It is a simple matter to show from Eq. (5.3) that for binary systems this simplification indeed obtains. For the more general case of ternary systems, the solution of Eqs. (5.3) is more complicated.

In conclusion, we might add a few words about the general direction along which the results of the present paper should be extended. Firstly, the formal solution for the correlation parameters given in Eqs. (3.15)–(3.18) should be explicitly evaluated to a higher order in the expansion parameter (T_c/T) than presently carried out. Secondly, the system interactions responsible for the order-disorder phenomena are not fully represented by the given form of the H(config). The system Hamiltonian needs to be extended to include the static strain energies, as well as the dynamical lattice effects such as phonons. In the same spirit the inclusion of higher-body potentials than the two-body ones used presently is also indicated.

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Lattice-Dynamic Calculation for Alkali Metals*

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We present a model calculation of lattice dynamics for alkali metals. The lattice potential consists of the electrostatic energy and the screened electron-ion interaction. The screened potential is formed by linearly screening a Heine-Abarenkov–type ion potential, and the Hartree dielectric function is modified to include approximately exchange and correlation effects. The model parameters are determined according to the experimental elastic constants. Expressions for elastic constants are derived by taking the long-wave limit of the secular equation. From our results in lattice dynamics, we find that the shear waves are dominated by the electrostatic potential, but for the longitudinal waves the contributions from both potentials are comparable and opposite in size. The agreement between the calculated and the observed dispersion curves is good for Na and K where neutron-scattering data are available. We have also calculated the effective ion-ion potential for the alkali metals. All of these potentials exhibit a minimum near the equilibrium position and some long-range oscillations caused by electron-ion interaction.

I. INTRODUCTION

SINCE the inelastic neutron scattering technique was applied for direct measurement of dispersion curves, it becomes apparent that the Born–von Kármán rigidion model is inadequate in treating lattice dynamics. This is especially so for metals where the problem comes from the conduction electrons. The electron-ion interaction is a many-body interaction characterized by the long-range screening of ions by electrons. This long-range force shows up for alkali metals. In a Born–von Kármán analysis of the observed dispersion curves, force constants up to the fifth neighbors for Na [1] and K [2] have to be included.

Clearly a proper lattice-dynamic calculation for metals must take into account the effective electron-ion interaction. Toya[3] first attempted such a calculation for monovalent metals by extending the Hartree-Fock calculation for the electron-phonon interactions. For simple metals the electron-ion interaction can be treated by the method of pseudopotentials, an effective electron-ion potential first derived by Phillips and Kleinman[4] in an orthogonalized-plane-wave (OPW) expansion for the conduction electrons. The pseudopotential model has been applied quite successfully in calculating atomic and electronic properties.[5,6] There are many lattice-dynamic calculations for alkali metals, notably that of Harrison,[5] Sham,[7] and Vosko *et al.*[8] Their good results establish the validity of using the pseudopotentials for alkali metals. The pseudopotential can be obtained from *a priori* calculation or from measured metal properties such as the atomic energy levels[6] and the liquid metal resistivities.[9] In this paper, we study the lattice

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[5] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

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[7] L. J. Sham, Proc. Roy. Soc. (London) **A283**, 33 (1965).

[8] S. H. Vosko, R. Taylor, and G. H. Keech, Can. J. Phys. **43**, 1187 (1965).

[9] N. W. Ashcroft and D. C. Langreth, Phys. Rev. **156**, 685 (1967); **159**, 500 (1967); see also N. W. Ashcroft, Cornell University Materials Science Center Report No. 555, 1966 (unpublished).

dynamics of alkali metals by using the pseudopotential method in a phenomenological approach. This work differs from the others in that the model potential is determined according to the experimental elastic constants. Our model potential contains three parameters, two in the bare-ion potential and one in the screening dielectric function.

The idea of determining lattice models by elastic constants is well known. Usually the elastic constants are used to compute force constants between neighbor atoms. However, this greatly limits the usefulness of this approach because there are only a few independent elastic constants, e.g., three for cubic crystals. Consequently, it is impossible to account for long-range interactions. Krebs[10] has calculated the dispersion curves for alkali metals based on a model which includes the central force for the nearest and second-nearest neighbors and the electron screening of the long-range Coulomb interaction between point ions. The two force constants and the strength of the screening are determined from elastic constants. However, some recent calculations[5,11] reveal that the interaction of the electrons with the core potential is important in determining elastic constants and dispersion curves. The present model has included the electron and core interaction and since a certain form for the crystal potential is utilized, the force constants of any atom can be expressed in terms of the model parameters. Actually, if the specific form of the lattice potential is known, the calculation could be most conveniently carried out in k space. There is no need of deriving force constants.

