PHYSICAL REVIEW VOLUME 140, NUMBER 5A 29 NOVEMBER 1965

Force Constants of Sodium

SATYA PRAKASH AND S. K. JOSHI*
Physics Department, Allahabad University, Allahabad, India

(Received 28 June 1965)

Force constants for sodium are calculated on the basis of a formulation presented by White some years ago. The force constants are taken to be the sum of the three contributions from overlap repulsive forces, the Coulomb interaction between ions, and the ion-electron-ion interaction. The Slater-Koster formalism is used to estimate the electronic contribution. The calculated force constants agree fairly well with the experimental values obtained by Woods and co-workers. The results are discussed.

I. INTRODUCTION

IN metals, the presence of a mobile Fermi gas has such drastic influence on the interaction between ions that it becomes imperative to consider them in any calculation of the force constants of metals. An interesting approach for calculating these force constants from fundamental principles was put forth by White[1] some time back. He calculated the force constants of the fcc metal copper and compared his results with the force constants inferred by Jacobsen[2] from thermal diffuse x-ray scattering. In this paper we report a calculation of the atomic force constants of the bcc metal sodium using the approach put forth by White. Our motivations in taking up this calculation were twofold. First, White's approach, though interesting, has not been applied to any other metal than copper. Experimental values of force constants of copper are not known with as high an accuracy as those of sodium. Secondly, sodium has a spherical Fermi surface and a small ion core; therefore, it approximates the assumptions embodied in White's approach better than copper.

II. THEORY

The principle of the method is quite simple. One assumes that a single nucleus is displaced by an infinitesimal amount. The electronic wave functions of the metal will change as a result of this distortion and there will be a change in the charge distribution. These changes will cause a certain force to be exerted on the other nuclei. This allows a calculation of the atomic force constants, which are the force components on one nucleus resulting from a unit displacement of the other nucleus along an axis in a crystal in equilibrium.

We now follow the established practice of dividing the contributions to force constants into three parts: (1) the contribution from Coulomb interaction between ion cores, (2) the contribution from the core-core exchange repulsion, and (3) the contribution via conduction electrons. We take up each of these contributions separately.

1. Coulomb Interaction between Ions

We assume the inner electrons to be tightly bound to the core and to move rigidly with it. For a small displacement δ of the core, the resulting electrostatic effects can be well approximated by a dipole of moment $e\delta$. The exchange and correlation effects between the conduction electrons and the core are accounted for in a simple but crude way. The virtual displacement of the ion core will push out a crescent of conduction electrons in the direction of displacement, and a similar crescent of electrons will appear at the back. The electrostatic effect of this change in conduction electron distribution is exactly the same as if a sphere of the size of the ion core and of positive charge density equal in magnitude to that of conduction electrons is given a displacement δ. This produces a dipole field which augments the ion-core field by nearly 9%. The atomic force constants contributed by the ion-core Coulomb interaction plus the excluded electron gas are shown in the second column of Table IV. The notation for the force constants will become clear from the representative force-constant matrices given in Table I for first, second, and third neighbors.

2. Core-Core Exchange Repulsion

The contributions of overlap forces to the force constants were calculated by assuming that for sodium the overlap potetntial is represented by[3]

$$\Phi^{(R)}=1.25\times10^{-12}\exp[(1.75-r)/0.345]. \qquad (1)$$

TABLE I. Force-constant matrices for first, second, and third neighbors in a bcc lattice.

Atom position	Force-constant matrix
$(1,1,1)a$	$\begin{pmatrix}\alpha & \beta & \beta\\ \beta & \alpha & \beta\\ \beta & \beta & \alpha\end{pmatrix}$
$(2,0,0)a$	$\begin{pmatrix}\alpha' & 0 & 0\\ 0 & \beta' & 0\\ 0 & 0 & \beta'\end{pmatrix}$
$(2,2,0)a$	$\begin{pmatrix}\beta'' & \gamma'' & 0\\ \gamma'' & \beta'' & 0\\ 0 & 0 & \alpha''\end{pmatrix}$

---

* Present address: Physics Department, University of California, Riverside, California.

