NORMAL VIBRATIONS OF SODIUM*)

By

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§ 1. Introduction

Frequencies of the normal vibrations of a metal[1] are usually calculated by assuming short range forces alone, taking interactions of neighbouring ions only into account. Force constants are introduced as parameters, which are adjusted to the observed elastic constants or the DEBYE temperature.

This treatment is not, however, very reliable as exemplified by its application to the computation of the frequencies of Cu. JACOBSEN[2] has evaluated nine force constants according to the theory of BORN and BEGBIE between nearest, second nearest and third nearest neighbouring ions of Cu from the frequency *versus* wave vector relations determined by the temperature-diffuse X-ray scattering. The force constants between nearest and third nearest neighbours have thus been found of the same order of magnitude, indicating the longe range character of the forces between ions in metals[3].

The potential between ions in a metal is the sum of (i) the coulomb repulsion v_C, (ii) the interaction induced by valence electrons v_E, inclusive of the electron-electron interactions, and (iii) the sum v_R of the exchange repulsion and VAN DER WAALS attraction. The v_C and v_E are those of long range force so that all interactions of ions in the distance must be reckoned except in the case of the complete shielding. However, the compensation by valence electrons for the perturbing ionic field accompanying lattice vibrations is not complete, so that the resultant perturbing field is of primary importance, as discussed in the foregoing paper[4].

The frequencies of lattice vibrations of a metal may be evaluated without introducing any arbitrary parameters, if the contributions v_C, v_E and v_R to the adiabatic potential are computed directly. The con-

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tribution v_C may be computed by the EWALD's method[5] and that v_R, which decreases very rapidly with distance, by taking only the neighbouring ions into account. The contribution v_E has been derived in the foregoing paper[4] by the extention of the HARTREE-FOCK method to the electron-lattice vibration interaction. The frequencies of the normal vibrations of Na which propagate along the three principal directions are thus calculated in the present paper and compared with those from usual calculations mentioned above. The appropriate elastic constants at the long wave-length limit are found coincident with those derived by WIGNER, SEITZ[6] and FUCHS[7], while the formulation is verified for short wave-length.

§ 2. The Equations for the Normal Modes and Frequencies

The displacement $\mathbf{u}_l(u_{lx}, u_{ly}, u_{lz})$ of an ion from the equilibrium position $\mathbf{R}_l^0$, accompanying the lattice vibration of wave number q, is given as

$$\mathbf{u}_l = N^{-1/2}\mathbf{e}_q\left\{a_q \exp(i\mathbf{q}\mathbf{R}_l^0)+a_q^* \exp(-i\mathbf{q}\mathbf{R}_l^0)\right\}, \tag{2.1}$$

where a_q is the amplitude of the wave, $\mathbf{e}_q$ its polarization vector and N is the number of ions in unit volume. The adiabatic potential $\delta\mathscr{V}$ for the vibration is

$$\delta\mathscr{V} = \frac{1}{4}\sum_{l\neq l'}{}' \sum_{xy}\left\{v(\mathbf{R}_l-\mathbf{R}_{l'})\right\}_{xy}(u_{lx}-u_{l'x})(u_{ly}-u_{l'y}). \tag{2.2}$$

The $v(\mathbf{R}_l-\mathbf{R}_{l'})$ in Eq. (2.2) is the interaction potential between ions at positions $\mathbf{R}_l$ and $\mathbf{R}_{l'}$, which consist of three parts, *i.e.*,

$$v = v_E+v_C+v_R,$$

where v_E, v_C and v_R are defined in §1, and the subscripts xy, *etc.* of $\{v(\mathbf{R}=(X, Y, Z))\}_{xy}$ signify partial differential coefficient $\partial^2 v/\partial X\partial Y$, *etc.* The dipole-dipole or dipole-quadrupole interacions between ion-cores are neglected in comparison with the exchange repulsions.