We will describe the lattice model and the method of evaluating the parameters in Secs. II and III. The model parameters are used to compute dispersion curves for alkali metals. To complement the dispersion curves we have also calculated the effective ion-ion potential. Finally, we will discuss the problem of using model potentials determined from elastic constants to calculate metal properties.

II. LATTICE POTENTIAL

In lattice dynamics we are interested in the change of lattice energy due to displacement of the ion from its equilibrium position. Generally the total potential is separated into the electrostatic energy, the ion-core exchange energy, and the screened electron-ion potential, the so-called band-structure energy. The electrostatic energy can be treated by an extended Ewald's method.[12] The core exchange term is often taken to be a Born-Mayer–type potential. Such a potential, with parameters determined from alkali halide data, has been applied in lattice-dynamic calculations.[7,9] However, this potential is expected to be much smaller for metals due to the different core configuration[13] and will be neglected here.[14]

Our main concern is the effective electron-ion interaction, for which we use the model pseudopotential. The idea of pseudopotential was first formulated by Phillips and Kleinman.[4] They show that in an OPW expansion for the conduction electrons, the Hamiltonian of the lattice is rearranged so that an effective potential can be defined for the ion. Owing to the orthogonality condition, this potential is small within the core and can be treated by perturbation method. In order to introduce our model potential, we will describe briefly the calculation of the band-structure energy E_{bs}.

If the total ion potential $W(r)$ is written as a superposition of the individual ion potentials $w(r)$, i.e.,

$$W(r)=\sum_i w(r-r_i)\,, \tag{1}$$

the electron-phonon matrix element can be written simply as

$$\begin{aligned}\langle k+q|W(r)|q\rangle &= W_q\\ &= S(q)U_b(q)\,,\end{aligned} \tag{2}$$

where $S(q)$ is the structure factor of the crystal and $U_b(q)$ is the Fourier transform of $U_b(r)$, the pseudopotential for an individual ion. For $U_b(r)$ we adopt the model-potential form proposed by Heine and Abarenkov (HA)[6]:

$$\begin{aligned}U_b(r) &= -V_0\,, \quad \text{for} \quad r<R_M\\ &= -Ze^2/r\,, \quad \text{for} \quad r>R_M\end{aligned} \tag{3}$$

where R_M is a measure for the effective core radius and V_0 is the core potential. Generally V_0 is a function of the electron energy and can be computed from the atomic energy levels. Here we take V_0 simply as a constant; this implies that our potential is a local pseudopotential. For alkali metals the core and valence states are well separated, a local pseudopotential may not be a serious restriction. Accordingly, we have

$$U_b(q)=-\frac{4\pi}{\Omega q^2}\left[\frac{V_0\sin qR_M}{q}+(Ze^2-V_0R_M)\cos qR_M\right], \tag{4}$$

where Ω is the volume of the unit cell.

The problem of electron screening was first treated by Bardeen[15] by a perturbation method. To obtain the screening contribution to E_{bs}, we have to calculate the screening potential only to the first order. In this case each ion potential can be screened independently. For a

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[10] K. Krebs, Phys. Rev. **138**, 143 (1965).

[11] P. S. Ho, Cornell University Materials Science Center Report No. 696, 1967 (unpublished).

[12] K. Fuchs, Proc. Roy. Soc. (London) **A157**, 444 (1936).

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

[14] We have completed a similar model calculation by taking the exchange term also into account. The exchange term was taken to be of the form $A\exp(-r/\rho)$. A, V_0, and R_M were the model parameters. Since the alkali halide value of ρ was used, it resulted in a considerable underestimate of the screened potential. The results were reported in Cornell University Materials Science Center Report No. 700, 1967 (unpublished).

