Pressure Effects on the Superconducting Transition Temperature of Pb

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McMillan's theory of the transition temperature of strong-coupling superconductors is extended to allow calculation of pressure effects on T_c from measured shifts in the transverse and longitudinal peaks in the phonon density of states. Using multiple-cutoff Lorentzians as a model for the phonon spectrum, we show that the pressure dependence of α_ν^2, the square of the electron-phonon coupling strength for the phonon mode ν, can be expressed largely in terms of pressure-induced shifts in the phonon peaks and that the remaining dependence can be calculated using pseudopotential theory. The results are evaluated for Pb using pressure data from two different electron-tunneling studies. When the data of Franck and Keeler are applied to the theory, the results are in good agreement with experiment. However, data from the work of Zavaritskii *et al.* yield a value of the pressure dependence of T_c which differs by more than a factor of 2 from that found experimentally. In addition to these results, we have used our pseudopotential calculation to evaluate α_ν^2 and find for Pb $\alpha_t^2=1.28$ meV and $\alpha_l^2=1.36$ meV. These values compare favorably to $\alpha_t^2=1.11$ meV and $\alpha_l^2=1.34$ meV which have been calculated directly from tunneling data by McMillan and Rowell.

I. INTRODUCTION

THE effect of pressure on the superconducting transition temperature has been studied experimentally for a large number of materials.[1] One might hope that the effect could be explained from first principles through direct examination of the self-energy equations of strong-coupling superconductors.[2,3] However, it is generally appreciated that the equations themselves are difficult to solve, and that many trial solutions are required in order to sort out the relative significance of the different properties of the normal state which enter the theory.

The problem of calculating T_c has been approached by McMillan[4] from a semiempirical point of view, and he found that the transition temperature of a strong-coupling superconductor can be approximated in closed form as a relatively simple function of the Coulomb interaction, the electron-phonon coupling strength, and the phonon spectrum. Olsen, Andres, and Geballe[5] have recently shown that McMillan's general results can be used to estimate the pressure dependence of T_c. Their predictions are in qualitative agreement with experiment for a number of non-transition-metal superconductors.

In this paper, we examine in some greater detail the effects of pressure on McMillan's expression for T_c and apply these results to Pb using appropriate models for the phonon spectrum and the electron-phonon interaction. We show that the pressure dependence of α^2, the strength of the electron-phonon interaction, can be expressed largely in terms of pressure-induced shifts in the phonon spectrum, and that the remaining dependence can be evaluated in terms of pseudopotential theory. The pressure dependence of T_c is evaluated for Pb using experimental data for pressure-induced shifts in the transverse and longitudinal peaks of the phonon density of states. We also make use of our pseudopotential calculation to obtain an independent estimate of α^2.

II. THEORY

By fitting to experimental data a theoretically motivated form of an expression for T_c for strong-coupling superconductors, McMillan showed that a wide range of metals and alloys obey the approximate relationship[6]

$$T_c=\frac{\omega_c}{1.73}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right], \tag{1}$$

where ω_c is the upper cutoff frequency (in units of °K) of the phonon density of states, and μ^* is the Morel and Anderson[7] pseudopotential describing Coulomb coupling. λ is a dimensionless electron-phonon coupling constant defined by

$$\lambda=\sum_\nu^3\lambda_\nu=\sum_\nu^3 2\int_0^{\omega_c}\alpha_\nu^2(\omega)F_\nu(\omega)\frac{d\omega}{\omega}, \tag{2}$$

where $\alpha_\nu(\omega)$ is the strength of an average electron-phonon interaction, and $F_\nu(\omega)$ is the phonon density of states for the phonon mode ν.

We adopt the point of view that Eq. (1) is essentially correct and examine the relationship between pressure-induced changes in T_c, ω_c, and λ_ν. Since the same value of $\mu^*=0.1$ is appropriate to all the polyvalent metals,[4] we expect this parameter to be independent of pressure. Taking the logarithmic derivative of Eq. (1) and sub-

[1] M. Levy and J. L. Olsen, in *High Pressure Physics*, edited by by A. Van Itterbeek (North-Holland Publishing Co., Amsterdam, 1965).
[2] V. Ambegaokar and L. Tewordt, Phys. Rev. **134**, A805 (1964).
[3] D. J. Scalapino, Y. Wada, and J. C. Swihart, Phys. Rev. Letters **14**, 102 (1965).
[4] W. L. McMillan, Phys. Rev. **167**, 331 (1968).
[5] J. L. Olsen, K. Andres, and T. H. Geballe, Phys. Letters **26A**, 239 (1968).
[6] This expression differs from Eq. (18) of Ref. 4 in that we have used ω_c in place of Debye θ, this being closer in form to the original theoretical solution [see Eq. (15) of Ref. 4].
[7] P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

stituting this value of μ^*, we find

$$\frac{d\ln T_c}{dP}=\frac{d\ln\omega_c}{dP}+\frac{1.23}{(\lambda-0.11)^2}\sum_\nu^3\frac{d\lambda_\nu}{dP}. \tag{3}$$