[1] H. C. White, Phys. Rev. **112**, 1092 (1958).

[2] E. H. Jacobsen, Phys. Rev. **97**, 654 (1955).

[3] W. Cochran, Proc. Roy. Soc. (London) **A276**, 308 (1963).

Here the interionic separation r is measured in angstroms. This leads to negligible force constants beyond the second neighbors. The resulting contribution is shown in the first column of Table IV. Recently Vosko[4] has pointed out that the contribution of overlap forces in sodium is negligibly small even for the first neighbors.

3. Conduction Electrons

Here we come to the core of the problem. We calculate the change in the conduction-electron charge density due to the virtual displacement of the ion core. We will borrow White's treatment of the problem using Slater-Koster formalism for a localized perturbation and adapt it for a body-centered cubic structure.

The perturbed wave function ψ for the electron is expanded in terms of the unperturbed wave functions u_k

$$\psi=\sum_k F_k u_k\,, \tag{2}$$

where the sum is over all propagation vectors $\mathbf{k}$ in the $3s$ conduction band. The Schrodinger equation for ψ is

$$H_0\psi+V\psi=E\psi\,. \tag{3}$$

H_0 is the unperturbed Hamiltonian and V is the perturbation. These two equations yield

$$F_{k'}E_{k'}+\sum_k F_k\langle k'|V|k\rangle=EF_{k'}\,. \tag{4}$$

Here E_k is the energy corresponding to the unperturbed wave function u_k, and $\langle k'|V|k\rangle=\int u_{k'}{}^*Vu_k d\tau$. We can express u_k in terms of Wannier functions $a(\mathbf{r}-\mathbf{R}_j)$:

$$u_k=1/\sqrt{N}\sum_{R_j}e^{i\mathbf{k}\cdot\mathbf{R}_j}a(\mathbf{r}-\mathbf{R}_j)\,. \tag{5}$$

The summation is over all the lattice sites of the crystal, which has N atoms. From (4) and (5) we get

$$F_{k'}=[1/(E-E_{k'})]\sum_{R_i}A(\mathbf{R}_i)e^{-i\mathbf{k}'\cdot\mathbf{R}_i}\,, \tag{6}$$

with

$$A(\mathbf{R}_i)=(1/N)\sum_{k,R_j}[R_i|V|R_j]e^{i\mathbf{k}\cdot\mathbf{R}_j}F_k \tag{7}$$

and

$$[R_i|V|R_j]=\int a^*(\mathbf{r}-\mathbf{R}_i)Va(\mathbf{r}-\mathbf{R}_j)d\tau\,. \tag{8}$$

With the help of (6) and (7) we get

$$A(\mathbf{R}_i)=(1/\sqrt{N})\sum_{R_j,R_p}[R_i|V|R_j]\times G_E(\mathbf{R}_j,\mathbf{R}_p)A(\mathbf{R}_p)\,, \tag{9}$$

where

$$G_E(\mathbf{R}_j,\mathbf{R}_p)=\frac{1}{\sqrt{N}}\sum_{k'}e^{i\mathbf{k}'\cdot(\mathbf{R}_j-\mathbf{R}_p)}\frac{1}{E-E_q}\,. \tag{10}$$

In (10) E is one of the perturbed energies closest to unperturbed eigenvalue E_q. As indicated by White,[1] it is a valid simplification in our first-order calculation of the effect of an infinitesimal perturbation to restrict the sum over k' to only those unperturbed states which are degenerate and have energy closest to the perturbed energy E. The consistency condition for Eq. (9) provides the general determinantal equation for energy,

$$\det\{(E-E_q)\delta_{R_i,R_p}-(1/N)\sum_{R_j}(R_i|V|R_j]\times\sum_{k'}e^{i\mathbf{k}'\cdot(\mathbf{R}_j-\mathbf{R}_p)}\}=0\,. \tag{11}$$