Defining $v_E(\mathbf{R}_l=0)+v_C(\mathbf{R}_l=0)$ and $v_R(\mathbf{R}_l=0)$ as

$$\sum_l\left\{v_E(\mathbf{R}_l)+v_C(\mathbf{R}_l)\right\}_{xy} = 0, \tag{2.3a}$$

$$\sum_l\left\{v_R(\mathbf{R}_l)\right\}_{xy} = 0, \tag{2.3b}$$

we have from Eq. (2.2)

$$\delta\mathscr{H} = -\frac{1}{2}\sum_{ll'}\sum_{xy}\left\{v(\mathbf{R}_l-\mathbf{R}_{l'})\right\}_{xy}u_{lx}u_{ly}\ , \tag{2.4}$$

or, substituting Eq. (2.1) for $\mathbf{u}_l$ into Eq. (2.4),

$$\delta\mathscr{H} = \delta\mathscr{H}^E+\delta\mathscr{H}^C+\delta\mathscr{H}^R \tag{2.5}$$

$$\delta\mathscr{H}^E = -\frac{1}{2}|a_q|^2\sum_{xy}\left\{[xy]^E+[xy]^{E*}\right\}e_{qx}e_{qy}\ , \tag{2.5E}$$

$$\delta\mathscr{H}^C = -\frac{1}{2}|a_q|^2\sum_{xy}\left\{[xy]^C+[xy]^{C*}\right\}e_{qx}e_{qy}\ , \tag{2.5C}$$

$$\delta\mathscr{H}^R = -\frac{1}{2}|a_q|^2\sum_{xy}\left\{[xy]^R+[xy]^{R*}\right\}e_{qx}e_{qy}\ , \tag{2.5R}$$

where coupling coefficients $[xy]^E$, *etc.*, are given as,

$$[xy]^E = \sum_l\left\{v_E(\mathbf{R}_l)\right\}_{xy}\exp(i\mathbf{q}\mathbf{R}_l)\ , \tag{2.6E}$$

$$[xy]^C = \sum_l\left\{v_C(\mathbf{R}_l)\right\}_{xy}\exp(i\mathbf{q}\mathbf{R}_l)\ , \tag{2.6C}$$

$$[xy]^R = \sum_l\left\{v_R(\mathbf{R}_l)\right\}_{xy}\exp(i\mathbf{q}\mathbf{R}_l)\ . \tag{2.6R}$$

For a crystal of cubic symmetry, $[xy]^E=[xy]^{E*}$, *etc.*, and the equations for the normal modes of vibration of wave number vector $\mathbf{q}$ are given from Eq. (2.5) as (M: the atomic mass)

$$\begin{aligned}
[xx]e_{qx}+[xy]e_{qy}+[xz]e_{qz} &= -M\omega^2e_{qx}\ ,\\
[yx]e_{qx}+[yy]e_{qy}+[yz]e_{qz} &= -M\omega^2e_{qy}\ ,\\
[zx]e_{qx}+[zy]e_{qy}+[zz]e_{qz} &= -M\omega^2e_{qz}\ ,
\end{aligned} \tag{2.7}$$

where $[xy]=[xy]^E+[xy]^C+[xy]^R$ and the circular frequencies ω are given by the secular equation

$$\begin{vmatrix}
[xx]+M\omega^2 & [yx] & [zx]\\
[xy] & [yy]+M\omega^2 & [zy]\\
[xz] & [yz] & [zz]+M\omega^2
\end{vmatrix} = 0\ . \tag{2.8}$$

Eqs. (2.7) and (2.8) are simplified by the geometrical symmetry for the waves propagating along the principal directions, *i.e.*, $\mathbf{q}=(q,0,0)$, $\mathbf{q}=(q,q,0)$ and $\mathbf{q}=(q,q,q)$.

(i) $(q,0,0)$; in this case $[yy]=[zz]$ and $[xy]=[yz]=[zx]=0$. The modes and their frequencies are given as,

$$(L)\quad \mathbf{e}_q=(1,0,0)\ ,\quad M\omega^2=-[xx]\ , \tag{2.9L}$$

$$(T_1)\quad \mathbf{e}_q=(0,1,0)\,,\qquad M\omega^2=-[yy]\,, \tag{2.9T_1}$$

$$(T_2)\quad \mathbf{e}_q=(0,0,1)\,,\qquad M\omega^2=-[yy]\,. \tag{2.9T_2}$$

(ii) $(q,q,0)$; $[xx]=[yy]$, $[xz]=[yz]=0$, and hence,

$$(L)\quad \mathbf{e}_q=(1/\sqrt{2},\,1/\sqrt{2},\,0)\,,\qquad M\omega^2=-\left\{[xx]+[xy]\right\}\,, \tag{2.10L}$$

$$(T_1)\quad \mathbf{e}_q=(1/\sqrt{2},\,-1/\sqrt{2},\,0),\qquad M\omega^2=-\left\{[xx]-[xy]\right\}\,, \tag{2.10T_1}$$

