Dependence of Phonon Frequencies on the Pseudopotential Form Factor for Aluminum*

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(Received 30 April 1969)

The phonon frequencies were calculated for aluminum from a theory based on Coulomb interactions among the ions, Born-Mayer repulsion between nearest-neighbor ion cores, and a local pseudopotential interaction between ions and conduction electrons. For both a Harrison modified point-ion potential and a local Heine-Abarenkov potential, the parameters of the theory were determined to give the best over-all fit to the measured phonon dispersion curves. For the two pseudopotentials so determined, the Born-Mayer repulsion was found to be negligible, the screened form factors w_q are the same for $0\leq q\leq 1.8k_F$ and are in good agreement with Fermi-surface data, and the calculated phonon frequencies are the same. The calculated frequencies depend sensitively on $|w_q|$ for $0\leq q\leq 2k_F$, and also depend strongly on some average of $|w_q|$ for larger q.

I. INTRODUCTION

As a result of several recent studies, we can conclude that a local pseudopotential theory gives a good qualitative account of the phonon spectra of simple metals.[1–9] In some cases a parametrized local pseudopotential was determined so as to obtain agreement between calculated and measured phonon frequencies.[1,4] In another work the phonon spectrum of potassium was used to derive the screened pseudopotential form factor.[10]

The question arises as to how accurately, or how uniquely, the form factor is determined by the phonon spectrum. This question is studied here for the example of aluminum. In our approach the total adiabatic potential for the ions is composed of the ion-ion Coulomb interaction (calculated for point ions of charge $+Ze$), Born-Mayer central-potential repulsion between ion cores (taken for nearest neighbors only for Al), and the screened ion-electron interaction (represented by a local pseudopotential with Hartree screening and the Hubbard-Sham[11,2] correction for exchange and correlation). The contributions to the dynamical matrices, whose eigenvalues give the phonon frequencies, have been given previously.[2,8]

We studied two local pseudopotentials, namely, the Harrison modified point-ion potential and a local Heine-Abarenkov potential. In each case, the Born-Mayer repulsion parameters and the pseudopotential parameters were determined to obtain the best over-all fit to the measured[12] phonon frequencies for Al. The calculations are outlined in Sec. II, and the results and conclusions are summarized in Sec. III.

II. CALCULATIONS FOR ALUMINUM

For simple metals the bare single-ion local pseudopotential should be Coulombic outside the ion core and a small potential (representing an operator) inside the core. The Harrison[1] model takes a point-ion Coulomb potential, plus a repulsive exponential function which tends to cancel the Coulomb potential in the core region. The bare-ion form factor may be written

$$w_{Bq}(H)=\frac{1}{\Omega_a}\left[-\frac{4\pi Ze^2}{q^2}+\frac{\beta}{(1+q^2\rho^2)^2}\right], \tag{2.1}$$

where Ω_a is the volume per atom, and β, ρ are positive parameters relating to the core part. The local Heine-Abarenkov[13] model takes a Coulomb potential outside of the core of radius σ, and a well of depth δ inside the core. The bare-ion form factor is

$$w_{Bq}(HA)=-\frac{4\pi}{\Omega_a q^2}\left[\frac{\delta\sin q\sigma}{q}+(Ze^2-\delta\sigma)\cos q\sigma\right]. \tag{2.2}$$

The screened form factor w_q, in either case, is

$$w_q=w_{Bq}/[1+(f_q-1)(1-g_q)], \tag{2.3}$$

$$g_q=q^2/2(q^2+\xi k_F^2). \tag{2.4}$$

Here f_q is the Hartree dielectric function, $1-g_q$ is the Hubbard-Sham approximate correction due to nonuniform electron gas exchange and correlation effects, ξ is a parameter determined from the electron gas

* Work supported by the U. S. Atomic Energy Commission.
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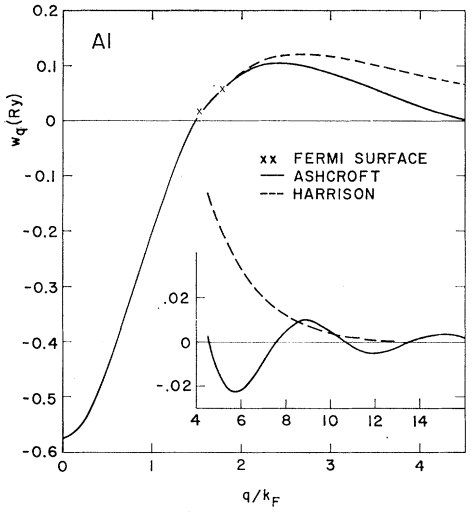

FIG. 1. Screened form-factor curves for the two pseudopotentials whose parameters were determined to give the best over-all fit to the measured phonon frequencies of Al.

compressibility,[14,15] and k_F is the magnitude of the Fermi wave vector. We note for any local pseudopotential which is Coulombic at large distances from the ion core, the screened form factor given by (2.3) has the property

$$w_q \to -\tfrac{2}{3}\epsilon_F \quad \text{as} \quad q \to 0, \tag{2.5}$$

where $\epsilon_F = \hbar^2 k_F^2/2m$.

