Kohn Effect in Na and other Metals

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It is pointed out that if the Kohn effect is looked for, not as an obvious kink in the phonon dispersion curves of metals as originally suggested, but as a damped sinusoidal variation of the interplanar force constants with separation, then (1) the effect has been observed in many metals and (2) for Na, which is very close to a free-electron metal, the measured force constants oscillate with the expected wavelength (π/k_F). From the data for Al and Pb, it would appear that even though the Fermi surface is quite close to a free-electron sphere in the extended zone, electrons do not scatter isotropically around this surface, but presumably stay within their respective Brillouin zones even at temperatures of the order of the Debye θ.

INTRODUCTION

PHONONS in a metal may be thought of as the plasma oscillations (of varying wavelength) of the positive ions immersed in the electron Fermi sea. The restoring force varies with wavelength and frequency because the surrounding electron gas screens the space charge associated with oscillations of different wavelengths to a different extent.[1] It is then the wave number (q) dependence (and in principle, the frequency dependence)[2] of the dielectric constant of the electron gas that determines the main features of the phonon spectrum in metals. Kohn recently pointed out that the dielectric function has a logarithmic singularity at $q/2=k_F$, the Fermi wave number, which indicates "an abrupt decrease in the ability of the electrons to screen the embedded charge distribution as soon as q exceeds $2k_F$."[3] This singularity should cause an anomaly or "kink" in the phonon spectrum, originally estimated to be $\sim 1\%$, at a value of q such that $|\mathbf{q}+\mathbf{g}|=2k_F$, where $\mathbf{g}$ is a reciprocal lattice vector. Subsequently, a more careful estimate[4,5] of the magnitude of the "Kohn effect" showed that it usually will be unobservably small. Only in special cases where, as in Pb, the electron phonon interaction is unusually large, might one observe the effect as originally described; recent observations[6,7] in Pb show striking anomalies which have been ascribed to the Kohn effect.

It is the purpose of this note to point out (1) that the Kohn effect has in fact been indirectly observed in many metals, including Na,[8] Al,[9] Ta,[10] Nb,[11] and Mo,[12] as an oscillatory variation of the interplanar force constants with separation and (2) to demonstrate the asymptotic form of this variation at large distances (on a free-electron model) and show that it compares favorably with the data for Na.

MODEL

For phonons propagating along directions of high symmetry, such as a body-diagonal or cube-edge direction in a cubic lattice, the physical motion corresponds to a rigid displacement of those planes of atoms normal to the propagation direction. The problem becomes formally equivalent to a linear chain[13] for which, as is well known, the successive Fourier coefficients of the dispersion curve are simply related to the interaction of an atom with successively more distant neighbors.[14] In the metals mentioned above, the experimentally determined interplanar force constants do not decrease monotonically with the interplanar separation, but fluctuate in sign in a manner that suggests they might be describable by a damped sine curve. The model discussed below shows that these fluctuations are related to the "Friedel wiggles"[15] in the screening of a monopole impurity by a (degenerate) electron gas and are, in fact, an integral of the long-range part of the spatial transform of the dielectric function used by Kohn.[16]

We want to consider the force on an ion in the zeroth plane due to a small rigid displacement $\mathbf{l}$ of the entire nth plane, all other planes being held fixed. ($\mathbf{l}$ will be along the propagation direction for a longitudinal mode, and perpendicular to it for a transverse mode.) In the spirit of the nearly-free-electron ap-

[1] Cf. D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963).

[2] As even the highest phonon frequencies are two orders of magnitude lower than the electron plasma frequencies in good metals, it is entirely adequate to consider the zero-frequency dielectric constant in what follows.