$$(T_2)\quad \mathbf{e}_q=(0,0,1)\,,\qquad M\omega^2=-[zz]\,. \tag{2.10T_2}$$

(iii) (q,q,q); this case is symmetrical in x,y,z. Therefore it follows that $[xx]=[yy]=[zz]$ and $[xy]=[yz]=[zx]$, and hence

$$(L)\quad \mathbf{e}_q=(1/\sqrt{3},\,1/\sqrt{3},\,(1/\sqrt{3})\,,\quad M\omega^2=-\left\{[xx]+2[xy]\right\}\,, \tag{2.11L}$$

$$(T_1)\quad \mathbf{e}_q=(1/\sqrt{2},\,-1/\sqrt{2},\,0)\,,\quad M\omega^2=-\left\{[xx]-[xy]\right\}\,, \tag{2.11T_1}$$

$$(T_2)\quad \mathbf{e}_q=(1/\sqrt{6},\,1/\sqrt{6},\,-2/\sqrt{6}),\ M\omega^2=-\left\{[xx]-[xy]\right\}\,. \tag{2.11T_2}$$

The transversal modes T_1 and T_2 for $\mathbf{q}=(q,0,0)$ and $\mathbf{q}=(q,q,q)$ degenerate as readily seen from the symmetry properties.

§ 3. The Coupling Coefficients $[xy]$

The coefficients $[xy]$ are given explicitly in this section. The $[xy]^E$ is given immediately from Eqs. (4.11), (5.1), (7.3), (7.9) and (7.10) in the preceding paper[4b] for the contribution from the valence electrons to the adiabatic potential, as

$$[xy]^E=[xy]^{E\mathrm{I}}+[xy]^{E\mathrm{II}}\,, \tag{3.1}$$

$$[xy]^{E\mathrm{I}}=Ne^2\left\{+\frac{4\pi}{3}\delta_{xy}\right\}\,, \tag{3.1EI}$$

$$[xy]^{E\mathrm{II}}=Ne^2\left\{-4\pi\sum_h\frac{(q_x+K_{hx})(q_y+K_{hy})}{|\mathbf{q}+\mathbf{K}_h|}G(t)^2F(t)^{-1}f(t)\right\}\,, \tag{3.1EII}$$

where $\mathbf{K}_h(K_{hx},K_{hy},K_{hz})$ is the reciprocal lattice vector and $t=|\mathbf{q}+\mathbf{K}_h|/2k_F$, k_F being the wave number vector of an electron at the FERMI surface. With the wave function

$$\psi(\mathbf{k})=U_0(\mathbf{r})\exp(i\mathbf{kr})$$

of an electron of wave number vector $\mathbf{k}$ and of its HARTREE energy $E_0(\mathbf{k})=E_0+(\hbar^2/2m)k^2$, the functions $G(t)$, $F(t)$ and $f(t)$ are given as discussed in the preceding paper[4b],

$$G(t)=\left\{1+\gamma\left(V(r_s)-E_0\right)\frac{3}{\beta\zeta_0}t^2\right\}g(2k_Fr_st)\,, \tag{3.2}$$

$$F(t)=\left\{(D_0/D)(2/\beta)t^2+(1-Bt^2)f(t)\right\}\,, \tag{3.3}$$

and

$$f(t)=\frac{1}{2}+\frac{1-t^2}{4t}\log\left|\frac{1+t}{1-t}\right|\,, \tag{3.4}$$

where $\gamma=U_0^2(r_s)$, $\beta=e^2k_F/\pi\zeta_0$, ζ_0 the FERMI energy in the HARTREE approximation, $g(x)=3(\sin x-x\cos x)/x^3$, $V(r_s)$ the HARTREE potential energy at the surface of atomic sphere of radius r_s, D or D_0 the density of states with or without the exchange and correlation energies taken into account, and B, which allows for the effect of the exchange and correlation interactions on the screening field, is assumed to be independent of $\mathbf{q}+\mathbf{K}_h$. The function $G(t)$ should vanish at $K_h(h\neq0)$, but that given above is not vanish, though its value at $t=|K_{110}|/2k_F$ is so small ($\sim$0.0005) that we may disregard the deviations.