We assume that the ion core at the origin is displaced along the x_1 axis and that the perturbation V has a dipole symmetry about $x_1=0$ plane, i.e., $V(x_1,x_2,x_3)=-V(-x_1,x_2,x_3)$. Also because of the symmetric nature of Wannier functions, $[0|V|0]=0$. The cubic symmetry of the lattice causes the matrix elements $[0|V|R_j]$ between the origin site and the four first neighbors on one side of the $x_1=0$ plane to be equal. The corresponding matrix elements for the other four nearest neighbors on the other side of this plane are also equal, and the matrix element for these sites is the negative of the matrix element for the first four. All the other matrix elements are assumed to be zero. With these approximations the ninth-order determinantal equation reduces to a second-order equation.

If we take a microcrystal of cubic shape, the Born–von Kármán cyclic boundary condition gives for the allowed vectors

$$\mathbf{k}=(\pi/na)(k_1\mathbf{i}_1+k_2\mathbf{i}_2+k_3\mathbf{i}_3)\,. \tag{12}$$

Here k_1, k_2, k_3 are integers; $\mathbf{i}_1$, $\mathbf{i}_2$, $\mathbf{i}_3$ are unit vectors along x_1, x_2, x_3 directions, respectively, a is the spacing of the atomic planes, and there are $2n$ planes along a crystal edge. The permitted $\mathbf{k}$ vectors are given by

$$+k_1\pm k_2\leqslant n\,,\quad \pm k_2\pm k_3\leqslant n\,,\quad \pm k_3\pm k_1\leqslant n\,. \tag{13}$$

Now if we work within the free-electron approximation for the conduction electrons in a crystal of volume v,

$$u_k=(1/\sqrt{v})e^{i\mathbf{k}\cdot\mathbf{r}}\,. \tag{14}$$

The unperturbed energy is

$$E_q=\pi^2h^2q/2m^*n^2a^2\,, \tag{15}$$

where m^* is the effective mass and

$$q=k_1{}^2+k_2{}^2+k_3{}^2\,. \tag{16}$$

The perturbed-energy values given by (11) are in this case

$$(E-E_q)=\pm(c_3c_4)^{1/2}\,, \tag{17}$$

with $c_3=(1/N)[1|V|0]\times$(total number of $\mathbf{k}$ vectors),

$$c_4=\frac{64}{N}[1|V|0]\sum\left(\sin^2\frac{\pi k_1}{n}\cos^2\frac{\pi k_2}{n}\cos^2\frac{\pi k_3}{n}\right)\,. \tag{18}$$

The summation in (18) is over all sets of integers k_i which have the same value of k^2. If we label the various first-neighbor sites as shown in Fig. 1, we can write from (9) and (10)

$$A(1)=A(2)=A(3)=A(4)=-A(5)=-A(6)=-A(7)=-A(8)=[c_3/(E-E_q)]A(0)\,. \tag{19}$$

---

[4] S. H. Vosko, Phys. Letters 13, 97 (1964).

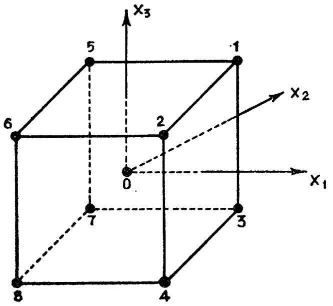

FIG. 1. The body-centered-cubic structure.

$A(0)$ is determined by using the normalization property of the perturbed wave function ψ_q. This gives

$$1=\frac{|A(0)|^2}{(E-E_q)^2}\sum\left[1+\frac{64c_3^2}{(E-E_q)^2}\sin^2\frac{\pi k_1}{n}\cos^2\frac{\pi k_2}{n}\cos^2\frac{\pi k_3}{n}\right].$$

