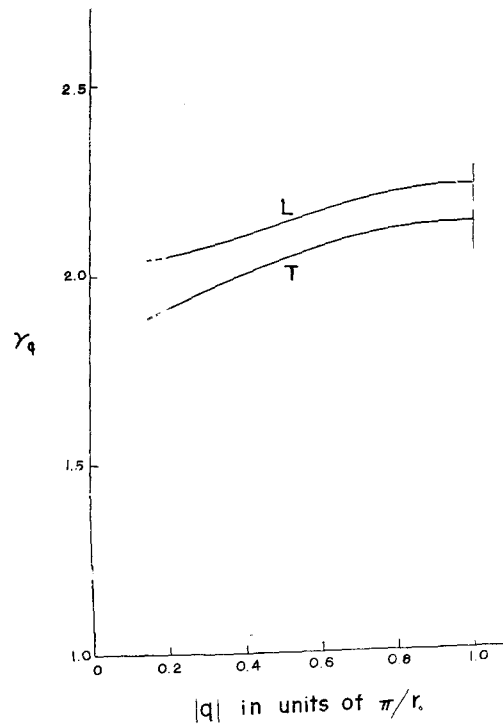
Fig. 11. The γ_q *versus* wave number vector $\mathbf{q} = \pi/r_0\,(\bar{q}, 0, 0)$ for Cu in the case of (b) $E_0 = -3.7$ eV.
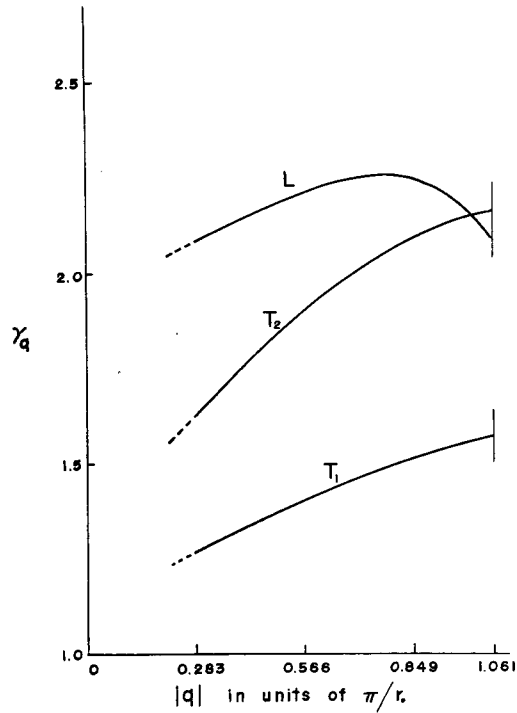
Fig. 12. The γ_q *versus* wave number vector $\mathbf{q}=\pi/r_0\,(\bar{q},\bar{q},0)$ for Cu in the case of (b) $E_0=-3.7$ eV.
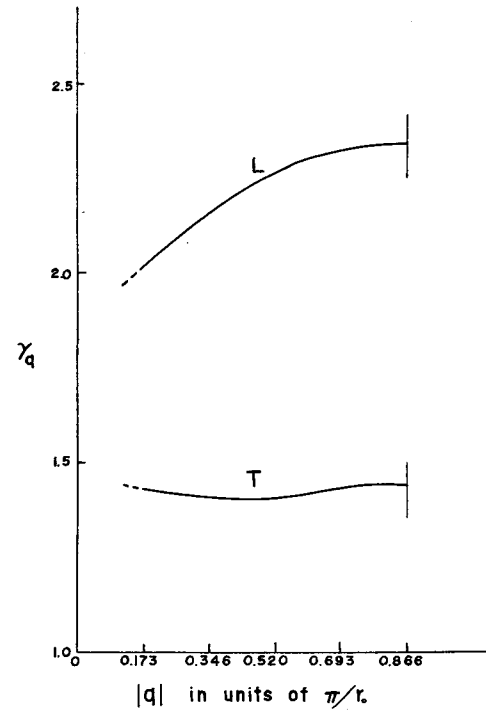
Fig. 13. The γ_q *versus* wave number vector $\mathbf{q}=\pi/r_0\,(\bar{q},\bar{q},\bar{q})$ for Cu in the case of (b) $E_0=-3.7$ eV.
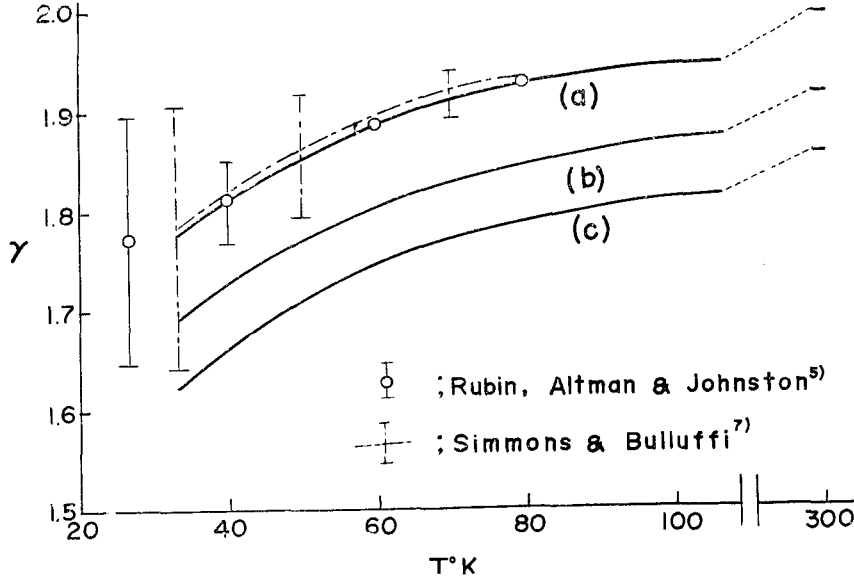
Fig. 14. Grüneisen $\gamma = \alpha V/xC_V$ *versus* temperature for Cu: (———) theoretical in the cases of (a) $E_0 = -3.33$ eV, (b) $E_0 = -3.70$ eV and (c) $E_0 = -4.07$ eV, respectively; ----- SIMMONS and BALLUFFI (ref. 7); ○ Rubin, Altman and Johnston (ref. 5).