The $[xy]^C$ is readily formulated by the EWALD's method[5] with the result,

$$[xy]^C=Ne^2\left[-G_{xy}+H_{xy}+\begin{cases}\dfrac{16}{3\sqrt{\pi}}\varepsilon^3\delta_{xy} & \text{for } (b.c.c.)\\ \dfrac{8}{3\sqrt{\pi}}\varepsilon^3\delta_{xy} & \text{for } (f.c.c.)\end{cases}\right]\,, \tag{3.5}$$

where

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

and

$$H_{xy}=\begin{matrix}4\\2\end{matrix}\Big\}\sum_{l\neq0}'\left[-f(l)\delta_{xy}+g(l)\frac{l_xl_y}{l^2}\cos\pi(\bar{\mathbf{q}},\mathbf{l})\right]\,,\qquad\begin{matrix}(b.c.c.)\\(f.c.c.)\end{matrix}$$

with

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

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

and

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

In the above equations, the lattice point vector $\mathbf{R}_l$, the reciprocal lattice point vector $\mathbf{K}_h$ and the wave number vector $\mathbf{q}$ are expressed as ($2r_0$: the lattice constant)

$$\mathbf{R}_l = r_0(l_x, l_y, l_z), \quad l = \sqrt{l_x^2+l_y^2+l_z^2}, \quad (l_x, l_y, l_z \text{ are all odd or all even for b. c. c.})$$

$$\mathbf{K}_h = \pi/r_0(h_x, h_y, h_z), \quad ((h_x+h_y+h_z) \text{ is even for b. c. c.})$$

and

$$\mathbf{q} = \pi/r_0(\bar{q}_x, \bar{q}_y, \bar{q}_z),$$

respectively. The constant ε should be chosen so that the two series $\sum_h$ and $\sum_{l\neq 0}'$ rapidly converge.

The v_R is given, according to BORN and MAYER[8], as

$$v_R(\mathbf{R}_l) = C_{11}b \cdot \exp\{(2r_B - R_l)/\rho\}, \tag{3.6}$$

where $b=10^{-12}$ erg., $\rho=0.345\cdot10^{-8}$ cm, $C_{11}=1.25$ and $r_B=0.875\cdot10^{-8}$ cm. The $[xy]^R$ is expressed from Eqs. (3.6) and (2.6R), as

$$[xy]^R = \frac{C_{11}b}{\rho}\sum_{l\neq 0}'\exp\{(2r_B-R_l)/\rho\}\cdot\left\{-\frac{1}{R_l}\delta_{xy} + \left(\frac{1}{\rho}+\frac{1}{R_l}\right)\frac{X_l Y_l}{R_l^2}\right\}\cdot\{\exp(i\mathbf{q}\mathbf{R}_l)-1\}. \tag{3.7}$$

By the definitions (2.3a) and (2.3b), the $[xy]$'s have to satisfy the equations

$$\lim_{q\to 0}\{[xy]^E+[xy]^C\} = 0 \tag{3.8}$$

and

$$\lim_{q\to 0}[xy]^R = 0, \tag{3.9}$$

as actually the case according to Eqs. (3.1), (3.5) and (3.7), since

$$\lim[xy]^E = Ne^2\left\{+\frac{4\pi}{3}\delta_{xy}4 - \pi\sum_h\frac{K_{hx}K_{hy}}{|\mathbf{K}_h|^2}\right\},$$

neglecting the contributions from $G(t=K_h/2k_F)$, $\mathbf{h}\neq 0$, which do not vanish because of the approximate formulation, and

$$\lim[xy]^C = Ne^2\left\{-\frac{4\pi}{3}\delta_{xy} + 4\pi\sum_h\frac{K_{hx}K_{hy}}{|\mathbf{K}_h|^2}\right\}.$$

Eq. (3.9) is apparent from Eq. (3.7).

§ 4. Numerical Results

Frequencies are calculated as functions of wave number vector by Eqs. (2.8), (2.9), (2.10), (2.11), (3.1), (3.5) and (3.7) along the (100), (110), and (111) directions. The results are given in Table I, II, and III, in which C, R, EI, EII or T means the contribution from $[xy]^C$, $[xy]^R$, $[xy]^{EI}$, $[xy]^{EII}$, or their total $[xy]$ in units of Ne^2/M respectively, and the circular frequency ω is given in the last column in units of $(Ne^2/M)^{1/2}$. The column $h\neq 0$ of EII gives the contributions from *Umklapp processes* satisfying the condition $|\mathbf{q}+{}^h\mathbf{K}|<|\mathbf{K}_{110}|$. For Na, $r=1$, $V(r_s)-E_0^C=0.08\,\mathrm{eV}$, $\zeta_0=3.17\,\mathrm{eV}$, $D/D_0=0.90$, $B=1.25$ and $r_s=3.96$ BOHR radius[9].