Therefore,

$$|A(0)|^2=c_4[1|V|0]/2N. \tag{20}$$

In the case of sodium, there is one $3s$ conduction electron; the lower half of the conduction band will be filled with discrete energy states. The perturbation will split every energy state into two levels, one displaced upwards and the other downwards. The corresponding perturbed wave functions are ψ_q^+ and ψ_q^-. Let the corresponding linear combination of the unperturbed wave functions u_k be u_q^+ and u_q^-. Then

$$\psi_q^{\pm}=u_q^{\pm}+p_q^{\pm}, \tag{21}$$

where $u_q^{\pm}=\sum_k F_k^{\pm}u_k^{\pm}$ (the summation is for all k degenerate at E_q), and $p_q^{\pm}=\sum_{k'}F_{k'}^{\pm}u_{k'}^{\pm}$ (the summation is for all k' nondegenerate at E_q). The change in the charge density of the conduction electrons produced by the displacement δ along x_1 axis of the ion at the origin is given by

$$\Delta\rho=-2e\sum\{\psi_q^{+*}\psi_q^{+}-u_q^{+*}u_q^{+}+\psi_q^{-*}\psi_q^{-}-u_q^{-*}u_q^{-}\}. \tag{22}$$

Here the summation is over all q in the lower half of the conduction band except $q=0$, which is a nondegenerate state and remains unperturbed. The factor 2 stems from spin degeneracy. Use of (21) and retention of only first-order terms give

$$\Delta\rho=-2e\sum[2\,\mathrm{Re}(u_q^{+*}p_q^{+})+2\,\mathrm{Re}(u_q^{-*}p_q^{-})]=\sum\Delta\rho_q; \tag{23}$$

"Re" means the real part. We write the expression for $\Delta\rho$ in terms of the following real functions

$$Q_q=v^{1/2}\sum u_k,$$
$$iR_q=v^{1/2}\sum\left[\sin\frac{\pi k_1}{n}\cos\frac{\pi k_2}{n}\cos\frac{\pi k_3}{n}\right]u_k. \tag{24}$$

The summations in the above expressions are over all k degenerate at E_q. Now if in the expression for p_q we represent the summation in the following form,

$$\sum_{(k'\text{ nondegenerate at }E_q)}=\sum_{(q'\neq q)}\sum_{(k'\text{ degenerate at }E_{q'})},$$

we can write, because $E-E_{q'}$ goes to $E_q-E_{q'}$ as δ tends to zero:

$$\Delta\rho=-\frac{32[1|V|0]}{Nv}\sum_q\sum_{q'}\frac{Q_{q'}R_q+Q_qR_{q'}}{E_q-E_{q'}}. \tag{25}$$

The summation for q' is over all the $3s$ conduction-band states and q is summed over the lower half of the $3s$ band, barring $q=0$. If we interchange q and q' in (25), the numerator remains the same and the denominator changes sign. $\Delta\rho$ will therefore be zero if we sum (25) over all q' (except $q'=0$) in the lower half of the conduction band only. The crystal volume $v=4Na^3$, and we introduce R given by

$$R=-em^*[1|V|0]/2\hbar^2\pi^2a. \tag{26}$$

The final expression for $\Delta\rho$ can then be written in the form

$$\Delta\rho=-32\frac{n^2}{N}R\sum_q\sum_{q'}\frac{Q_{q'}R_q+R_{q'}Q_q}{q'-q}. \tag{27}$$

Because of the arguments given above in Eq. (27), q is summed over all its values except $q=0$ in the lower half of the conduction band and q' is summed over all

TABLE II. $Q_q(\mathbf{r})$ and $R_q(\mathbf{r})$ for $\mathbf{r}$ along [111] axis; $\mathbf{r}=(\alpha,\alpha,\alpha)a$.