SIMMONS and BULLUFFI[7]. The agreement between the theoretical and the experimental values is satisfactory.

It should be noted that the respective contributions of the first, second and third terms of (37) to γ_q differ markedly from those of alkali metals, notwithstanding the same order of magnitudes of the resultant values.

Conclusion

The dispersion relation of circular frequency ω *versus* wave number vector **q** and polarization vector $\mathbf{e}_q$, which the present author has previously derived by extending HARTREE-FOCK method, is proved to be valid as a function of lattice constant or atomic volume, hence $\gamma_q \equiv -d \log \omega/d \log V$ of any vibrational mode is readily evaluated.

Grüneisen constant γ is given by the mean of γ_q with weights $(\hbar\omega/\kappa T)^2 \times \exp(\hbar\omega/\kappa T)\{\exp(\hbar\omega/\kappa T)-1\}^{-2}$. The γ of alkali metals thus derived at high temperatures $T \geq \Theta$ are 1.24, 1.46, 1.76 and 1.93 for Na, K, Rb and Cs, respectively, which are compared with the respective experimental values 1.25 ~1.37, 1.34~1.41, 1.48~1.86 and 1.29~1.60. The γ at lower temperatures is

also worked out predictively. In the case of Na, the γ decreases monotonously as T tends to $0°K$, but in the case of K, it has a maximum at about $T=10°K$.

Frequency versus wave vector relations as well as $\gamma(T)$ of Cu are calculated similarly for the cases of the HARTREE energies of an electron $\mathbf{k}=0$ being $-3.33\,eV$, $-3.70\,eV$ and $-4.07\,eV$. As for the exchange repulsive potential between ion-cores, the central force potential of BORN-MAYER type is assumed, the two constants involved being adjusted to the observed longitudinal and transversal frequencies at the largest $\mathbf{q}$ of $(1, 1, 1)$ branch. The theoretical results are in conformity with experimental results by JACOBSEN[22], RUBIN, ALTMAN and JOHNSTON[5], and SIMMONS and BULLUFFI[7].

