PHYSICAL REVIEW VOLUME 139, NUMBER 1A 5 JULY 1965

Model Pseudopotential and the Kohn Effect in Lead

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(Received 15 February 1965)

A model local pseudopotential for lead is proposed and two parameters adjusted so that the pseudopotential leads to the correct vibration frequency for two selected modes. Two potentials are found to satisfy these conditions and one is selected which resembles the pseudopotential suggested from other experiments. Kohn anomalies in the spectrum are found which are of the same general magnitude of those observed. The model does not, however, lead to the correct stable structure, nor does it appear to describe well the effective interaction between ions at small distances. Similar adjustment of the model to fit the vibration spectrum of aluminum gives a pseudopotential similar to that computed from first principles and leads to the correct stable structure, but again does not give correctly the effective interaction potential at short distances.

I. INTRODUCTION

IN the self-consistent-field approximation, the energy eigenstates for electrons in a metal can be obtained by solving the Schrödinger equation,

$$T\psi+V\psi=E\psi\,, \tag{1.1}$$

where V is the self-consistent potential. If we know the core states $|\alpha\rangle$, which for a simple metal can be taken equal to the core states in the free ion to a good approximation, we may replace the Schrödinger equation by the pseudopotential equation,

$$T\varphi+W\varphi=E\varphi\,, \tag{1.2}$$

where the general form of the pseudopotential has been given by Austin, Heine, and Sham[1];

$$\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle=\langle\mathbf{k}+\mathbf{q}|V|\mathbf{k}\rangle+\textstyle\sum_\alpha f(\mathbf{k},\alpha)\langle\mathbf{k}+\mathbf{q}|\alpha\rangle\langle\alpha|\mathbf{k}\rangle\,, \tag{1.3}$$

and $f(\mathbf{k},\alpha)$ is a general function of $\mathbf{k}$ and α. [This form for plane-wave matrix elements of the pseudopotential can readily be obtained from the formulas given in Ref. 1.] This will lead to precisely the same eigenvalues E and the eigenfunction ψ may be obtained from the pseudoeigenfunction φ by orthogonalizing to the core states,

$$\psi=(1-\textstyle\sum_\alpha|\alpha\rangle\langle\alpha|)\varphi\,. \tag{1.4}$$

The advantage of the pseudopotential equation is that with appropriate choice of $f(\mathbf{k},\alpha)$ the pseudopotential will in some sense be small and approximate solutions may be found by perturbation techniques.

We have used this technique[2–4] to evaluate the conduction-electron energies and to sum them over occupied states in metals. This gives the total band-structure energy of the metal and may be determined as a function of the positions of the ions in the metal; this, in turn, allows the calculation of atomic properties of metals such as the vibration spectrum.

In these calculations we have found that the nonlocal nature of the pseudopotential, arising from the final term in Eq. (1.3), was very pronounced. This was reflected in a strong dependence of the matrix elements of Eq. (1.3) upon $\mathbf{k}$ as well as upon $\mathbf{q}$. We have therefore been skeptical of attempts to replace the true nonlocal pseudopotential by an effective local potential. However, Sham[5] has indicated that little error is introduced in the final results by replacing the nonlocal pseudopotential by an effective potential which is an average of the nonlocal potential over $\mathbf{k}$. We wish here to explore further the use of such an effective potential.

This has the advantage of considerably simplifying the computations. More importantly, from our point of view, it allows us to select a particularly simple model form and adjust two parameters so that the computed vibration spectrum fits that observed for lead. The calculation of the true pseudopotential for a metal as heavy as lead would be a considerable task and would be of questionable significance unless spin-orbit coupling were included. The phenomenological approach, by adjusting to fit experiment, takes some crude account of the influence of spin-orbit coupling upon the vibration spectrum.

On the other hand, the calculations are certainly not from first principles and comparison with experiment is not such a critical test. We partly compensate for this by carrying out the same calculations for aluminum and comparing with the pseudopotential obtained from first principles earlier.[4]

II. THE MODEL PSEUDOPOTENTIAL

We first separate the pseudopotential into individual (but overlapping) ionic pseudopotentials centered at the ion positions $\mathbf{r}_j$;

$$W(\mathbf{r})=\textstyle\sum_j w(\mathbf{r}-\mathbf{r}_j)\,. \tag{2.1}$$

This separation is valid to the order in W to which we compute. We are interested then in the structure of the individual pseudopotentials $w(\mathbf{r})$ which are, of course, nonlocal operators.

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[1] B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. **127**, 276 (1962).

[2] W. A. Harrison, Phys. Rev. **129**, 2503 (1963).