The contributions from exchange repulsions are about 10% of the adiabatic potentials as shown in the table, and negative for the modes T_1 of $(q,q,0)$, from which we may conclude that the b. c. c. structure

TABLE I. Frequencies ω *versus* wave number vector $\mathbf{q}=(\pi/r_0)\,(\bar{q},0,0)$

The C or R denotes the contributions from the coulomb repulsion between ions (Eq. (3.5)) or those from the exchange repulsions between ion-cores (Eq. (3.7)). The EI or EII is the values of Eq. (3.1 EI) or (Eq. 3.1 EII), representing the electron-ion and electron-electron interactions, and $T=C+R+EI+EII$. The units are $(Ne^2/M)=1.54\times10^{26}/\mathrm{sec}^2$. The circular frequencies are given in the last column in units of $(Ne^2/M)^{1/2}=1.24\times10^{13}/\mathrm{sec}$.

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

$\bar{q}$	C	R	EI	EII		T	ω
				$h=0$	$h\neq0$ (*Umklapp*)		
0.2	7.791	0.044	4.189	− 11.523	− 0.050	0.451	0.67
0.4	6.062	0.142	4.189	− 8.800	− 0.190	1.403	1.18
0.6	3.501	0.233	4.189	− 5.430	− 0.239	2.252	1.50
0.8	1.041	0.282	4.189	− 2.522	− 0.223	2.738	1.65
1.0	0	0.295	4.189	− 0.798	− 0.798	2.888	1.70

Transversal branch (T_1 or T_2), $\mathbf{e}_q=(0,1,0)$ or $\mathbf{e}_q=(0,0.1)$.

q	C	R	EI	EII		T	ω
				$h=0$	$h\neq0$ (*Umklapp*)		
0.2	− 3.895	0.027	4.189	0	− 0.039	0.282	0.53
0.4	− 3.031	0.098	4.189	0	− 0.263	0.993	1.00
0.6	− 1.750	0.189	4.189	0	− 0.748	1.880	1.37
0.8	− 0.521	0.265	4.189	0	− 1.330	2.603	1.61
1.0	0	0.295	4.189	0	− 1.596	2.888	1.70

is unstable for metals with large exchange repulsion. It is interesting to note that $[xy]^{II}$ contributes appreciably to the transversal modes of shorter wave-length through *Umklapp processes*.

The elastic constants may be determined from the ratio of the frequency and the wave number in the long wave-length limit; *i.e.* c_{11} or c_{44} from the ratio of the L or T_1 branch of $(q, 0, 0)$, and $c_{11}-c_{12}$ from the ratio of the T_1 branch of $(q, q, 0)$. The c_{11} or the compressibility $\kappa=\{c_{11}-(2/3)(c_{11}-c_{12})\}^{-1}$ thus determined coincides with that given by the theory of WIGNER and SEITZ[6], as we have seen in §§6 and 7 of the foregoing paper.

TABLE II. Frequencies ω *versus* wave number vector $(\mathbf{q}=\pi/r_0)(\bar{q}, \bar{q}, 0)$

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

$\bar{q}$	C	R	EI	EII		T	ω
				$h=0$	$h\neq 0$ (*Umklapp*)		
0.1	8.216	0.034	4.189	− 12.035	− 0.043	0.361	0.60
0.2	7.791	0.121	4.189	− 10.548	− 0.270	1.283	1.13
0.3	7.256	0.230	4.189	− 8.401	− 0.861	2.413	1.55
0.4	6.818	0.318	4.189	− 6.003	− 2.006	3.312	1.82
0.5	6.649	0.351	4.189	− 3.766	− 3.766	3.657	1.91

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

$\bar{q}$	C	R	EI	EII		T	ω
				$h=0$	$h\neq 0$ (*Umklapp*)		
0.1	− 4.170	− 0.004	4.189	0	− 0.009	0.006	0.08
0.2	− 4.118	− 0.016	4.189	0	− 0.029	0.026	0.16
0.3	− 4.051	− 0.030	4.189	0	− 0.062	0.046	0.21
0.4	− 3.994	− 0.042	4.189	0	− 0.096	0.057	0.24
0.5	− 3.972	− 0.046	4.189	0	− 0.111	0.060	0.245