In conclusion, it has been shown that the extention of the HARTREE-FOCK method enables us to calculate from first principles the thermal expansion coefficients or Grüneisen constants as functions of temperatures, as well as the absolute magnitude of electrical conductivities, frequencies of normal vibrations, and consequently elastic constants and heat capacities or DEBYE temperatures of monovalent metals. The agreements of the theoretical values with observations are found satisfactory.

The present method will further be applied to elucidate the nature of electrical conductivity of transition metals[23], the change of electrical conductivity under pressure, the temperature variation of compressibility and the martensitic transformation of Li and Na at low temperatures.

Appendix

TABLE A I.   The r_q *versus* wave number vector $\mathbf{q}=(\pi/r_0)(\bar{q},0,0)$, $\mathbf{q}=(\pi/r_0)(\bar{q},\bar{q},0)$ or $\mathbf{q}=(\pi/r_0)(\bar{q},\bar{q},\bar{q})$ for Na and K. The first column gives the value of $\bar{q}$, the second, third and fourth columns give respectively the contributions of the first (I), the second (II) and the third (III) terms of Eq. (37). The r_q's are given in the last column.

(i) $\mathbf{q}=(\pi/r_0)(\bar{q},0,0)$

(L)   Longitudinal mode $\mathbf{e}_q=(1,0,0)$.

$\bar{q}$		(I)	(II)	(III)	r_q
0.2	Na	0.448	0.192	0.984	1.623
	K	0.452	0.217	1.191	1.860
0.4	Na	0.446	0.197	0.981	1.624
	K	0.449	0.232	1.223	1.903
0.6	Na	0.446	0.194	0.828	1.468
	K	0.447	0.235	1.041	1.723
0.8	Na	0.448	0.182	0.563	1.193
	K	0.449	0.224	0.712	1.385
1.0	Na	0.449	0.177	0.443	1.069
	K	0.450	0.219	0.575	1.244

($T_{1,2}$)   Transversal mode $\mathbf{e}_q=(0,1,0)$ or $(0,0,1)$

$\bar{q}$		(I)	(II)	(III)	r_q
0.2	Na	0.454	0.158	0.153	0.764
	K	0.453	0.193	0.192	0.838
0.4	Na	0.452	0.165	0.260	0.878
	K	0.451	0.204	0.335	0.990
0.6	Na	0.450	0.172	0.364	0.987
	K	0.450	0.213	0.475	1.137
0.8	Na	0.449	0.176	0.422	1.047
	K	0.450	0.217	0.549	1.216
1.0	Na	0.449	0.177	0.443	1.060
	K	0.450	0.219	0.573	1.242

(ii) $\mathbf{q} = (\pi/r_0)(\bar{q}, \bar{q}, 0)$

(L) Longitudinal mode $\mathbf{e}_q = (1/\sqrt{2}, 1/\sqrt{2}, 0)$.

$\bar{q}$		(I)	(II)	(III)	r_q
0.1	Na	0.453	0.187	0.686	1.326
	K	0.450	0.223	0.790	1.463
0.2	Na	0.452	0.192	0.762	1.406
	K	0.448	0.234	0.917	1.598
0.3	Na	0.451	0.195	0.819	1.465
	K	0.446	0.239	1.011	1.697
0.4	Na	0.451	0.196	0.852	1.499
	K	0.445	0.243	1.069	1.757
0.5	Na	0.451	0.197	0.863	1.510
	K	0.445	0.244	1.089	1.778

(T_1) Transversal mode $\mathbf{e}_q = (1/\sqrt{2}, -1/\sqrt{2}, 0)$

$\bar{q}$		(I)	(II)	(III)	r_q
0.1	Na	0.786	-1.005	1.437	1.217
	K	0.639	-0.587	1.498	1.550
0.2	Na	0.752	-0.890	1.123	0.984
	K	0.628	-0.537	1.218	1.309
0.3	Na	0.767	-0.946	1.285	1.106
	K	0.637	-0.578	1.416	1.475
0.4	Na	0.799	-1.061	1.601	1.339
	K	0.655	-0.652	1.777	1.780
0.5	Na	0.812	-1.105	1.718	1.425
	K	0.661	-0.680	1.914	1.895