[15] J. Bardeen, Phys. Rev. **52**, 688 (1937). See also D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963).

local pseudopotential approximation the first-order matrix element of the screening potential can be shown to be

$$W_q{}^e = W_q[1/\epsilon(q)-1]. \tag{5}$$

For a noninteracting electron gas $\epsilon(q)$ is the Hartree dielectric function

$$\epsilon(q)=1+\chi(q)/q^2 \tag{6}$$

and

$$\chi(q)=\frac{3\pi Ze^2}{\Omega E_F}\left(1+\frac{4k_F{}^2-q^2}{4k_Fq}\ln\left|\frac{2k_F+q}{2k_F-q}\right|\right).$$

E_F is the Fermi energy and k_F is the Fermi wave vector. Subtracting $W_q{}^e$ from W_q we have the effective screened potential

$$\begin{aligned} W_q{}^S &= S(q)U_s(q)\\ &= S(q)U_b(q)/\epsilon(q)\,, \end{aligned} \tag{7}$$

where $U_s(q)$ is called the form factor of the screened potential. E_{bs} is the energy difference from the ion-ion interaction and the electron-electron interaction arising from the screening field of the ions. It can be shown[5] that

$$E_{\mathrm{bs}}=\tfrac{1}{2}\sum_k S^*(k)S(k)U^I(k)\,, \tag{8}$$

where

$$U^I(k)=\frac{\Omega k^2}{2\pi e^2}\,\frac{1-\epsilon(k)}{\epsilon(k)}U_b{}^2(k)$$

and the sum in E_{bs} covers all occupied electron states k.

One problem here is to calculate $\epsilon(q)-1$ for electrons at metallic densities; the Hartree dielectric function which neglects exchange and correlation will not be accurate enough. The difficulty arises from the electron-electron interactions. Various modified forms[16] have been suggested for the dielectric function; essentially, one writes

$$\epsilon(q)=1+\frac{\chi(q)}{q^2[1-\xi(q)\chi(q)]}\,, \tag{9}$$

where

$$\xi(q)=1/2(q^2+\eta k_F{}^2)\,.$$

η is a function of density only. Then

$$\frac{\epsilon(q)-1}{\epsilon(q)}=\frac{\chi(q)/q^2}{1+\chi(q)(1-\xi q^2)/q^2}. \tag{10}$$

One sees that the effect of electron interaction is approximately included in the factor $1-\xi q^2$. For large q, $1-\xi q^2\simeq\frac{1}{2}$ and $\chi(q)>0$, so $W_q{}^e$ increases and $W_q{}^S$ decreases. This is expected from the short-range exchange of electrons with parallel spins. For small q, $1-\xi q^2\simeq 1$, the electron interaction has little effect on screening. Overall the electron interaction makes E_{bs} slightly more negative. For electronic properties which depend mainly on $U_s(q)$ between 0 and $2k_F$, the effect may be small. However, we will see later that for atomic properties such as sound velocity and dispersion curves it becomes significant.

In some recent calculations,[8,9] η was computed from the compressibility of electron gas. Here we consider η as an adjustable parameter to be determined together with V_0 and R_M from the experimental elastic constants.

III. LONG-WAVE LIMITS IN THE SECULAR EQUATION

In order to determine the lattice potential, we wish to express the elastic constants in terms of the model parameters. This can be done by taking the long-wave limit of the secular equation[11]

$$\det|D_{\alpha\beta}(k)-M\omega_k{}^2\delta_{\alpha\beta}|=0\,, \tag{11}$$

where we consider only one atom of mass M per unit cell and ω_k is the phonon frequency along direction k. The dynamic matrix $D_{\alpha\beta}(k)$ can be obtained by expanding the lattice potential to the second order of the ion displacement from the equilibrium position. Let us first consider the contribution from the electrostatic energy. Detailed calculations of dispersion curves for a Coulomb lattice have been reported in the literature.[17] An important result is the Kohn sum rule.

$$\sum_{\lambda=1}^{3}\omega_{k\lambda}{}^2=\omega_p{}^2=\frac{4\pi Z^2e^2}{\Omega M}\,, \tag{12}$$

where ω_p is the ion plasma frequency and λ indicates the different phonon modes. For small k there are two transverse modes with frequency proportional to k and one longitudinal mode whose frequency can be written as

$$\omega_{kl}{}^2=\omega_p{}^2-(S_1{}^2+S_2{}^2)k^2\,,$$

where S_1 and S_2 are the sound velocities for the transverse waves; this expression follows from the sum rule. Clearly, the electrostatic energy alone fails to give a proper acoustic behavior for the longitudinal wave. This difficulty can be resolved by taking the screened potential into account.