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

$\bar{q}$	C	R	EI	EII		T	ω
				$h=0$	$h\neq 0$ (*Umklapp*)		
0.1	− 4.047	0.013	4.189	0	− 0.018	0.137	0.37
0.2	− 3.673	0.048	4.189	0	− 0.058	0.506	0.71
0.3	− 3.205	0.091	4.189	0	− 0.124	0.951	0.98
0.4	− 2.824	0.125	4.189	0	− 0.192	1.298	1.14
0.5	− 2.677	0.139	4.189	0	− 0.222	1.429	1.20

TABLE III. Frequencies ω *versus* wave number vector $\mathbf{q}=(\pi/r_0)(\bar{q},\bar{q},\bar{q},)$

Longitudinal branch (L), $\mathbf{e}_q=\left(\frac{1}{\sqrt{3}},\frac{1}{\sqrt{3}},\frac{1}{\sqrt{3}}\right)$.

$\bar{q}$	C	R	EI	EII		T	ω
				$h=0$	$h\neq 0$ (*Umklapp*)		
0.1	8.178	0.061	4.189	− 11.776	− 0.062	0.590	0.72
0.2	7.433	0.196	4.189	− 9.544	− 0.322	1.952	1.40
0.3	5.826	0.300	4.189	− 6.786	− 0.697	2.832	1.68
0.4	3.206	0.296	4.189	− 3.975	− 0.879	2.837	1.685
0.5	0	0.190	4.189	− 1.832	− 0.611	1.942	1.39

Transversal branch (T_1 or T_2), $\mathbf{e}_q=\left(\frac{1}{\sqrt{2}},-\frac{1}{\sqrt{2}},0\right)$ or $\left(\frac{1}{\sqrt{6}},\frac{1}{\sqrt{6}},-\frac{2}{\sqrt{6}}\right)$.

$\bar{q}$	C	R	EI	EII		T	ω
				$h=0$	$h\neq 0$ (*Umklapp*)		
0.1	− 4.089	0.007	4.189	0	− 0.0215	0.0855	0.29
0.2	− 3.716	0.029	4.189	0	− 0.164	0.338	0.58
0.3	− 2.913	0.071	4.189	0	− 0.576	0.771	0.88
0.4	− 1.603	0.129	4.189	0	− 1.373	1.345	1.16
0.5	0	0.190	4.189	0	− 2.443	1.942	1.39

The c_{44} is derived by expanding the coefficient $[yy]$ of $(q,0,0)$ with respect to q^2. The constant term (signified by subscript 0) in the expansion is

$$\begin{aligned}[yy]_0 &= [yy]_0^E+[yy]_2^C+[yy]_2^R \\ &= Ne^2\left[-\frac{4\pi}{3}+\left\{-4\pi\sum_h\frac{h_y^2}{h^2}\exp\left(-\frac{\pi^2}{4\varepsilon^2}h^2\right)\right.\right. \\ &\qquad \left.\left.+4\sum_{l\neq 0}'\left(-f(l)+g(l)\frac{l_y^2}{l^2}\right)+\frac{16}{3\sqrt{\pi}}\varepsilon^2\right\}+0\right] \\ &= Ne^2\left[-\frac{4\pi}{3}+\frac{4\pi}{3}\right]=0\,, \end{aligned} \tag{4.1}$$

and the coefficient of q^2 (signified with subscript 2)

$$[yy]_2=[yy]_2^E+[yy]_2^C+[yy]_2^R \tag{4.2}$$

with

$$[yy]_2^E\approx 0\,, \tag{4.2E}$$

and

$$[yy]_2^C = Ne^2\Big[4\pi\sum_h \frac{h_y^2}{h^2}\Big(4\frac{h_x^2}{h^4}-\frac{1}{h^2}+\frac{\pi^4}{8\varepsilon^4}h_x^2-\frac{\pi^2}{4\varepsilon^2}$$
$$+\frac{\pi^2}{\varepsilon^2}\frac{h_x^2}{h^2}\Big)\exp\Big(-\frac{\pi^2}{4\varepsilon^2}h^2\Big)-2\pi^2\sum_{l\neq 0}{}'\Big\{-f(l)+g(l)\frac{l_y^2}{l^2}\Big\}l_x^2\Big] \quad (4.2C)$$

The c_{44} is now given as,

$$c_{44} = -\frac{Nr_0^2}{\pi^2}\left\{[yy]_2^C+[yy]_2^R\right\},$$

which is exactly the same expression as given by FUCHS[7]. In the case of alkali metals, $V(r_s)-E_0$ is very small in general, so that $[yy]_2^F$ is nearly zero, which justifies the assumption made by FUCHS in his