The total band-structure contribution to the i, i' element of the dynamical matrix for wave vector $\mathbf{k} \neq 0$ is[8]

$$2\sum_{\mathbf{Q}} F_{|\mathbf{Q}+\mathbf{k}|}(\mathbf{Q}+\mathbf{k})_i(\mathbf{Q}+\mathbf{k})_{i'} - 2\sum'_{\mathbf{Q}} F_{|\mathbf{Q}|}Q_iQ_{i'}, \tag{2.6}$$

where the sums are over reciprocal-lattice vectors $\mathbf{Q}$ and the energy–wave-number characteristic is conveniently expressed as

$$F_q = -(\Omega_a q^2/8\pi e^2) w_q^2 (f_q - 1)[1 + (f_q - 1)(1 - g_q)]. \tag{2.7}$$

We note the function multiplying w_q^2 in (2.7) diverges as $q \to 0$, and converges as q^{-2} for large q. Thus, for a given $\mathbf{k}$ in (2.6), the $\mathbf{Q}=0$ term $F_k \mathbf{k}_i \mathbf{k}_{i'}$ is a very important contribution, which depends on $|w_q|$ in the small-q region; the sum over $\mathbf{Q} \neq 0$ is also an important contribution which samples $|w_q|$ quite thoroughly in the large-q region.

We used the following values of experimental quantities for Al:

$$Z = 3, \quad \Omega_a = 110.6 a_0^3, \quad \xi = 1.90, \quad \langle\omega^2\rangle = 17.1 (10^{26}\ \text{sec}^{-2}).$$

Here Ω_a and ξ are at $T = 0°\text{K}$ and $\langle\omega^2\rangle$ is the average over the zone of the phonon frequencies squared at 80°K.[16] In order to fit the calculated phonon frequencies to the measurements, we systematically varied the theoretical parameters and studied graphs of the results. This was not as difficult as it may appear, since it was easily determined that the over-all shape of calculated curves was quite poor in any case where a significant Born-Mayer repulsion was included. In particular, the Born-Mayer repulsion tends to straighten out the curves of ω versus k (i.e., reduce the magnitude of the curvature). Omitting the Born-Mayer repulsion then left two parameters for each pseudopotential; one of these parameters was determined by fitting $\langle\omega^2\rangle$ in a separate calculation,[8] and the other was varied to obtain good graphical fits to the frequencies along symmetry directions.

The pseudopotential parameters so determined are as follows:

Harrison: $\beta = 47.5$ Ry a_0^3, $\rho = 0.24 a_0$

Heine-Abarenkov: $\delta = 0$, $\sigma = 1.117 a_0$.

It is interesting that the Heine-Abarenkov well depth goes to zero for the best phonon frequency fit; this potential then becomes an Aschroft potential.[17] The screened form factors are shown in Fig. 1. It is also interesting that, for the two pseudopotentials, the w_q are identical for $0 \leq q \leq 1.8 k_F$. Furthermore, these two pseudopotentials are in good agreement with the form factors determined from Fermi-surface measurements,[18] as shown in Fig. 1.

We calculated the phonon frequencies to an estimated accuracy of 0.5% for each of these pseudopotentials. To obtain this accuracy the reciprocal-lattice sums which appear in the dynamical matrices in (2.6) must be extended to quite large reciprocal-lattice vectors $\mathbf{Q}$; in particular the sums must be carried to $|Q| = 14 k_F$

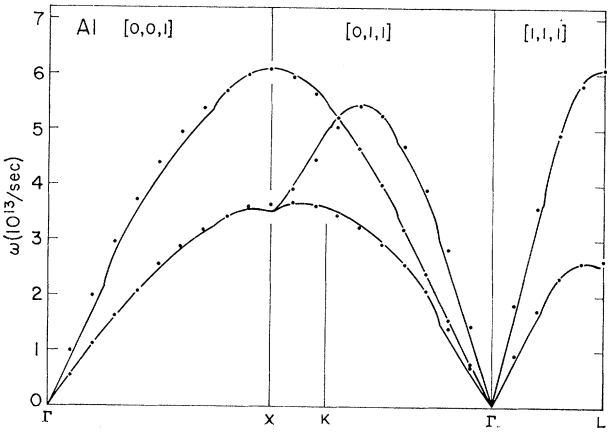

FIG. 2. Comparison of calculated and measured phonon frequencies for Al. The calculated curves (either pseudopotential) are shown by the solid lines, while the points represent the data of Ref. 12. The Kohn anomalies have been slightly exaggerated to make them more apparent in the theoretical curves.