(T_2) Transversal mode $\mathbf{e}_q = (0, 0, 1)$

$\bar{q}$		(I)	(II)	(III)	r_q
0.1	Na	0.453	0.159	0.145	0.758
	K	0.455	0.193	0.181	0.830
0.2	Na	0.454	0.157	0.127	0.738
	K	0.456	0.191	0.159	0.806
0.3	Na	0.454	0.158	0.138	0.750
	K	0.455	0.193	0.174	0.882
0.4	Na	0.161	0.161	0.155	0.759
	K	0.454	0.196	0.197	0.847
0.5	Na	0.453	0.162	0.160	0.775
	K	0.454	0.197	0.204	0.855

(iii) $\mathbf{q} = (\pi/r_0)(\bar{q}, \bar{q}, \bar{q})$

(L)   Longitudinal mode $\mathbf{e}_q = (1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$

$\bar{q}$		(I)	(II)	(III)	r_q
0.1	Na	0.448	0.187	0.612	1.247
	K	0.450	0.224	0.708	1.381
0.2	Na	0.446	0.194	0.693	1.333
	K	0.447	0.235	0.837	1.520
0.3	Na	0.445	0.197	0.755	1.397
	K	0.446	0.241	0.942	1.629
0.4	Na	0.446	0.196	0.783	1.425
	K	0.446	0.242	1.005	1.693
0.5	Na	0.447	0.193	0.775	1.415
	K	0.447	0.239	1.021	1.707

$(T_{1,2})$ Transversal mode $\mathbf{e}_q = (1/\sqrt{2}, -1/\sqrt{2}, 0)$ or $(1/\sqrt{6}, 1/\sqrt{6}, -2/\sqrt{6})$

$\bar{q}$		(I)	(II)	(III)	r_q
0.1	Na	0.445	0.163	0.265	0.873
	K	0.456	0.201	0.337	0.995
0.2	Na	0.452	0.176	0.470	1.098
	K	0.452	0.220	0.622	1.294
0.3	Na	0.449	0.185	0.638	1.272
	K	0.450	0.230	0.854	1.534
0.4	Na	0.448	0.190	0.731	1.369
	K	0.448	0.236	0.973	1.657
0.5	Na	0.447	0.193	0.775	1.415
	K	0.447	0.239	1.021	1.707

TABLE A II.   Circular frequency ω_q *versus* wave number vector
$\mathbf{q}=(\pi/r_0)(\bar{q},0,0)$, $\mathbf{q}=(\pi/r_0)(\bar{q},\bar{q},0)$ or $\mathbf{q}=(\pi/r_0)(\bar{q},\bar{q},\bar{q})$
for Cu.   The first column gives values of $\bar{q}$, the
second, third, fourth and fifth columns give respect-
ively the contributions of E_C+E_I, E_{II}, E_R and their
sum in Eq. (9) in units of Ne^2.   The circular frequ-
encies are given in the last column in units of
$(Ne^2/M)^{1/2}=1.35\times10^{13}$ sec^{-1}.

(i) $\mathbf{q}=(\pi/r_0)(\bar{q},0,0)$

(L)   Longitudinal mode $\mathbf{e}_q=(1,0,0)$

$\bar{q}$		E_C+E_I	E_{II}	E_R	sum	ω_q
0.2	(a)	12.202	− 12.417	1.305	1.091	1.044
	(b)	12.202	− 12.494	1.421	1.129	1.063
	(c)	12.202	− 12.573	1.539	1.168	1.081
0.4	(a)	11.227	− 12.102	4.695	3.819	1.954
	(b)	11.227	− 12.412	5.098	3.913	1.978
	(c)	11.227	− 12.727	5.509	4.010	2.002
0.6	(a)	9.978	− 11.816	8.828	6.990	2.644
	(b)	9.978	− 12.464	9.559	7.073	2.660
	(c)	9.978	− 13.134	10.300	7.144	2.673
0.8	(a)	8.93	− 11.66	12.13	9.39	3.06
	(b)	8.93	− 12.63	13.10	9.41	3.07
	(c)	8.93	− 13.63	14.08	9.38	3.06
1.0	(a)	8.52	− 11.59	13.38	10.30	3.21
	(b)	8.52	− 12.68	14.44	10.28	3.21
	(c)	8.52	− 13.82	15.50	10.21	3.20