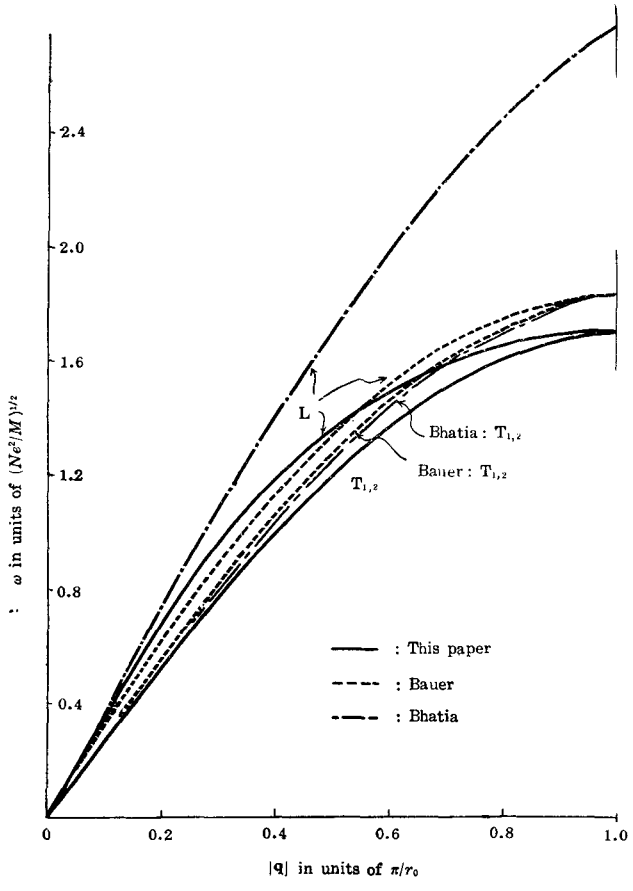

Fig. 1 Circular frequencies ω *versus* wave number vector $\mathbf{q} = \pi/r_0\,(\bar{q}, 0, 0)$.

derivation of the shear moduli. In the case of noble metals (Cu, Ag and Au), $V(r_s)-E_0$ is of the order of 3~4 eV and the coulomb term $[yy]_2^C$ is compensated a good deal by $[yy]_2^E$, as assumed by ZENER and HUNTINGTON.[10]

The $c_{11}-c_{12}$ is given similarly as

$$c_{11}-c_{12} = -\frac{Nr_0^2}{\pi^2}\left\{[xx]_2-[xy]_2\right\},$$

where $[xx]_2$ or $[xy]_2$ is the coefficient of q^2 in the expansion of $[xx]$ or $[xy]$ of $(q, q, 0)$. The result is the same as that obtained by FUCHS, as readily verified similarly as in the case of c_{44}.

Figs. I, II and III show the results in comparison with the calculations by BAUER[11] and by BHATIA[12]. BAUER has assumed central forces and introduced force constants α and γ corresponding to the interactions

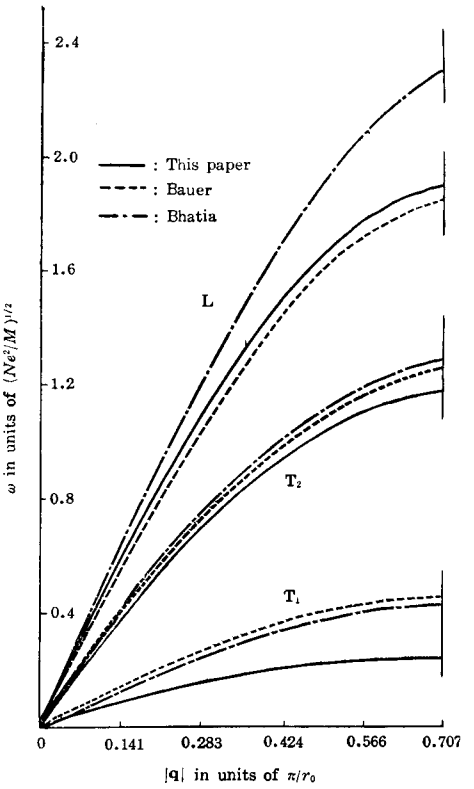

Fig. 2 Circular frequencies ω *versus* wave number vector $\mathbf{q} = \pi/r_0$ $(q, q, 0)$.