To derive the electrostatic part of the elastic constants, let us consider the shear waves along the [110] direction. For a bcc lattice the long-wave limits of these waves give

$$C_{44}{}^E=0.7423Z^2e^2/a^4 \tag{13}$$

and

$$C'^E=\tfrac{1}{2}(C_{11}{}^E-C_{12}{}^E)=0.0997Z^2e^2/a^4\,,$$

where a is the lattice parameter. Equation (13) is of course identical to the results of Fuchs.[12] Along the [100] direction, the longitudinal wave is directly related to C_{11} and the degenerate shear waves are related

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[16] D. J. W. Gelhart and S. H. Vosko, Can. J. Phys. **44**, 2137 (1966); J. Hubbard, Proc. Roy. Soc. (London) **A243**, 336 (1958).

[17] C. B. Clark, Phys. Rev. **109**, 1133 (1958); R. A. Coldwell-Horsfall and A. A. Mardudin, J. Math. Phys. **1**, 395 (1960).

to C_{44}. Applying the sum rule, we find that when $k\rightarrow 0$

$$(\omega_l^E)^2=\omega_p^2-0.7423(Z^2e^2/aM)k^2. \qquad (14)$$

Because of the presence of ω_p^2, we are not able to write the expression for C_{11}^E until it is cancelled by another identical term in the screened potential.

The screened potential part of the dynamic matrix can be expressed as

$$D_{\alpha\beta}^S(k)=\frac{1}{\Omega}\sum_G\left[U^I(k+G)(k+G)_\alpha(k+G)_\beta-U^I(G)G_\alpha G_\beta\right], \qquad (15)$$

where the sum includes all the reciprocal lattice vectors G. It is interesting to examine first the $G=0$ term in the long-wave limit. For the [100] longitudinal wave

$$(\omega_l^S)^2=-\omega_p^2+\frac{4\pi Z^2e^2k^2}{\Omega M}\left[\frac{\Omega E_F}{6\pi Ze^2}+R_M^2\left(1-\frac{2V_0R_M}{3Ze^2}\right)-\frac{1}{2\eta k_F^2}\right] \qquad (16)$$

and there is no contribution to the shear waves. Combining Eqs. (14) and (16), one sees that the [100] longitudinal wave becomes an acoustic wave; this is true for the other longitudinal waves as well. However, a stable wave still requires the k^2 term in ω_l^S plus additional contribution from the $G\neq 0$ terms to exceed the corresponding term in ω_l^E. This imposes certain limitations on the model potentials. We note that the first k^2 term in ω_l^S gives the Bohm-Staver frequency[18]

$$\omega_{BS}=(2ZE_F/3M)^{1/2},$$

which was first derived for an ionic "jellium" model with a Hartree electron gas. One sees then that the longitudinal sound velocity is the Bohm-Staver velocity modified by contributions from the effective ion potential (the second k^2 term), the approximate exchange and correlation contribution (the third k^2 term), and all the $G\neq 0$ terms in the electrostatic and screened potentials.

The contributions of the screened potential to the elastic constants from the nonzero G terms turn out to be

$$C_{11}^S=\frac{1}{\Omega}\sum_G{}'\left[U^I(G)+\frac{U^{I\prime}(G)}{2}\left(\frac{5G_x^2}{G}-\frac{G_x^4}{G^3}\right)+\frac{U^{I\prime\prime}(G)}{2}\frac{G_x^4}{G^2}\right],$$

$$C_{44}^S=\frac{1}{2\Omega}\sum_G{}'\left[U^{I\prime}(G)\left(\frac{G_x^2}{G}-\frac{G_x^2G_y^2}{G^3}\right)+U^{I\prime\prime}(G)\frac{G_x^2G_y^2}{G^2}\right],$$

$$C'^S=\frac{1}{2\Omega}\sum_G{}'\left[U^{I\prime}(G)\left(\frac{G_x^2}{G}-\frac{G_x^4+3G_x^2G_y^2}{2G^3}\right)+U^{I\prime\prime}(G)\frac{G_x^4-G_x^2G_y^2}{2G^2}\right],$$

where

$$U^{I\prime}(G)=\left.\frac{dU^I(k)}{dk}\right|_{k=G}, \qquad U^{I\prime\prime}(G)=\left.\frac{d^2U^I(k)}{dk^2}\right|_{k=G}, \qquad (17)$$