($T_{1,2}$)   Transversal mode $\mathbf{e}_q=(0,1,0)$ or $(0,0,1)$

$\bar{q}$		E_C+E_I	E_{II}	E_R	sum	ω_q
0.2	(a)	0.182	− 0.093	0.508	0.597	0.773
	(b)	0.182	− 0.107	0.535	0.610	0.781
	(c)	0.182	− 0.122	0.562	0.622	0.788
0.4	(a)	0.670	− 0.459	1.841	2.052	1.433
	(b)	0.670	− 0.524	1.939	2.085	1.444
	(c)	0.670	− 0.595	2.037	2.112	1.453
0.6	(a)	1.294	− 1.054	3.492	3.731	1.932
	(b)	1.294	− 1.200	3.679	3.773	1.942
	(c)	1.294	− 1.356	3.868	3.807	1.951
0.8	(a)	1.82	− 1.62	4.83	5.03	2.24
	(b)	1.82	− 1.84	5.09	5.08	2.25
	(c)	1.82	− 2.07	5.36	5.11	2.26
1.0	(a)	2.02	− 1.86	5.34	5.50	2.35
	(b)	2.02	− 2.11	5.63	5.55	2.36
	(c)	2.02	− 2.37	5.93	5.59	2.36

(ii) $\mathbf{q} = (\pi/r_0)\,(\bar{q}, \bar{q}, 0)$

(L)   Longitudinal mode $\mathbf{e}_q = (1/\sqrt{2}, 1/\sqrt{2}, 0)$

$\bar{q}$		$E_C + E_I$	E_{II}	E_R	sum	ω_q
0.2	(a)	12.121	$-$ 12.637	3.080	2.564	1.601
	(b)	12.121	$-$ 12.840	3.345	2.626	1.621
	(c)	12.121	$-$ 13.047	3.612	2.686	1.640
0.4	(a)	10.500	$-$ 12.354	8.573	6.720	2.592
	(b)	10.500	$-$ 12.995	9.296	6.801	2.610
	(c)	10.500	$-$ 13.658	10.026	6.868	2.621
0.6	(a)	7.41	$-$ 9.74	10.22	7.89	2.81
	(b)	7.41	$-$ 10.55	11.04	7.89	2.81
	(c)	7.41	$-$ 11.40	11.86	7.87	2.81
0.75	(a)	4.61	$-$ 5.99	8.28	6.90	2.63
	(b)	4.61	$-$ 6.60	8.87	6.88	2.62
	(c)	4.61	$-$ 7.23	9.47	6.85	2.62

(T_1)   Transversal mode $\mathbf{e}_q = (1/\sqrt{2}, -1/\sqrt{2}, 0)$

$\bar{q}$		$E_C + E_I$	E_{II}	E_R	sum	ω_q
0.2	(a)	0.055	$-$ 0.000	0.304	0.359	0.599
	(b)	0.055	$-$ 0.000	0.304	0.359	0.599
	(c)	0.055	$-$ 0.000	0.305	0.360	0.600
0.4	(a)	0.326	$-$ 0.182	1.305	1.449	1.204
	(b)	0.326	$-$ 0.210	1.333	1.449	1.204
	(c)	0.326	$-$ 0.239	1.365	1.452	1.205
0.6	(a)	0.94	$-$ 0.73	2.96	3.16	1.78
	(b)	0.94	$-$ 0.84	3.07	3.18	1.79
	(c)	0.94	$-$ 0.95	3.20	3.19	1.79
0.75	(a)	1.51	$-$ 1.31	4.26	4.46	2.11
	(b)	1.51	$-$ 1.49	4.47	4.49	2.12
	(c)	1.51	$-$ 1.67	4.68	4.51	2.12