[3] W. A. Harrison, Phys. Rev. **129**, 2512 (1963).

[4] W. A. Harrison, Phys. Rev. **136**, 1107 (1964).

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

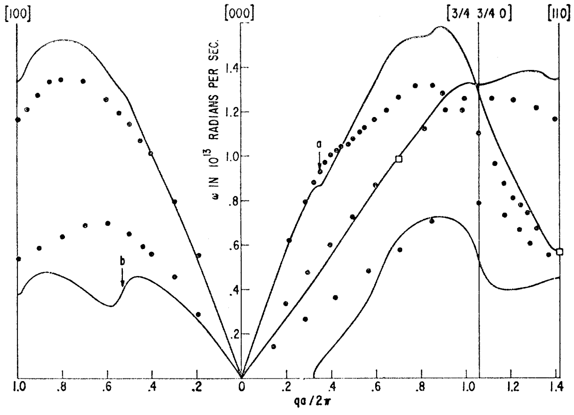

FIG. 1. Curves represent the computed vibration spectrum of lead using the high-β pseudopotential, $\beta=96.9$ Ry a.u.^{3}, $r_c=0.31$ a.u. Experimental points are taken from Brockhouse, Arase, Caglioti, Rao, and Woods (Ref. 13). Two prominent Kohn anomalies in the computed curves are indicated by arrows and are discussed in the text. Points at which the pseudopotential was fit to experiment are indicated by boxes.

We have noted earlier[6] that for many electronic properties, we are interested only in matrix elements $\langle\mathbf{k}+\mathbf{q}|w|\mathbf{k}\rangle$ between two states lying on the Fermi surface. This subclass of matrix elements could be characterized by a single parameter q lying between zero and $2k_F$, twice the Fermi wave number. Thus a single curve for each metal gave an important set of matrix elements and these were evaluated for the simple metals Li, Be, Na, Mg, Al, K, Ca, and Zn.[6] We further found that these curves could be fit quite well by a one-parameter form,

$$\langle\mathbf{k}+\mathbf{q}|w|\mathbf{k}\rangle\approx[-4\pi Ze^2/q^2+\beta]/[\Omega_0\epsilon(q)]. \qquad (2.2)$$

Here Z is the valence of the ion; β is the strength (the one undetermined parameter) of a delta function approximating the influence of the core; Ω_0 is the atomic volume; and $\epsilon(q)$ is the Hartree dielectric function for free electrons.

In calculations of atomic properties we will require matrix elements for q larger than $2k_F$, and Eq. (2.2) does not behave properly in this range. As q becomes large, the expression in Eq. (2.2) approaches the constant β/Ω_0, whereas our computed form factors always approach zero at large q. To obtain a more appropriate form at large q, we consider the form of the general pseudopotential given in Eq. (1.3). The decay of the repulsive final term on the right-hand side at large q arises from the factor $\langle\mathbf{k}+\mathbf{q}|\alpha\rangle$. For a core function which varies as Ae^{-r/r_c}, this factor approaches

$$\langle\mathbf{k}+\mathbf{q}|\alpha\rangle\rightarrow\frac{4\pi A}{\Omega_0}\int\frac{\sin qr}{qr}e^{-r/r_c}r^2dr=\frac{4\pi r_c{}^3A}{\Omega_0}\frac{1}{[1+(qr_c)^2]^2}$$

at large q. We are therefore motivated to propose matrix elements given by

$$\langle\mathbf{k}+\mathbf{q}|w|\mathbf{k}\rangle=[-4\pi Ze^2/q^2+\beta/(1+(qr_c)^2)^2]/[\Omega_0\epsilon(q)], \qquad (2.3)$$

with the two adjustable parameters β and r_c.

Given this form and the values of the parameters we may directly proceed to the computation of any property of interest using the methods described earlier.[3] The energy-wave number characteristic which determines the atomic properties is found to be

$$E(q)=-\frac{q^2}{8\pi Ze^2\Omega_0}\left[-\frac{4\pi Ze^2}{q^2}+\frac{\beta}{[1+(qr_c)^2]^2}\right]^2\frac{\epsilon(q)-1}{\epsilon(q)}. \qquad (2.4)$$

The appearance of the $\epsilon(q)-1$ in the numerator comes from noting that the sum over all electronic states to obtain the energy is of the same form as the sum over states to obtain the screening field. The band-structure energy per electron is given by

$$E_{bs}=\sum_q S^*(\mathbf{q})S(\mathbf{q})E(q), \qquad (2.5)$$

where $S(\mathbf{q})$ is the structure factor given by

$$S(\mathbf{q})=(1/N)\sum_j e^{-i\mathbf{q}\cdot\mathbf{r}_j}, \qquad (2.6)$$

the sum being over all N ion positions in the crystal.