(k_1,k_2,k_3)	$Q_q(\mathbf{r})$	$R_q(\mathbf{r})$
$(a,0,0)$	$6\cos(\pi\alpha a/n)$	$2\sin(\pi a/n)\sin(\pi\alpha a/n)$
$(a,a,0)$	$12\cos^2(\pi\alpha a/n)$	$8\sin(\pi a/n)\cos(\pi a/n)\sin(\pi\alpha a/n)\cos(\pi\alpha a/n)$
(a,a,a)	$8\cos^3(\pi\alpha a/n)$	$8\sin(\pi a/n)\cos^2(\pi a/n)\sin(\pi\alpha a/n)\cos^2(\pi\alpha a/n)$
$(a,b,0)$	$24\cos(\pi\alpha a/n)\cos(\pi\alpha b/n)$	$8\{\sin(\pi a/n)\cos(\pi b/n)\sin(\pi\alpha a/n)\cos(\pi\alpha b/n)$ $+\sin(\pi b/n)\cos(\pi a/n)\sin(\pi\alpha b/n)\cos(\pi\alpha a/n)\}$
(a,b,b)	$24\cos(\pi\alpha a/n)\cos^2(\pi\alpha b/n)$	$8\{\sin(\pi a/n)\cos^2(\pi b/n)\sin(\pi\alpha a/n)\cos^2(\pi\alpha b/n)$ $+2\sin(\pi b/n)\cos(\pi a/n)\cos(\pi b/n)\sin(\pi\alpha b/n)\cos(\pi\alpha a/n)\cos(\pi\alpha b/n)\}$
(a,b,c)	$48\cos(\pi\alpha a/n)\cos(\pi\alpha b/n)\cos(\pi\alpha c/n)$	$16\{\sin(\pi a/n)\cos(\pi b/n)\cos(\pi c/n)\sin(\pi\alpha a/n)\cos(\pi\alpha b/n)\cos(\pi\alpha c/n)$ $+\sin(\pi b/n)\cos(\pi c/n)\cos(\pi a/n)\sin(\pi\alpha b/n)\cos(\pi\alpha c/n)\cos(\pi\alpha a/n)$ $+\sin(\pi c/n)\cos(\pi a/n)\cos(\pi b/n)\sin(\pi\alpha c/n)\cos(\pi\alpha a/n)\cos(\pi\alpha b/n)\}$

values in the upper half of the band and in addition over $q'=0$. In evaluating (27) special care must be taken to give proper weights to contributions to $\Delta\rho$ from **k** vectors lying on the surface, edges, or corners of the Brillouin zone.

We have evaluated $Q_q(\mathbf{r})$ and $R_q(\mathbf{r})$ for **r** along the three symmetry directions [100], [110], and [111]. The forms of $R_q(\mathbf{r})$ and $Q_q(\mathbf{r})$ are given in Table II for $(\alpha,\alpha,\alpha)a$ and for six possible combinations of (k_1,k_2,k_3). Calculations of $\Delta\rho$ were carried out for microcrystals of different sizes by varying n. It is found that beyond $n=6$ (i.e., a crystal having 432 atoms), $\Delta\rho$ is substantially independent of n. This is apparent from Fig. 2 where we have plotted $\Delta\rho$ against the number of atoms in the crystal at a point $\mathbf{r}=(a,0,0)$. In Fig. 3 we have plotted $\Delta\rho$ as a function of r along the three principal symmetry directions [100], [110], and [111] for a body-centered crystal of 432 atoms. From Fig. 3 we have constructed Fig. 4, where we have shown the variation of $\Delta\rho$ with polar angle at $r=0.5a$. The figure shows that at $r=0.5a$, the change $\Delta\rho$ is independent of azimuthal angle and shows a $\cos\theta$-type dependence on polar angle θ. We have plotted $\Delta\rho$ in units of $-R$. R involves $[1|V|0]$, which could be fixed from the condition that no net dipole moment is produced by the virtual displacement of the ion at the origin, as observed from a distant external point. Thus the dipole moment due to $\Delta\rho$ should cancel that due to the ion core plus the excluded electrons.