and the prime indicates that the $G=0$ term is omitted. We like to point out that Eqs. (16) and (17) hold not only for bcc metals; they could be used to calculate elastic constants for any cubic metal. Finally, after some manipulation, we obtain the following expression for C_{11} in a bcc lattice

$$C_{11}=\frac{Z^2e^2}{a^4}\left[10.13\frac{a_0}{aZ^{1/3}}+50.27\frac{R_M^2}{a^2}\left(1-\frac{2V_0R_M}{3Ze^2}\right)-\frac{1.654}{\eta Z^{1/3}}-1.485\right]+C_{11}^S, \qquad (18)$$

where a_0 is the Bohr radius. The successive terms in the bracket come from the Bohm-Staver frequency, the pseudopotential, the exchange and correlation effects of the screening electrons, and the electrostatic energy. For alkali metals, they are of comparable magnitude, e.g., for Rb they are respectively, 0.957, 2.718, -0.814, and -1.485 in units of e^2/a^4.

IV. DISPERSION CURVES

In the last section we have expressed the elastic constants in terms of the model parameters. For alkali metals we find that we can always choose a set of parameters to yield elastic constants to within 3% of the observed values. In Table I we show the result of a

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[18] D. Bohm and T. Staver, Phys. Rev. 84, 836 (1952).

typical calculation for Rb. In Table II we present the model parameters and some relevant data for alkali metals; the HA model potentials are also included for comparison. Our calculation is based on the data for Li,[19] Na,[20] and Rb[21] at 78°K and for K[22] at 4.2°K. For Cs there is no measurement available so we take the HA model parameters. We have not attempted to eliminate the lattice thermal effects by taking the linearly extrapolated data at 0°K as in the quasiharmonic approximation; instead data available at the lowest temperature are used here. One reason is the presence of the phase transformations for Li and Na below 78°K.[23] Furthermore, this facilitates the comparison of our result with the experimental dispersion curves for Na at 90°K and for K at 9°K. As for K, the temperature dependence of the elastic constants is linear to 4.2°K, our result would differ very little from that obtained in the quasiharmonic approximation.

Table I. Model calculation of elastic constants (in 10^{10} dyn/cm^2) for Rb at 78°K. The model parameters used are $V_0=0.402$ Ry, $R_M=1.74$ Å, $\eta=2.02$.

	Electrostatic energy	Screened potential $G=0$ term	$G\neq 0$ terms	Sum	Exp[b] value
C_{11}[a]	-3.458	6.642	-0.007	3.177	3.171
C_{44}	1.729	0	0.257	1.986	1.980
C'	0.232	0	0.031	0.263	0.256

[a] We have taken off the ω_p^2 terms in Eqs. (14) and (16) in order to calculate the contributions to C_{11} from the electrostatic energy and the $G=0$ term in the screened potential.

[b] Based on the 78°K data in Ref. 21.

Table II. Model parameters and some relevant data for alkali metals. (Units for the elastic constants are 10^{10} dyn/cm^2.)

	Li	Na	K	Rb	Cs
V_0 (Ry)[a]	0.845	0.542	0.413	0.401	
	(0.672)	(0.610)	(0.480)	(0.448)	(0.410)
R_M (Å)[a]	1.18	1.22	1.59	1.74	
	(1.48)	(1.80)	(2.22)	(2.33)	(2.54)
η[b]	1.58	1.78	1.87	2.02	
	(2.19)	(2.23)	(2.29)	(2.32)	(2.35)
C_{11}[c]	14.8	8.50	4.16	3.17	
C_{44}	10.8	5.88	2.86	1.98	
C'	1.16	0.729	0.377	0.256	
a (Å)	3.482	4.234	5.239	5.609	6.060

[a] The values of V_0 and R_M in the brackets are the corresponding values given in Ref. 6. Here we have taken the A_0 values which are the core pseudopotentials for s electrons.

[b] Values for η in the bracket are calculated from the compressibility of the electron gas. See Ref. 9.

[c] The C_{11} values given here are the isothermal values which have been converted from the adiabatic constants. There is no conversion necessary for C_{44} and C'.