In particular, we may compute the vibration spectrum (including of course the electrostatic as well as the band-structure energy) as described earlier[3,4] using various values of β and r_c and select those values which give the best fit to the spectrum.

III. ADJUSTING THE PARAMETERS

We followed the procedure of fixing r_c and varying β to obtain the correct frequency for a selected mode at a selected wave number. We found often that for fixed r_c the frequency of the mode in question varied roughly quadratically with β. Thus for some choices of r_c, there

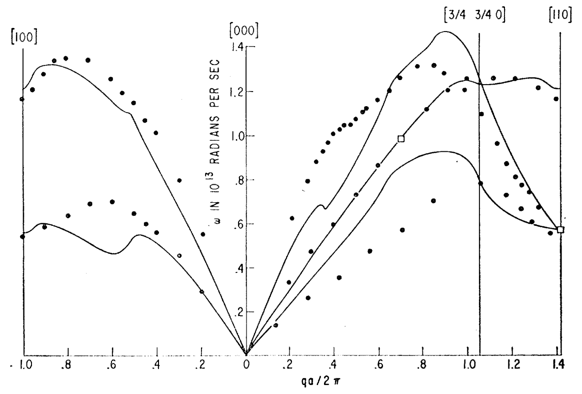

FIG. 2. Curves represent the computed vibration spectrum of lead using the low-β pseudopotential, $\beta=19.6$ Ry a.u.^{3}, $r_c=0.30$ a.u. Experimental points are taken from Brockhouse, Arase, Caglioti, Rao, and Woods (Ref. 13). Points at which the pseudopotential was fit to experiment are indicated by boxes.

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[6] W. A. Harrison, Phys. Rev. **131**, 2433 (1963).

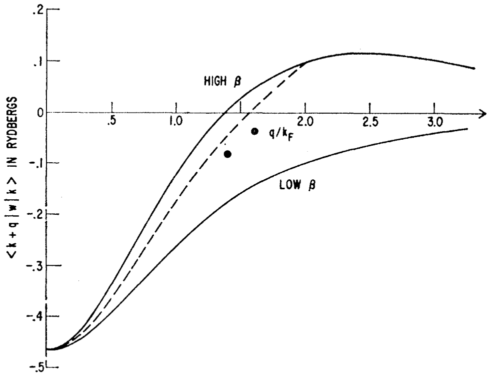

FIG. 3. Computed form factors for lead for the two model pseudopotentials which lead to the dispersion curves of Figs. 1 and 2. The dashed line gives the pseudopotential estimated earlier (Ref. 8) from the resistivity of lead alloys. The two points represent form factors estimated by Anderson and Gold (Ref. 7) from studies of the Fermi surface.

was no value of β giving the correct frequency; such values of r_c were of no interest. For other choices of r_c there were two values of β; we retain both values. We then followed the same procedure for different values of r_c until we obtained agreement also for a second selected mode. Agreement for the second mode was obtained at different values of r_c for the high- and for the low-β solutions. These two experimental frequencies lead to two different possible pseudopotentials.

In lead, after some experimentation, we selected the two modes: transverse mode propagating in the [110] direction with polarization in the [001] direction and with wave number q given by $qa/2\pi=0.707$; and transverse mode propagating in the [110] direction with polarization in the $[1\bar{1}0]$ direction and with wave number q given by $qa/2\pi=1.414$. Agreement with these two modes was obtained with $r_c=0.3$ atomic units (a.u.), $\beta=19.6$ Ry a.u.^{3} and with $r_c=0.31$ a.u., $\beta=96.9$ Ry a.u.^{3} [Note that β has units of energy times volume; our unit of volume is a Bohr radius (a.u.) cubed (0.529 Å)^3.] The corresponding computed dispersion curves are given in Figs. 1 and 2. The most striking aspect of these curves is the structure, which is to be associated with the Kohn effect. We will discuss this aspect later.

We may note at once that there is some calculational error reflected in the failure of the T_{110} and longitudinal modes propagating the [110] direction to become degenerate at $qa/2\pi=1.414$ in the high-β curves. This reflects a failure to reach convergence in summing over q though we summed to q equal to $16\pi/a$, corresponding to some 500 reciprocal lattice vectors and their satellites, and added an approximate correction for the remainder. This represents a systematic error of the order of the difference between the computed frequency of the degenerate modes, but is not of great importance for our considerations.

We note further that the frequency of some of the high-β modes has become imaginary, reflecting an instability in the lattice.