The contributions to force constants from $\Delta\rho$ were calculated by dividing $\Delta\rho$ curves into three regions: $r<1.6a$, $1.6a<r<2.5a$ and $2.5a<r<3.4a$. In the region $r<1.6a$, $\Delta\rho$ can be represented fairly well by a relation of the type

$$\Delta\rho=-18.36R\cos\theta\sin(r\pi/1.6a)e^{-1.33r/a}. \quad (28)$$

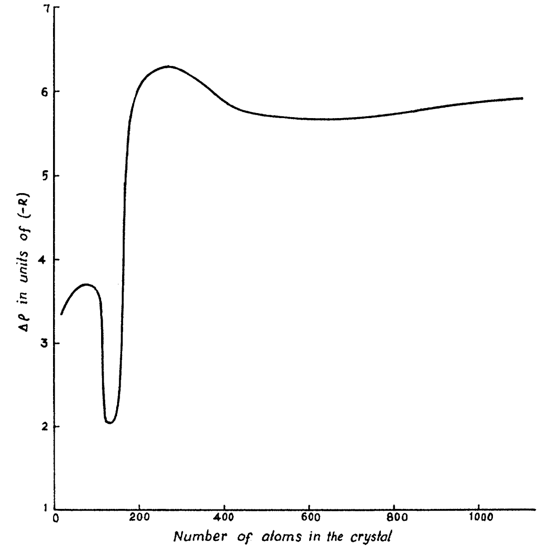

FIG. 2. The variation of $\Delta\rho$ with the number of atoms in a microcrystal of cubic shape at the point $\mathbf{r}=(a,0,0)$.

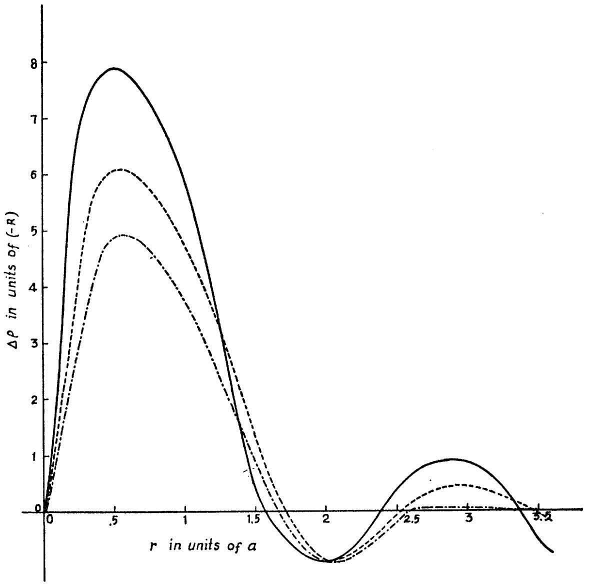

FIG. 3. $\Delta\rho$ versus r along the three symmetry directions of the bcc crystal. Full, dashed, and dash-dotted curves are for [100], [110], and [111] directions, respectively.

The electrostatic effect of this distribution is the same as that for a dipole of moment $-6.735a^4$ along x_1 axis. This value for dipole moment was obtained by following the procedure outlined by White in his paper. The contributions to force constants from this region are given in the first column of Table III.

We represent $\Delta\rho$ in the region $1.6a<r<2.5a$ by a spherical cap with radius $2a$, opening $\theta_0=60°$, and constant surface charge density $0.0661aR$. There will be a similar cap with equal negative charge density for

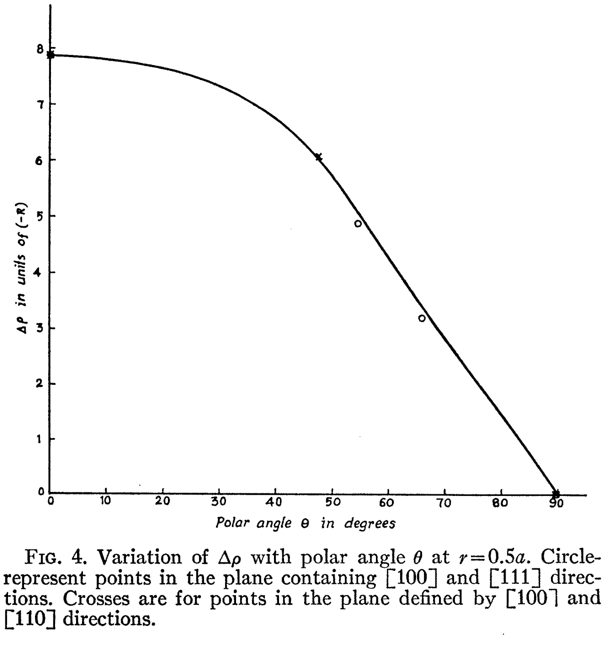

FIG. 4. Variation of $\Delta\rho$ with polar angle θ at $r=0.5a$. Circle-represent points in the plane containing [100] and [111] directions. Crosses are for points in the plane defined by [100] and [110] directions.