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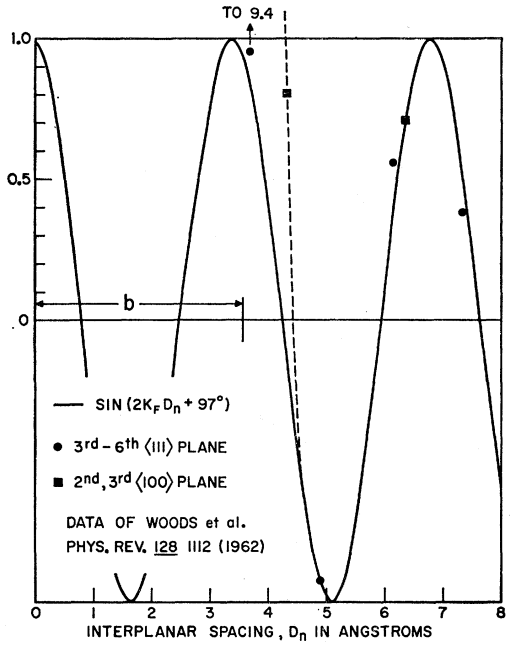

FIG. 1. Comparison of the experimental results for the interplanar force constants in Na with the model discussed in the text. The data points plotted are derived from the results of Woods *et al.* (Ref. 8) by multiplying by the square of the interplanar separation and correcting for the difference in atomic density between the ⟨111⟩ and ⟨100⟩ planes. The values have been normalized to obtain a best fit to the solid curve in the figure, the phase of which is also an adjustable parameter. It is expected (see text) that the agreement should be good beyond ~4.5 Å. The dashed line through the data closer into the origin shows how the tail of the main screening charge comes in.

proximation, the screening of this displaced plane by the Bloch electrons will be equivalent to the screening of a similar plane of dipoles $e\mathbf{l}$ by a free-electron gas.[17] Ultimately, we will only be concerned with the effect of the screening charge on ions at lattice positions; it then even becomes unnecessary to ever "fold back" the final results, which involve k_F measured in the extended zone, into the first Brillouin zone.

The main screening of the dipoles may be computed for our purpose using the (zero frequency) Thomas-Fermi dielectric constant[18]

$$\epsilon_{TF}(q)\simeq 1+(\lambda q)^{-2};\quad \lambda=(n/2em^{1/2})(\pi/3n)^{1/6}, \qquad (1)$$

where n is the electron density. For $lk_F\ll 1$ (as it always is for a typical phonon density), the screened dipole potential is just the derivative of the screened monopole "Yukawa" potential

$$V(r)=\frac{e\mathbf{l}\cdot\mathbf{r}}{r^3}\left(1+\frac{r}{\lambda}\right)\exp\left(-\frac{r}{\lambda}\right). \qquad (2)$$

The dipole perturbation is shielded by the electrons as effectively as a monopole perturbation, though the total shielding charge is, of course, zero in the dipole case. For Na, $\lambda=0.67$ Å$\simeq 0.2b$, where b is the nearest-neighbor distance. In addition to this "smooth" screening cloud, there is a small long-range, oscillatory, charge-density variation which may be thought of as permanent standing waves of probability density set up in the electron sea by each of the (well-shielded) dipole perturbations. We can obtain an expression for the long-range charge-density variation by differentiating Kittel's[19] monopole result:

$$\Delta\rho_k(\mathbf{r})=-8\pi l|f_k(\pi)|\cos\alpha\cos(2kr+\delta)/r^2. \qquad (3)$$

Here l is the dipole length, α the angle between $\mathbf{r}$ and $\mathbf{l}$, $f_k(\pi)$ the probability for backward scattering from a monopole and δ its phase angle. The magnitude of the charge-density oscillations induced by a dipole perturbation is less by the factor $2kl\lesssim 0.3$ than the analogous result for monopole scattering. By comparing the monopole calculations of Langer and Vosko[16] (their Fig. 4 is appropriate to Na), one estimates that Eq. (3) above will correctly describe $\Delta\rho_k(\mathbf{r})$ for distances $\gtrsim$ the fourth nearest-neighbor plane separation in the ⟨111⟩ direction in Na. (They also show that this oscillatory function is the long-range approximation to the Fourier transform of the dielectric function used by Kohn.) From Eq. (3), one obtains by direction integration, keeping only the longest range terms, the potential V and E_l, the component of electric field along $\mathbf{l}$, which after integration over k become

$$\begin{aligned} V&=4\pi^2 l\cos\alpha|f_{k_F}(\pi)|\sin(2k_Fr+\varphi)/r^3,\\ E_l&=-8\pi^2\cos^2\alpha|f_{k_F}(\pi)|k_Fl\cos(2k_Fr+\varphi)/r^3. \end{aligned} \qquad (4)$$

The final interplanar force constant is obtained by summing the field E_l produced at a particular site in the zeroth plane over all lattice points in the nth plane. For sufficiently distant planes this can be replaced by an integration. For longitudinal phonons, the force $F_n{}^L$ becomes

$$F_n{}^L=8\pi^3 de|f_{k_F}(\pi)|l\sin(2k_FD_n+\varphi)/D_n{}^2, \qquad (5)$$

where D_n is the interplanar distance and d is the density of ions in the plane.