Neither figure represents sufficiently better agreement with experiment than the other to enable us to select it. It is therefore appropriate to consider other information we have about the pseudopotential in lead.

We consider the form factor $\langle \mathbf{k}+\mathbf{q}|w|\mathbf{k}\rangle$ which is plotted in Fig. 3 for the two model pseudopotentials. Comparison is made there with two values of the form factor estimated by Anderson and Gold[7] by analysis of the Fermi surface. It is also made with the form factor we have estimated earlier[8] by consideration of the resistivity of various alloys of lead. In terms of the model used here, that given earlier for lead corresponds to $\beta=60$ Ry a.u.^{3}, $r_c=0$. On this basis we select the high-β solution as giving a better description of lead.

It should be noted again that no explicit account is taken here of the effects of spin-orbit coupling. Anderson and Gold[7] estimate a spin-orbit coupling parameter of 0.0961 Ry, comparable with the form factors determining the band gaps at zone faces. The effects of spin-orbit coupling thus should have an appreciable role in determining both the dispersion curves and the resistivity of alloys. By neglecting this effect and forcing the pseudopotential to give appropriate experimental results, we are making a very crude experimental correction for spin-orbit coupling. Some of the discrepancy in our computed dispersion curve will come from the crudeness of this correction as well as from the oversimplification of the problem with our effective potential.

A further interesting check on the method may be made by applying the same procedure to aluminum and comparing the resulting pseudopotential with that computed from first principles. Here spin-orbit coupling is so small that there is no difficulty in our neglecting it.

We attempted again a fit of the same modes used in lead, but with much less extensive exploration than was carried on in lead. We found that with $r_c \geq 0.3$ there was no β giving as low a frequency as that observed at the $q=0.707\times 2\pi/a$ mode. At $r_c=0.2$, there were solutions at $\beta=41.4$ and about 15. The former gave a good fit to the second mode and resembled the form factor which we had computed from first principles. We therefore computed the vibration spectrum for that case. The resulting dispersion curves are shown in Fig. 4.[9] We also show in Fig. 5 the corresponding form factor and that computed from first principles. The rather good fit in both cases suggests that the approach is a reasonable one. Presumably with further adjustment we could improve the agreement with the vibration spectrum of aluminum.

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[7] J. R. Anderson and A. V. Gold (to be published). The author is indebted to Professor Gold and Professor Anderson for informing him of these results prior to publication.

[8] W. A. Harrison, Rev. Mod. Phys. **36**, 256 (1964).

[9] J. L. Yarnell, J. L. Warren, and S. H. Koenig, *Lattice Dynamics* (Proceedings of the International Conference held at Copenhagen, Denmark, August, 1963), edited by R. F. Wallis (Pergamon Press Ltd., London, 1965), p. 57.

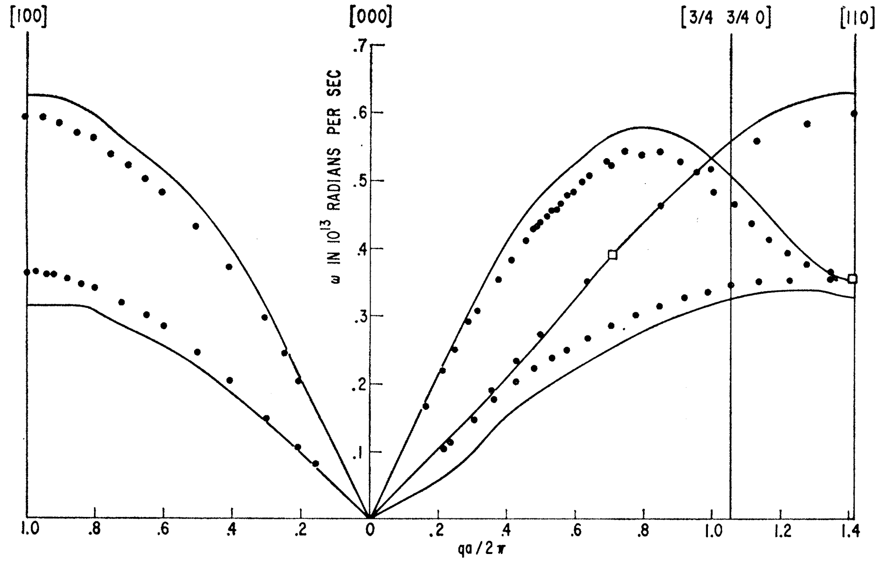

FIG. 4. Curves represent the computed vibration spectrum of aluminum using the model pseudopotential with $\beta=41.4$ Ry a.u.^{3} and $r_c=0.2$ a.u. Experimental points are from Yarnell, Warren, and Koenig (Ref. 9). Points at which the pseudopotential was fit to experiment are indicated by boxes.