TABLE III. Electronic contribution to force constants.

Force constant	Contribution due to conduction electrons in the region $r<1.6a$	$1.6a<r<2.5a$	$2.5a<r<3.4a$	Total electronic contribution
α	0	1232	−362	870
β	−4457	107	48	−4302
α'	−5789	−775	500	−6064
β'	2894	675	−255	3314
α''	1023	335	−129	1229
β''	−511	321	−498	−688
γ''	−1535	−103	−162	−1800

$x_1<0$. The electrostatic effects of such caps at external or internal points were represented by expansions in Legendre polynomials up to $P_5(\cos\theta_0)$. The dipole moment of the spherical caps along x_1 axis observed from a distant external point is $2.49a^4R$. The contributions to atomic force constants from this region are given in the second column of Table III.

In the region $2.5a<r<3.4a$ we represent $\Delta\rho$ by a spherical cap of radius $3a$, opening 45° and constant surface charge density $-0.033aR$ for $x_1>0$, and a similar cap with equal negative charge density for $x_1<0$. The contributions to force constants were estimated in a manner exactly the same as that described in the preceding paragraph. The dipole moment of the spherical cap observed from an external point is $-2.8a^4R$. The contributions to force constants from this region are shown in the third column of Table III. In the region beyond $3.4a$, the change $\Delta\rho$ is quite small and we neglect it in our calculation of force constants. The total electronic contribution to force constants is given in the last column of Table III. R was evaluated according to a process outlined earlier and its value was found to be $e\delta/7a^4$.

TABLE IV. Force constants of sodium.

Force constant	Overlap	Contribution from Ionic coulomb interaction +excluded electrons	Ion-electron-ion interaction	Total	Values of Woods *et al.*
α	109	0	870	979	1175
β	147	4643+418	−4302	906	1320
α'	76	6049+544	−6064	605	472
β'	−6	−3024−272	3314	12	104
α''	0	−1069−96	1229	64	0
β''	0	535+48	−688	−105	−38
γ''	0	1605+144	−1800	−51	−65

III. DISCUSSION

In Table IV we have displayed the contribution to force constants from the overlap forces, the ionic Coulomb interaction, and the ion-electron-ion interaction. The results are compared with the reliable values of force constants obtained by Woods *et al.*[5] by neutron-spectrometric methods. The agreement between the calculated and experimental force constants is surprisingly good in view of the approximations that have gone into our calculation. In deriving the electronic contribution to force constants we have made many crude approximations. Our neglect of all matrix elements other than $[1|V|0]$ is questionable. In addition the force constants were calculated from the knowledge of $\Delta\rho$ graphs along only three symmetric directions by procedures which are not very satisfactory.

The form of $\Delta\rho$ curves obtained by us is similar to those obtained by March and Murray[6] in their self-consistent calculation in a free-electron metal containing localized defects. The oscillations in the $\Delta\rho$ curves are shown to be the result of a singularity in the dielectric constant, so that the charge density at large distances contains oscillatory terms of the form $r^{-3}\cos 2k_Fr$, where k_F is the Fermi wave vector.[7]

ACKNOWLEDGMENTS

The authors are grateful to the State Council of Scientific and Industrial Research, Ultar Pradesh for financial help and to N. Singh for discussion.

---

[5] A. D. B. Woods, B. N. Brockhouse, R. H. March, A. T. Stewart, and R. Bowers, Phys. Rev. **128**, 1112 (1962).

[6] N. H. March and A. M. Murray, Proc. Roy. Soc. (London) **A261**, 119 (1961).

[7] J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids **12**, 196 (1960).