Table III. Contributions to ω^2 in [110] directions for K. (All ω^2 are expressed in terms of ω_p^2 and the unit for k is $2\pi/a$.)

k	Electrostatic energy	Screened potential	ω^2	ω_{exp}^2 [a]
		Longitudinal wave $\Sigma_1[kk0]$		
0.1	0.98717	-0.95435	0.03282	0.03370
0.2	0.95328	-0.82802	0.12526	0.12239
0.3	0.91076	-0.66220	0.24865	0.23168
0.4	0.87585	-0.52050	0.35535	0.31164
0.5	0.86239	-0.46462	0.39777	0.35458
		Transverse wave $\Sigma_3[kk0]$		
0.1	0.01130	0.00166	0.01296	0.01035
0.2	0.04108	0.00579	0.04687	0.05324
0.3	0.07826	0.01043	0.08869	0.09313
0.4	0.10865	0.01374	0.12239	0.12764
0.5	0.12033	0.01500	0.13533	0.13850
		Transverse wave $\Sigma_2[kk0]$		
0.1	0.00153	-0.00002	0.00151	...
0.2	0.00565	-0.00021	0.00544	...
0.3	0.01098	-0.00072	0.01026	...
0.4	0.01551	-0.00141	0.01410	...
0.5	0.01728	-0.00173	0.01555	...

[a] Reference 2.

The dispersion curves are obtained by solving the secular equation along various k directions. In Table III we list part of the result for K. Usually there is a convergence problem in calculating $D_{\alpha\beta}{}^S(k)$ due to the oscillation of $U_b(k)$ at large k, which is caused by the discontinuity of the potential at R_M [see Eq. (4)]. Here we do not encounter much difficulty since the discontinuity in our potential is relatively small (check the V_0 values in Table II). Nevertheless, we have included enough terms, all 458 reciprocal lattice vectors within $6b$ ($b=2\pi/a$), to ensure proper convergence for the lattice sums. We have also studied the Kohn effect, an anomaly on the dispersion curves arising from the logarithmic singularity of $\epsilon(k)$ at $2k_F$. The size of this effect turns out to be very small for the alkali metals and probably not observable.

In Figs. 1 and 2 we plot the dispersion curves along

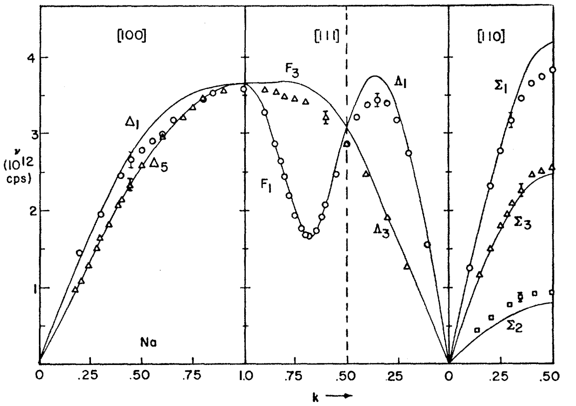

Fig. 1. Comparison of the calculated and observed dispersion curves for Na. k is plotted in units of b, $\sqrt{3}b$, and $\sqrt{2}b$ along [100], [111], and [110] directions, respectively.

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[19] H. C. Nash and C. S. Smith, J. Phys. Chem. Solids **9**, 113 (1959).

[20] R. H. Martinson, Ph.D. thesis, Cornell University, 1966 (unpublished).

[21] E. J. Gutman and J. Trivisonno, J. Phys. Chem. Solids **28**, 805 (1967).

[22] W. R. Marquardt and J. Trivisonno, J. Phys. Chem. Solids **26**, 273 (1965).

[23] For Li see H. Hovi, E. Mantysalo, and K. Tinsanan, Acta Met. **14**, 67 (1966); for Na see C. S. Barrett, Acta Cryst. **9**, 671 (1956).

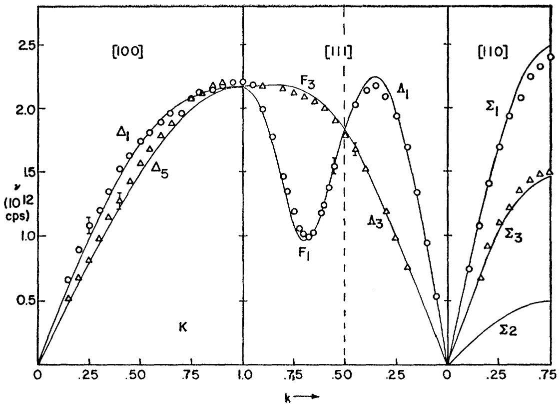

FIG. 2. Comparison of the calculated and observed dispersion curves for K. k is plotted in units of b, $\sqrt{3}b$, and $\sqrt{2}b$ along [100], [111], and [110] directions, respectively.