The greater degree of success in the case of aluminum than in lead might indicate that in fact spin-orbit coupling may be an important source of error in lead. Comparison of the form factors would indicate that the use of perturbation theory in computing the energies should have comparable validity for both metals.

An additional point should be made concerning the sensitivity of the vibration spectrum to the pseudopotential. In aluminum, the speed of transverse sound propagating in the [100] direction is reduced to about half of that obtained from the electrostatic energy alone. This reflects a cancellation of about three-quarters of the electrostatic energy by band-structure energy. In lead the corresponding reduction in the speed of sound is by a factor of 3 representing even stronger cancellation. We conclude first that the dispersion curves strongly reflect the details of the pseudopotential; we conclude second that the greater cancellation in the case of lead may be an additional cause of difficulty in matching the observed dispersion curves.

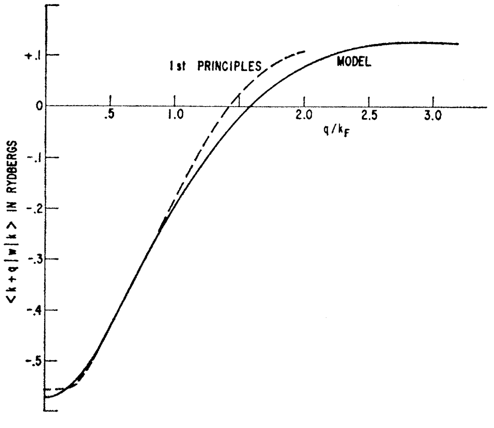

FIG. 5. Form factors for aluminum. The solid line represents the model pseudopotential with $\beta=41.4$ Ry a.u.^{3} and $r_c=0.2$ a.u. The dashed curves represent those computed from first principles (Ref. 4).

IV. THE KOHN EFFECT

We next turn to the remarkable structure, particularly in the lead curves, arising from the Kohn effect.[10] Our earlier opinion[3] was that the observed structure in the dispersion curves did not come from the singularity in the dielectric function at $2k_F$. We based this conclusion first on the fact that the singularity is not visible in the energy-wave number characteristics we computed for zinc (and subsequently for sodium, magnesium, and aluminum). This remains true in our present calculation; Figure 6 shows the $E(q)$ curves for lead and aluminum which we are using here. The initial peaks arise from the vanishing of the structure factor, and nothing in the curves near $q=2k_F$ suggests the singularity which becomes so visible when we compute the dispersion curves in detail. Our second reason for being skeptical of the interpretation of the observed wiggles as Kohn anomalies was the calculation by Woll and Kohn[11] which indicated that the expected irregularities were indeed very small. Their calculations were based upon the electron-phonon interaction given much earlier by Bardeen,[12] which seems to seriously underestimate the matrix element for back scattering. Because of an extreme sensitivity (we will see that it is exponential) of the size of the anomaly upon these matrix elements, they greatly underestimated the size of the effect.

Without making a detailed study of the Kohn effect, a few interesting points can be made. In computing the dispersion curves in second-order perturbation theory,

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[10] W. Kohn, Phys. Rev. Letters **2**, 393 (1959).

[11] E. J. Woll, Jr., and W. Kohn, Phys. Rev. **126**, 1693 (1962).

[12] J. Bardeen, Phys. Rev. **52**, 688 (1937).

we always find the positions of the anomalies at wave numbers arising from the free-electron surface. The true Fermi surface, however, deviates appreciably from the free-electron sphere and the anomalies are therefore displaced. We would only obtain the correct positions if the influence of the pseudopotential were carried to higher order.

The singularity designated by *a* in Fig. 1 represents such a case. A consideration of the topology of the Fermi surface indicates that this anomaly comes from transfer of electrons across the hole in the third-band structure. This transfer is indicated in Fig. 7. Brockhouse *et al.*[13] have associated the irregularity at slightly larger wave number with this transfer and have indicated that the difference in position is consistent with our understanding of the lead Fermi surface.

The singularity in our computed curves designated by *b* in Fig. 1 comes from transfer of electrons right at the zone face, as indicated in Fig. 7. In terms of bands this means transfer of electrons between the third and fourth bands. However, it is believed[14] that there is no Fermi surface in the fourth band and hence it is not surprising that the corresponding Kohn anomaly is suppressed. We have not, however, explored the effects of including Fermi-surface distortions in detail.