APPLICATION TO Na

Sodium, with one electron per atom, is known to have a spherical Fermi surface with an effective mass very close to the free-electron value; it should be the material best suited for comparison with Eq. (5). We have taken the data[8] for the interplanar force constants that describe longitudinal phonons propagating along the ⟨100⟩ and ⟨111⟩ directions, adjusted the data for the two directions by dividing by the appropriate d, multiplied by $D_n{}^2$, and tried to obtain the best fit of these points to a curve of the form $\sin(2k_FD_n+\varphi)$, where $k_F=0.92\times 10^8$ cm^{-1} was set at the value ap-

[17] H. C. White, Phys. Rev. 112, 1092 (1958).
[18] Cf. C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), p. 112.
[19] See Ref. 18, p. 348.

propriate to a free-electron gas with the number density of sodium. The result is shown in Fig. 1. Points closer in to the origin deviate from the curve, consistent with the criterion discussed above.

An equation analogous to Eq. (5) can, of course, be obtained for transverse modes. The result, within the same approximation, is

$$F_n{}^T = 4\pi^3 |f_{k_F}(\pi)| l^2 e d \cos(2k_F D_n + \varphi)/D_n{}^3 k_F. \quad (6)$$

The term in D_n^{-2} vanishes identically in the integration, though it presumably wouldn't if the lattice summation were properly done. The experimental data for the transverse phonons show a distance variation between D_n^{-2} and D_n^{-3}, and are shifted in phase when compared with the data in the figure in the direction that is a compromise between Eqs. (5) and (6).

OTHER METALS

The interplanar forces constants derive from the dielectric constant of the electron gas of the metal in question since they are essentially the forces between pairs of ions embedded in the electron distribution. The existence of the long-range oscillations in real space of these force constants indicates a discontinuity in the wave-number-dependent dielectric constant, that due to the sharpness of the Fermi surface. This is, in essence, the Kohn effect. The amplitude of the oscillations may vary from metal to metal because of differing electron-ion core interactions and be much larger than the result computed for free electrons; this variation is contained in $f_k(\pi)$ and is discussed in some detail by Taylor.[5]

For Al and Pb the long-range oscillatory forces are much more pronounced than in Na.[6,9] In Pb, force-constant oscillations have been observed in the ⟨100⟩ direction with a period of two lattice planes, which decay as the inverse square of the interplanar separation and which extend out to the eleventh plane (25 Å). Since both Al and Pb are quite good free-electron metals,[20,21] i.e., since the energy surfaces are obtained surprisingly well by folding the respective free-electron Fermi sphere back into the first Brillouin zone, one might expect that the analysis that works so well for Na should work for Pb and Al (in the extended zone). The ⟨100⟩ period in Pb, however, is about twice as long as that expected for a free-electron Fermi surface containing four electrons per atom. Similar discrepancies occur in Al. This suggests that at the temperatures at which the data were taken (300°K for Al, 100°K for Pb), the electron-phonon scattering does not mix electrons in different zones; pockets of electrons with smaller Fermi diameters must contribute to the force constants. It also suggests that perhaps "magnetic breakdown" [22] such as observed in Mg[23] (in which large area de Haas-van Alphen orbits are observed in external magnetic fields sufficiently large so that the magnetic perturbation is larger than the splitting at the zone boundaries) may also show up as a change in the long-range behavior of the interplanar force constants upon application of a large magnetic field.

Woods and co-workers[11,12] have reported phonon dispersion results for Nb and Mo (which are adjacent in the periodic table) and pointed out that while the nearest-neighbor force constants are similar, the long-range interactions are much different. On the other hand, they show that the long-range behavior of Nb and Ta, both column Vb metals, is quite similar. This, of course, would be expected on the basis of our discussion, since the Fermi momenta would be expected to be quite different for Nb and Mo, but similar for Nb and Ta.

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