the symmetry directions for Na and K, respectively, and in Fig. 3 we show the curves for Li, Rb, and Cs. The neutron scattering data for Na and K are also included for comparison; the dispersion curves for the other alkali metals have yet to be measured. We wish to point out that the results shown here are good in comparison with other calculations,[5,7,8] which we have not shown here for keeping the clarity of the figures. It is also interesting to compute the elastic constants for Cs. We have used the model potential determined by Ashcroft[9] in addition to the HA potential. The results are shown in Table IV. Similar to the other alkali metals, the shear constants are found to be dominated by the electrostatic energy. For C_{11} and the bulk modulus B, there is reasonable agreement for these calculations. We feel that a measurement of elastic constants for Cs, especially at low temperatures, will be very useful for a model calculation of its properties.

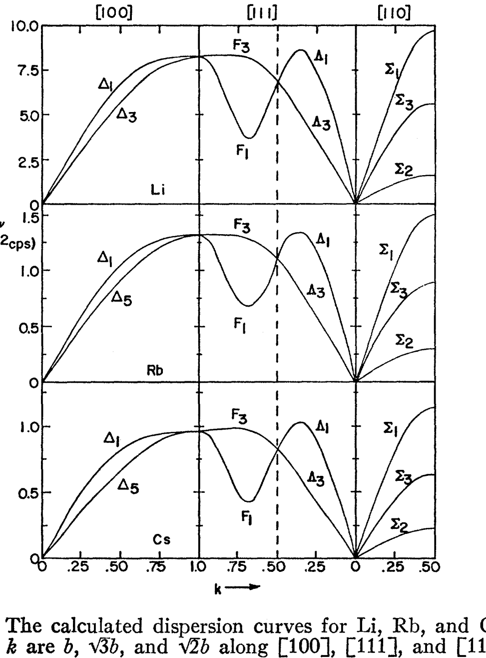

FIG. 3. The calculated dispersion curves for Li, Rb, and Cs. Units for k are b, $\sqrt{3}b$, and $\sqrt{2}b$ along [100], [111], and [110] directions, respectively.

V. EFFECTIVE ION-ION POTENTIALS

Using the model potentials, we can calculate the effective ion-ion potential $\varphi(r)$ in the real space. This potential is useful for visualizing the ionic interactions in the metal and has been applied for computing liquid metal properties.[9] To calculate $\varphi(r)$ one rearranges E_{bs} into two terms, one of which comes from the indirect ion-ion interaction via the electrons, and the other depends only on the volume of the crystal and will not contribute directly to the interionic potential. $\varphi(r)$ then becomes a two-body, central-force potential which consists of the indirect plus the electrostatic interactions, i.e.,

$$\varphi(r)=\frac{Z^2e^2}{r}+\frac{\Omega}{(2\pi)^3}\int U^I(k)e^{i\mathbf{k}\cdot\mathbf{r}}d^3k$$

$$=\frac{Z^2e^2}{r}-\frac{\Omega}{2\pi^2 r}\int_0^\infty \frac{\chi(k)U_b{}^2(k)}{k^2+\chi(k)(1-\xi k^2)}k\sin kr\,dk\,. \quad (19)$$

However, the elastic constants do not have to obey the Cauchy relation due to the presence of the volume-dependent term in the total potential. The calculated $\varphi(r)$ for alkali metals are shown in Fig. 4. We notice a resemblance in these potentials; all of them show a minimum between the first- and the second-neighbor positions. The magnitude of the minimum is approximately 0.03 eV and is smaller for heavier elements. The results agree quite well with two recent calculations.[9,24] The similarity of the interionic potential is reflected in the dispersion as seen from Figs. 1–3, a fact that was observed in the neutron scattering experiments.[1,2] Generally the potentials display long-range oscillations, but except that of Li, these oscillations diminish rapidly after the sixth-neighbor position. This is consistent

TABLE IV. Calculated elastic constants (in 10^{10} dyn/cm²) for Cs.