The size of the singularity *a* appears to be roughly correct. Other irregularities which we find in our computed curves seem not to be visible on the scale of accuracy of the experiments. It is interesting to look more quantitatively at the size of the singularities. For a downward singularity[11] such as *a* or *b*, there are two points of zero slope and the "size" of the singularity may reasonably be defined as the difference in wave number between these two points. We may estimate that difference.

To do this we must sketch the calculation of vibration frequencies. We assume a periodic displacement of the ions given by

$$\delta\mathbf{r}_j = \mathbf{a}\cos(\mathbf{Q}\cdot\mathbf{r}_j - \omega t).$$

This gives rise to an average kinetic energy per ion of $Ma^2\omega^2/4$, where M is the mass of an ion. It also gives rise to potential energy consisting of an electrostatic energy δE_{es} and a band-structure energy determined from Eq. (2.5). The latter is found to be

$$\delta E_{bs} \approx (Za^2/4)\sum q^2E(q)$$

per ion except for angular factors appearing in the summand. This sum is over all lattice wave numbers $\mathbf{q}_0$ ($\mathbf{q}_0$ is 2π times a reciprocal lattice vector) and satellite points $\mathbf{q}_0 \pm \mathbf{Q}$. The average kinetic and potential energies are set equal and we may solve for the frequency.

$$\omega^2 \approx 4\delta E_{es}/Ma^2 + (Z/M)\sum q^2E(q). \qquad (4.1)$$

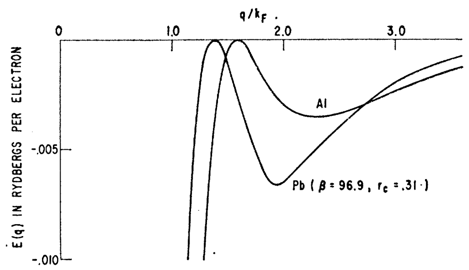

Fig. 6. Energy-wave number characteristics for aluminum and lead computed from the model pseudopotentials. The lead curve represents the high-β model potential.

The Kohn anomaly arises as we vary the phonon wave number $\mathbf{Q}$ and a satellite point $\mathbf{q}_0 \pm \mathbf{Q}$ crosses the value $2k_F$. Here there is a logarithmic singularity in the dispersion curve arising from the corresponding singularity in the $\epsilon(q)$ factors in $E(q)$. Equation (2.4) gives the model form for $E(q)$ and contains the dielectric function twice; the singularity in the $\epsilon(q)$ appearing in the numerator is of more importance since $\epsilon(q)$ is near unity at $q = 2k_F$. We seek the points at which $d\omega/dQ$, or equivalently $d\omega^2/dQ$, is equal to zero and therefore wish to extract the singular term in $d\omega^2/dQ$ which arises from the $\epsilon(q)$ in the numerator of Eq. (2.4). The singular term in $d\epsilon(q)/dq$ may be found by direct differentiation of $\epsilon(q)$[15] near $q = 2k_F$. We find the singular contribution to $d\omega^2/dq$ given by

$$\left.\frac{d\omega^2}{dq}\right|_{\text{sing.}} = \frac{Z}{M}q^2\frac{dE(q)}{dq} = \frac{Z}{M}\frac{q^2E(q)}{\epsilon(q)-1}\frac{d\epsilon}{dq}$$
$$= \frac{Z}{2M}\frac{q^2}{k_F}E(q)\ln\left|1-\frac{q}{2k_F}\right|. \qquad (4.2)$$

The points where $d\omega^2/dq$ will vanish are just those points at which the magnitude of the singular term, Eq. (4.2), is equal to the magnitude of $d\omega^2/dQ$ in the absence of the singularity; we characterize the latter by a speed

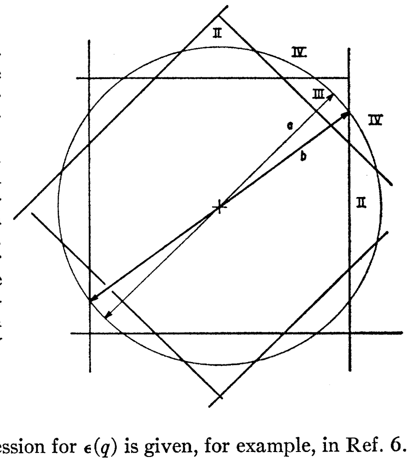

Fig. 7. The free-electron Fermi sphere for lead with Brillouin-zone planes intersecting a (100) plane. Energy-band indices associated with various segments are indicated by Roman numerals. The electron transfer corresponding to the Kohn anomalies indicated by *a* and *b* in Fig. 1 are shown by arrows.

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[13] B. N. Brockhouse, T. Arase, G. Caglioti, K. R. Rao, and A. D. B. Woods, Phys. Rev. **128**, 1099 (1962).