(T_2)   Transversal mode $\mathbf{e}_q = (0, 0, 1)$

$\bar{q}$		$E_C + E_I$	E_{II}	E_R	sum	ω_q
0.2	(a)	0.393	$-$ 0.315	1.041	1.119	1.058
	(b)	0.393	$-$ 0.360	1.099	1.133	1.064
	(c)	0.393	$-$ 0.408	1.157	1.142	1.069
0.4	(a)	1.741	$-$ 2.065	4.003	3.679	1.918
	(b)	1.741	$-$ 2.323	4.255	3.673	1.917
	(c)	1.741	$-$ 2.598	4.508	3.652	1.911
0.6	(a)	4.22	$-$ 5.58	8.14	6.77	2.60
	(b)	4.22	$-$ 6.20	8.70	6.74	2.60
	(c)	4.22	$-$ 6.84	9.30	6.68	2.58
0.75	(a)	6.45	$-$ 8.60	11.08	8.93	2.99
	(b)	6.45	$-$ 9.46	11.97	8.91	2.99
	(c)	6.45	$-$ 10.37	12.76	8.85	2.98

(iii) $\mathbf{q} = (\pi/r_0)(\bar{q}, \bar{q}, \bar{q})$

(L) Longitudinol mode $\mathbf{e}_q = (1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$

$\bar{q}$		$E_C + E_I$	E_{II}	E_R	sum	ω_q
0.1	(a)	12.456	$-$ 12.635	1.348	1.169	1.081
	(b)	12.456	$-$ 12.720	1.464	1.200	1.095
	(c)	12.456	$-$ 12.807	1.581	1.230	1.109
0.2	(a)	12.167	$-$ 13.123	4.878	3.923	1.981
	(b)	12.167	$-$ 13.474	5.298	3.991	1.998
	(c)	12.167	$-$ 13.835	5.721	4.052	2.013
0.3	(a)	11.81	$-$ 13.94	9.24	7.11	2.67
	(b)	11.81	$-$ 14.66	10.04	7.16	2.68
	(c)	11.81	$-$ 15.41	10.84	7.24	2.69
0.4	(a)	11.53	$-$ 14.72	12.77	9.58	3.10
	(b)	11.53	$-$ 15.77	13.87	9.63	3.10
	(c)	11.53	$-$ 16.86	14.98	9.65	3.11
0.5	(a)	11.42	$-$ 15.04	14.12	10.50	3.24
	(b)	11.42	$-$ 16.22	15.33	10.54	3.25
	(c)	11.42	$-$ 17.44	16.56	10.54	3.25

($T_{1,2}$) Transversal mode $\mathbf{e}_q = (1/\sqrt{2}, -1/\sqrt{2}, 0)$ or $(1/\sqrt{6}, 1/\sqrt{6}, -2/\sqrt{6})$

$\bar{q}$		$E_C + E_I$	E_{II}	E_R	sum	ω_q
0.1	(a)	0.056	$-$ 0.019	0.198	0.235	0.485
	(b)	0.056	$-$ 0.022	0.203	0.237	0.487
	(c)	0.056	$-$ 0.025	0.210	0.241	0.491
0.2	(a)	0.200	$-$ 0.060	0.715	0.854	0.924
	(b)	0.200	$-$ 0.069	0.736	0.867	0.931
	(c)	0.200	$-$ 0.079	0.759	0.880	0.938
0.3	(a)	0.38	$-$ 0.10	1.35	1.63	1.28
	(b)	0.38	$-$ 0.12	1.39	1.66	1.29
	(c)	0.38	$-$ 0.13	1.44	1.68	1.30
0.4	(a)	0.22	$-$ 0.19	1.87	2.20	1.48
	(b)	0.52	$-$ 0.22	1.94	2.23	1.49
	(c)	0.52	$-$ 0.26	2.01	2.27	1.50
0.5	(a)	0.57	$-$ 0.21	2.07	2.43	1.53
	(b)	0.57	$-$ 0.25	2.13	2.45	1.57
	(c)	0.57	$-$ 0.28	2.20	2.48	1.58