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for the Harrison potential, and to $|Q|=20k_F$ for the Ashcroft potential. The slower convergence of the Ashcroft potential may be expected from the large-q behavior shown in Fig. 1.

The most important result of our calculations is that the two calculated phonon dispersion curves are essentially identical. More specifically, for the two pseudopotentials, $\langle\omega^2\rangle$ is the same and the phonon frequencies along symmetry lines differ in magnitude by about 0.5% on the average and by 1.5% at most. The calculated frequencies are compared with experimental results in Fig. 2. The average magnitude of the deviation of theory from the 57 experimental points shown in Fig. 2 is 3%.

Within the accuracy of our calculations, then, the two pseudopotentials give an equally good representation of Fermi-surface data and phonon frequencies. But the two form factors are quite different for $q>2k_F$, and this large-q region gives important contributions to the phonon frequencies. The large-q contributions may be illustrated by calculating the phonon frequencies under the assumption $w_q=0$ for $q\geq nk_F$, where n is a number to be chosen. Results of this calculation are shown in Fig. 3 for the Harrison potential.

Introducing a discontinuity in the form-factor curve leads to Kohn-type anomalies in the phonon dispersion curves. When $n=2$ the anomalies are in the same places as Kohn anomalies, since the latter are due to the weakly singular behavior of the screening function at $q=2k_F$. The dashed curve of Fig. 3, corresponding to $n=2$, shows giant anomalies which are due to cutting off w_q at $q=2k_F$, and shows the importance of the large-q contributions to the phonon frequencies. For larger n, the anomalies become smaller and more numerous. The example of $n=6$ is shown by the solid line in Fig. 3; this curve is still drastically different from the accurate results shown for $n=14$.

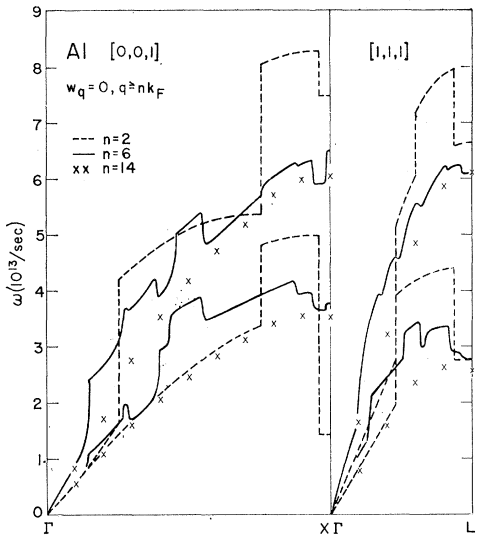

FIG. 3. The effect on the calculated phonon frequencies of cutting off the form factor for q larger than nk_F. The curves shown are for the Harrison potential; the points shown for $n=14$ correspond to points on the accurate curves of Fig. 2.

III. SUMMARY AND CONCLUSIONS

We have calculated the phonon frequencies of aluminum from a theory based on long-range Coulomb interactions among the ions, short-range Born-Mayer repulsion between ion cores, and a local pseudopotential interaction between ions and conduction electrons. For both a Harrison and a Heine-Abarenkov local pseudopotential, the parameters of the theory were determined to give the best over-all fit to the measured phonon frequencies. This fitting procedure led to the following results:

(a) For each pseudopotential, the Born-Mayer repulsion is essentially zero.

(b) For each pseudopotential, the screened form factor is in good agreement with experimental Fermi-surface data.

(c) The phonon frequencies calculated for the two pseudopotentials are essentially identical.

It is not surprising that the Born-Mayer repulsion is negligible for Al. In comparison with Na, for which the Born-Mayer repulsion is small,[2,8] Al has a much smaller ion core and has more conduction electrons to hold the cores apart. It is also not surprising that the two form factors are identical for $0\leq q\leq 1.8k_F$; as we noted from Eq. (2.6), fitting the phonon spectrum for $\mathbf{k}$ throughout the Brillouin zone places strong requirements on $|w_q|$ for $|q|$ lying in the zone ($0\leq q\leq 1.0k_F$ for Al). We note the range of pseudopotentials studied in our phonon-frequency calculations had form factors vastly different from those of our final fitted pseudopotentials, shown in Fig. 1.

Finally, it is somewhat surprising that the two pseudopotentials give the same phonon frequencies (to order 1%), when their form factors are so different for $q>2k_F$ (Fig. 1), and the calculated frequencies depend so strongly on the contributions from $q>2k_F$ (Fig. 3).

ACKNOWLEDGMENTS

The author is grateful to Nelson Gillis for valuable discussions, and to Reginald Stedman for a table of the measured phonon frequencies for aluminum.