[14] The most recent and thorough discussion of this point is given in Ref. 7.

[15] An explicit expression for $\epsilon(q)$ is given, for example, in Ref. 6.

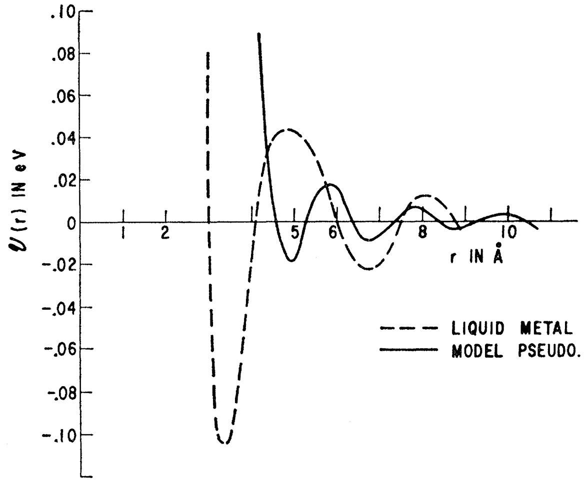

FIG. 8. The effective interaction between ions for lead obtained from the model pseudopotential (high-β) and that obtained from a study of the pair-distribution function for liquid lead by Johnson, Hutchinson, and March (Ref. 16).

of sound.

$$\left.\frac{d\omega^2}{dq}\right|_{\text{nonsing.}}=2\omega v_s.$$

Then the size of the singularity is the distance δq between the two points of vanishing slope.

$$\begin{aligned}\delta q&=4k_F|1-(q/2k_F)|\\&=4k_F\exp(-M\omega v_s/ZE(q)k_F).\end{aligned}\quad(4.3)$$

It should be recalled that angular factors in the summand were dropped which appear in the denominator and can make the exponential much smaller for some modes.

Using numbers appropriate to the anomaly *a* of Fig. 1, $\omega=0.9\times10^{13}$ rad/sec and $v_s=2\times10^5$ cm/sec, we obtain $\delta q=0.004k_F$ or 0.005 on the scale of the abscissa; the angular factors were unity for this case. This appears to be roughly that obtained in the calculation. Note that the corresponding anomaly in Fig. 2 was considerably larger because of the decreased (computed) velocity and frequency.

Perhaps of more significance than the exact size of the anomalies is their extreme sensitivity to, for example, the pseudopotential. A decrease in the matrix element of the pseudopotential at $2k_F$ by 20% reduces the size of the anomaly by a factor of 50.

With such extreme sensitivity of the size of the anomaly upon the pseudopotential, it is difficult to put a meaningful estimate on the size of the singularities in a particular material. We must attribute some of our success in obtaining singularities of the correct size in lead to chance. On the other hand, it is gratifying to see that the observation of singularities in lead should not be regarded as surprising as we initially thought.

V. OTHER PROPERTIES

Once we have obtained the energy-wave number characteristic $E(q)$ for a given metal it is quite straightforward to compute many atomic properties of the metal.[3] We have not carried this very far with our model potential for lead, but have obtained two interesting results.

First, we compared the energies of fcc, bcc, and hcp (with variable axial ratio) structures using the model pseudopotential for lead. We found that both potentials gave hcp as the stable structure instead of the observed fcc. At the same time the model potential for aluminum gave correctly the fcc structure. Exploration of other light metals using reasonable model pseudopotentials has similarly given the wrong structure in most cases, though not in the cases of sodium, magnesium, and aluminum. It remains to be seen whether more accurate pseudopotentials will remedy this situation, but it seems very possible at this point that the approximations inherent in our approach are too severe to reliably predict stable structures and that sodium, magnesium, and aluminum[4] were fortunate choices.

We have also computed the effective ion-ion interaction[2] $V(r)$ for lead using the model potential. This is essentially a sum of the Coulomb interaction between ions and the Fourier transform of $E(q)$. The resulting potential is shown in Fig. 8 along with an effective interaction for lead given by Johnson, Hutchinson, and March[16] which was obtained from the measured pair-distribution function in liquid lead. There are several aspects of the comparison which may be noted. First, the general magnitudes of the potentials we obtain are the same. In contrast, our first calculation of the interaction potential in zinc[3] gave the first minimum deeper by an order of magnitude than those given by Johnson *et al.* This does not reflect any major difference in the magnitudes of energy-wave number characteristics from which the potentials for zinc and lead are derived; but rather differences in the curvatures which are amplified in taking the Fourier transform. It seems very possible at this point that we overestimated the size of the oscillations in the hand calculation for zinc, and more recent machine calculations on other metals have given results of the same general magnitude as those found by Johnson *et al.*