TABLE A III. The r_q *versus* wave number vector $\mathbf{q}=(\pi/r_0)(\bar{q}, 0, 0)$, $\mathbf{q}=(\pi/r_0)(\bar{q}, \bar{q}\, 0)$ or $\mathbf{q}=(\pi/r_0)(\bar{q}, \bar{q}, \bar{q})$ for Cu. The first column gives the value of $\bar{q}$, the second, third and fourth columns give respectively the contributions of the first (I), the second (II) and the third (III) terms of Eq. (37). The r_q's are given in the last column.

(i) $\mathbf{q}=(\pi/r_0)(\bar{q}, 0, 0)$

(L) Longitudinal mode $\mathbf{e}_q=(1, 0, 0)$

$\bar{q}$		(I)	(II)	(III)	r_q
0.2	(a)	− 0.099	2.181	0.079	2.161
	(b)	− 0.129	2.124	0.059	2.054
	(c)	− 0.159	2.094	0.037	1.972
0.4	(a)	− 0.115	2.190	0.093	2.168
	(b)	− 0.151	2.192	0.073	2.113
	(c)	− 0.187	2.174	0.050	2.037
0.6	(a)	− 0.132	2.288	0.112	2.269
	(b)	− 0.176	2.263	0.094	2.182
	(c)	− 0.221	2.269	0.071	2.119
0.8	(a)	− 0.145	2.333	0.130	2.317
	(b)	− 0.197	2.324	0.114	2.242
	(c)	− 0.250	2.351	0.091	2.192
1.0	(a)	− 0.149	2.343	0.136	2.330
	(b)	− 0.202	2.341	0.123	2.262
	(c)	− 0.260	2.375	0.099	2.214

$(T_{1,2})$ Transversal mode $\mathbf{e}_q=(0, 1, 0)$ or $(0, 0, 1)$

$\bar{q}$		(I)	(II)	(III)	r_q
0.2	(a)	0.074	1.833	0.026	1.933
	(b)	0.062	1.829	0.023	1.913
	(c)	0.048	1.798	0.018	1.864
0.4	(a)	0.052	1.932	0.037	2.020
	(b)	0.035	1.940	0.033	2.008
	(c)	0.018	1.919	0.027	1.964
0.6	(a)	0.032	2.016	0.046	2.094
	(b)	0.013	2.035	0.042	2.090
	(c)	− 0.008	2.024	0.034	2.050
0.8	(a)	0.020	2.069	0.053	2.142
	(b)	− 0.002	2.095	0.048	2.141
	(c)	− 0.025	2.091	0.040	2.106
1.0	(a)	0.015	2.091	0.055	2.162
	(b)	− 0.008	2.121	0.050	2.163
	(c)	− 0.032	2.119	0.042	2.129

(ii) $\mathbf{q} = (\pi/r_0)(\bar{q}, \bar{q}, 0)$

(L) Longitudinal mode $\mathbf{e}_q = (1/\sqrt{2}, 1/\sqrt{2}, 0)$

$\bar{q}$		(I)	(II)	(III)	r_q
0.2	(a)	— 0.101	2.184	0.000	2.173
	(b)	— 0.137	2.142	0.071	2.076
	(c)	— 0.172	2.127	0.049	2.004
0.4	(a)	— 0.138	2.315	0.117	2.293
	(b)	— 0.184	2.293	0.098	2.207
	(c)	— 0.230	2.303	0.074	2.147
0.6	(a)	— 0.148	2.339	0.130	2.322
	(b)	— 0.199	2.332	0.114	2.247
	(c)	— 0.253	2.360	0.091	2.198
0.75	(a)	— 0.100	2.149	0.114	2.163
	(b)	— 0.144	2.127	0.102	2.085
	(c)	— 0.191	2.141	0.067	2.016