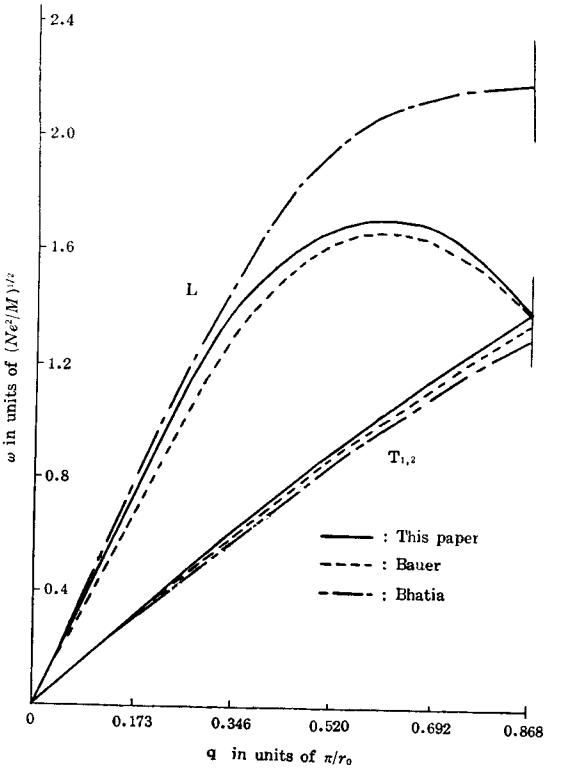

Fig. 3 Circular frequencies ω *versus* wave number vector $\mathbf{q} = \pi/r_0$ (q, q, q).

between the nearest and second nearest neighours, which are determined as $\alpha=r_0c_{44}$ and $\gamma=\alpha/4$. The dispersion relations by BAUER are given by dotted line. BHATIA, on the other hand, has taken into account in a simple way the effects of valence electrons on the ionic motion, but only the interactions between nearest neighbours. Three parameters introduced was adjusted by the three independent elastic constants c_{11}, c_{12} and c_{44}. Broken lines in Figs. show the results by BHATIA.

§ 5. Verification of the Formulation for Short Wave-Length

We will now examine the validity of our formulation for shorter wave-length. For the mode $\mathbf{q}=(\pi/r_0, 0, 0)$, $\mathbf{e}_q=(1, 0, 0)$ or $\mathbf{q}=(0, \pi/r_0, 0)$, $\mathbf{e}_q=(1, 0, 0)$ in the metals of *b. c. c.* structure, each ion is displaced alternately by $+u$ or $-u$ in the direction of x-axis from the equilibrium position, where $u=N^{-\frac{1}{2}}(a_q+a_q^*)$ by Eq. (1). The contribution from the coulomb repulsions of ions vanishes as seen in Table I, and those of valence electrons to the potential for the vibration may be calculated by cellur method[13], admitting that the coulomb energy of valence electrons is approximately balanced by the exchange and correlation energies just as in perfect crystals. The circular frequency is given as

$$M\omega^2 = 2\varepsilon(u)/u^2 + (\text{increase of the exchange repulsions}), \quad (5.1)$$

where $\varepsilon(u)$ is the perturbing energy when an ion is displaced from the centre of the atomic sphere, given, by taking the boundary condition as $(d\psi(r)/dr))_{r=r_s}=0$, as

$$\begin{aligned} 2\varepsilon(u)/u^2 &= (1/r_s)(dv_I/dr)_{r=r_s} - (2m/\hbar^2)\left\{v_I(r_s)-\mathscr{E}_0\right\}^2 \\ &= Ne^2\left\{4\pi/3-(2\pi/3)(r_s/a_H)^3(e^2/2a_H)^{-2}(v_I(r_s)-\mathscr{E}_0)^2\right\} \end{aligned} \quad (5.2)$$

where $v_I(r)$ ($-e^2/r$ for $r\gtrsim r_s$) is the potential of an ion, and $\mathscr{E}_0$ is the energy of an electron with an ion at the centre of the atomic sphere and the same boundary condition as above. For Na, $r_s=3.96a_H$ and $v_I(r_s)-\mathscr{E}=1.48$ eV, which give by Eqs. (5.1) and (5.2),

$$\omega = 1.73\,(Ne^2/M)^{1/2}$$

in good agreement with $\omega=1.70\,(Ne^2/M)^{1/2}$ in Table I.

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