	HA model[a]	AL model[b]	Other[c] calculation
C_{11}	2.81	2.58	2.45
C_{44}	1.51	1.91	1.59
C'	0.183	0.188	0.185
B	2.56	2.33	2.20
V_0 (Ry)	0.410	0	
R_M (Å)	2.54	1.55	
η	2.35	2.35	

[a] The model parameters are taken from Ref. 6.
[b] The model parameters are taken from Ref. 9.
[c] The elastic constants in this column are given by H. B. Huntington, *The Elastic Constants of Crystals* (Academic Press Inc., New York, 1958), p. 76. C_{44} and C' actually come from M. Bailyn's calculation, the bulk modulus is Bridgman's experimental value, and C_{11} is obtained from B and C'.

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[24] W. M. Shyu and G. D. Gaspari, Phys. Rev. 163, 667 (1967).

with the range of the electron-ion interaction observed in Na and K dispersion curves. The oscillations are caused by the singularity of the form factor at $2k_F$, thus related to the Kohn anomaly. Our results obtained here indicate that the Kohn effect will be small for alkali metals, a point which we have reached previously.

VI. DISCUSSION

We have presented a calculation of lattice dynamics and interionic potentials for alkali metals. In this calculation the main interest is in the screened electron-ion interaction, for which we use a linear screening of the ion pseudopotential with a modified dielectric function to account for the approximate exchange and correlation effects. We have formulated the elastic constants in terms of the model parameters which are in turn determined according to the experimental data at low temperatures. This proves to be a valid approach for alkali metals as judging from our results in calculating the atomic properties. Since the elastic constants measure only the derivatives of the lattice potential, the form of the potential being determined must be chosen first, and this limits our method to a phenomenological approach. However, our choice of the HA model potential and the parameters is not unique; the formulation developed here could very well be applied to other lattice potentials.

In the lattice dynamics of alkali metals we see that the effect of the screened potential is mainly in the longitudinal waves; for the shear waves the electrostatic interaction dominates (see Table III). Since the contribution from the electrostatic energy can be calculated exactly, it is not difficult to obtain reasonably good agreement for the shear waves. This is also true for elastic constants. This point is important to realize when one attempts to deduce the screened potential from the dispersion curves. In our calculation the discrepancy occurs mainly in the longitudinal waves at large k. In fact, the calculated frequency is generally higher than the observed values; this indicates that the screened potential has been underestimated. The problem appears to lie in determining the parameter η from elastic constants. From Eq. (10) one sees that the function $\epsilon(k)-1$ is not very sensitive to η for small k, so the value of η determined from long-wave limits of elastic constants may not be satisfactory. We found that η has rather strong influence on the phonon frequency at large k, as well as on the long-range oscillations of the ion-ion potential. To avoid this difficulty, one may wish to calculate η from a longitudinal phonon frequency measured at large k or even from Fermi surface data. Also one should not overlook the question about the validity of using the modified dielectric function to account for the electron-electron interactions in the whole range of k.

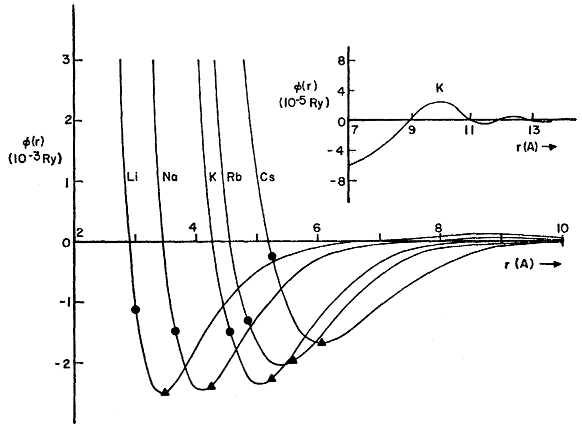

FIG. 4. The effective ion-ion potentials for alkali metals. We have designated the first-neighbor position by a ● and the second-neighbor position by a ▲. The inserted figure shows, as a typical example, the long-range oscillations in the interionic potential of K.

There are other aspects that we wish to improve in the present calculation. First is to include the anharmonic effects, thus making the model suitable for calculating temperature and pressure effects. Second is to replace the valence charge Z, which we take as unity, by an effective charge Z_{eff} to account for the effect of the "orthogonal hole" in the OPW expansion. For alkali metals Z_{eff} exceeds unity by a few percent[6]; this will increase both the electrostatic energy and the screened potential (negatively). The effect is expected to be mainly on the electronic properties. The last is to calculate other metallic properties, particularly the electronic properties, to complement the atomic properties here. This will enable us to evaluate better the present model calculation.

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