(T_1) Transversal mode $\mathbf{e}_q = (1/\sqrt{2}, -1/\sqrt{2}, 0)$

$\bar{q}$		(I)	(II)	(III)	r_q
0.2	(a)	0.077	1.400	0.000	1.476
	(b)	0.077	1.267	0.000	1.344
	(c)	0.076	1.186	0.000	1.262
0.4	(a)	0.050	1.526	0.021	1.596
	(b)	0.040	1.421	0.019	1.480
	(c)	0.030	1.357	0.015	1.402
0.6	(a)	0.033	1.618	0.038	1.688
	(b)	0.016	1.534	0.034	1.584
	(c)	— 0.002	1.484	0.028	1.511
0.75	(a)	0.035	1.670	0.048	1.745
	(b)	0.002	1.597	0.044	1.643
	(c)	— 0.019	1.554	0.036	1.571

(T_2) Transversal mode $\mathbf{e}_q = (0, 0, 1)$

$\bar{q}$		(I)	(II)	(III)	r_q
0.2	(a)	0.035	1.638	0.046	1.719
	(b)	0.015	1.567	0.041	1.623
	(c)	0.006	1.525	0.034	1.552
0.4	(a)	0.044	1.931	0.091	1.978
	(b)	0.079	1.891	0.083	1.895
	(c)	0.117	1.882	0.071	1.836
0.6	(a)	0.101	2.151	0.118	2.168
	(b)	0.147	2.134	0.107	2.094
	(c)	0.196	2.152	0.090	2.045
0.75	(a)	0.120	2.231	0.126	2.236
	(b)	0.169	2.220	0.113	2.104
	(c)	0.221	2.244	0.073	2.096

(iii) $\mathbf{q} = (\pi/r_0)(\bar{q}, \bar{q}, \bar{q})$

(L) Longitudinal mode $\mathbf{e}_q = (1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$,

$\bar{q}$		(I)	(II)	(III)	r_q
0.1	(a)	$-$ 0.077	2.097	0.081	2.101
	(b)	$-$ 0.110	2.051	0.064	2.005
	(c)	$-$ 0.143	2.031	0.044	1.932
0.2	(a)	$-$ 0.122	2.261	0.106	2.245
	(b)	$-$ 0.164	2.231	0.088	2.155
	(c)	$-$ 0.206	2.230	0.064	2.088
0.3	(a)	$-$ 0.150	2.262	0.126	2.338
	(b)	$-$ 0.198	2.348	0.107	2.256
	(c)	$-$ 0.249	2.366	0.082	2.199
0.4	(a)	$-$ 0.167	2.423	0.138	2.394
	(b)	$-$ 0.220	2.421	0.119	2.319
	(c)	$-$ 0.276	2.451	0.093	2.268
0.5	(a)	$-$ 0.172	2.444	0.142	2.414
	(b)	$-$ 0.288	2.446	0.123	2.341
	(c)	$-$ 0.286	2.481	0.097	2.292

(T_{1,2}) Transversal mode $\mathbf{e}_q = (1/\sqrt{2}, -1/\sqrt{2}, 0)$ or $(1/\sqrt{6}, 1/\sqrt{6}, -2/\sqrt{6})$

$\bar{q}$		(I)	(II)	(III)	r_q
0.1	(a)	0.079	1.440	0.013	1.532
	(b)	0.072	1.341	0.012	1.425
	(c)	0.065	1.263	0.009	1.337
0.2	(a)	0.082	1.431	0.012	1.525
	(b)	0.076	1.426	0.010	1.412
	(c)	0.069	1.252	0.008	1.329
0.3	(a)	0.085	1.420	0.010	1.515
	(b)	0.079	1.315	0.009	1.403
	(c)	0.073	1.239	0.007	1.319
0.4	(a)	0.074	1.457	0.015	1.546
	(b)	0.066	1.349	0.013	1.428
	(c)	0.060	1.310	0.011	1.381
0.5	(a)	0.073	1.460	0.015	1.548
	(b)	0.066	1.357	0.013	1.436
	(c)	0.058	1.283	0.010	1.352

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