The oscillations of the computed interaction potential at large distances are the Friedel oscillations which reflect the same singularity in the dielectric function which gives rise to the Kohn effect. The fact that the computed magnitudes agree roughly with those found by Johnson *et al.*, is consistent with our computed Kohn anomalies being roughly of the size observed. The period of the computed oscillations is half the Fermi wave length and they decay as $1/r^3$. The curves derived from the liquid should have slightly longer periods

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[16] M. D. Johnson, P. Hutchinson, and N. H. March, Proc. Roy. Soc. (London) **A282**, 283 (1964).

because the density of the liquid is lower and hence the Fermi wave length is larger. However, the periods of the curves of Johnson *et al.* appear to be 50% bigger which is a puzzling result.

Our computed curve does not show a minimum at the near-neighbor distance (3.5 Å) as does the Johnson curve. This minimum is not necessary for the stability of the metal since there are volume-dependent terms in the energy in addition to those included in the interaction potential and that potential itself depends upon the volume. However, such a minimum did occur in our treatment of aluminum[4] using the full nonlocal pseudopotential and is absent in the interaction derived from the model potential for aluminum. We conclude that the behavior of the interaction potential at short distances is not well given by the model potential we have used. Perhaps the appropriate behavior could be obtained, however, without use of a nonlocal potential if a different form were used.

VI. CONCLUSIONS

Our experimentation with a model pseudopotential has met with mixed success. We have found it possible to fit the vibration spectrum reasonably well with two parameters and presumably would do better with more. Furthermore, a pseudopotential is found which looks very much like that obtained by consideration of the electronic properties alone. The fact that the scheme seems to work somewhat better for aluminum than for lead might suggest that spin-orbit coupling plays an important role in lead and cannot be accounted for well with the simple pseudopotential. At the same time, a model potential, at least in the form we have chosen, seems not to duplicate all the results of the nonlocal potential. In particular, the effective interaction between ions is not well given.

The most striking finding is the account which the model in lead gives of the observed Kohn anomalies. This account is not sensitive to the detailed form of the model used but only to the form factor for back scattering. The size of the anomalies found would be much the same had we simply extracted the form factor for back scattering from our previously given form factors or if we had attempted an extrapolation of the form factors obtained by Anderson and Gold from studies of the Fermi surface. The model lends additional support in indicating that these form factors are consistent with the general form of the vibration spectrum.

PHYSICAL REVIEW VOLUME 139, NUMBER 1A 5 JULY 1965

Measurement of the Mössbauer Recoilless Fraction in β-Sn for 1.3 to 370°K*†

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(Received 15 February 1965)

Doppler-shift measurements of Mössbauer recoilless fractions f in β-Sn show discrepancies of the order of 20 to 30% and sometimes bear quoted errors of ±10%. Such discrepancies can be caused by using incorrect values of α, the internal conversion coefficient; τ_m, the mean life of the excited state; Γ_A and Γ_S, the absorber and source linewidths; and B, the nonresonant background present in the detector at the energy of the Mössbauer γ rays. In the present work, the use of a black resonant absorber and the technique x-γ delayed coincidences combine to eliminate dependence on these parameters in first approximation. In particular, the results $f=0.455\pm0.010$ at 77.3°K and $f=0.72\pm0.01$ at 4.2°K are obtained. The errors are systematic, and are due largely to uncertainties in evaluating the residual resonant transmission of the black absorber, the total magnitude of which is about 5% for $T\leq100$°K. For the experimental temperature range of $1.3\leq T\leq370$°K, f values are obtained at over 300 points for two different source samples. The results are as much as 20% higher than some previously reported values, and also do not agree well with the theoretical calculations of DeWames, Wolfram, and Lehman for $T\leq150$°K. On the other hand, when the data are expressed in terms of a Debye temperature Θ derived at each temperature from the Debye formula for f, the Θ values show remarkably little variation with temperature, and fall on a smooth curve. The results at low temperature help to clarify the data of Wiedemann, Kienle, and Pobell in the superconducting region and immediately above.

1. INTRODUCTION

NUMEROUS authors have reported data on the temperature dependence of the recoilless fraction f in the Mössbauer effect. It is naturally of interest to compare these experimental f values to theoretical predictions, since this can be considered as a direct test of various forms of the phonon frequency spectrum. f is given by the relation

$$f=e^{-2W}, \tag{1}$$

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* This work was supported in part by the U. S. Air Force Office of Scientific Research and the National Science Foundation.

† Based in part on a dissertation submitted to Washington University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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