To proceed further requires a specific model of the phonon spectrum. Thus, from this point onward we shall restrict our discussion to the case of Pb. We obtain an analytic expression for λ_ν for Pb by assuming the multiple-cutoff Lorentzian model of Scalapino, Schrieffer, and Wilkins[8] for the phonon density of states:

$$F_\nu(\omega)=A_\nu\left[\frac{1}{(\omega-\omega_1{}^\nu)^2+(\omega_2{}^\nu)^2}-\frac{1}{(\omega_2{}^\nu)^2+(\omega_3{}^\nu)^2}\right], \quad |\omega-\omega_1{}^\nu|<\omega_3{}^\nu$$
$$=0, \quad |\omega-\omega_1{}^\nu|>\omega_3{}^\nu \tag{4}$$

where

$$A_\nu=\frac{1}{2}\left[\frac{1}{\omega_2{}^\nu}\arctan\frac{\omega_3{}^\nu}{\omega_2{}^\nu}-\frac{\omega_3{}^\nu}{(\omega_2{}^\nu)^2+(\omega_3{}^\nu)^2}\right]^{-1}$$

normalizes $F_\nu(\omega)$; and $\omega_1{}^t=4.4$ meV, $\omega_2{}^t=0.75$ meV, $\omega_3{}^t=1.5$ meV, $\omega_1{}^l=8.5$ meV, $\omega_2{}^l=0.5$ meV, and $\omega_3{}^l=1.0$ meV have been chosen to approximate the phonon spectrum as determined by inelastic neutron scattering data on Pb.[9] If $\alpha_\nu{}^2$ is assumed to be independent of frequency, then Eq. (2) can be integrated directly,

$$\lambda_\nu=\frac{2\alpha_\nu{}^2A_\nu}{(\omega_1{}^\nu)^2+(\omega_2{}^\nu)^2}\left[2\frac{\omega_1{}^\nu}{\omega_2{}^\nu}\arctan\frac{\omega_3{}^\nu}{\omega_2{}^\nu}-\left(\frac{(\omega_1{}^\nu)^2-(\omega_3{}^\nu)^2}{(\omega_2{}^\nu)^2+(\omega_3{}^\nu)^2}\right)\ln\left(\frac{\omega_1{}^\nu+\omega_3{}^\nu}{\omega_1{}^\nu-\omega_3{}^\nu}\right)\right]. \tag{5}$$

Substituting values of $\alpha_\nu{}^2$ derived from tunneling data[10] ($\alpha_t{}^2=1.11$ meV and $\alpha_l{}^2=1.34$ meV), we find $\lambda_t=0.51$ and $\lambda_l=0.32$. The fact that we obtain $\sum_\nu{}^3\lambda_\nu=1.34$ using the tunneling $\alpha_\nu{}^2$'s and the cutoff Lorentzian model for $F_\nu(\omega)$, as compared to $\lambda=1.33\pm0.02$ calculated from $\alpha^2(\omega)F(\omega)$ derived wholly from tunneling data,[10] is an indication that this phonon model is well suited to our purposes.

To determine the pressure dependence of λ_ν, we make the simplifying assumption that only $\alpha_\nu{}^2$ and the center of the Lorentzian distribution $\omega_1{}^\nu$ are shifted by pressure. Then

$$\frac{d\lambda_\nu}{dP}=\lambda_\nu\frac{d\ln\alpha_\nu{}^2}{dP}+\frac{4\alpha_\nu{}^2A_\nu\omega_1{}^\nu}{(\omega_1{}^\nu)^2+(\omega_2{}^\nu)^2}\times\left[\frac{\omega_3{}^\nu}{(\omega_2{}^\nu)^2+(\omega_3{}^\nu)^2}-\frac{\omega_1{}^\nu}{(\omega_1{}^\nu)^2+(\omega_2{}^\nu)^2}\ln\left(\frac{\omega_1{}^\nu+\omega_3{}^\nu}{\omega_1{}^\nu-\omega_3{}^\nu}\right)-\frac{1}{\omega_2{}^\nu}\left(\frac{(\omega_1{}^\nu)^2-(\omega_2{}^\nu)^2}{(\omega_1{}^\nu)^2+(\omega_2{}^\nu)^2}\right)\arctan\frac{\omega_3{}^\nu}{\omega_2{}^\nu}\right]\frac{d\ln\omega_1{}^\nu}{dP} \tag{6}$$

$$\approx\lambda_\nu\left(\frac{d\ln\alpha_\nu{}^2}{dP}-\frac{d\ln\omega_1{}^\nu}{dP}\right). \tag{7}$$

With the assumed values of $\omega_n{}^\nu$, the approximation made in obtaining Eq. (7) from Eqs. (5) and (6) is accurate to within 3%.

To calculate $d\ln\alpha_\nu{}^2/dP$, we examine the first moment of $\alpha_\nu{}^2(\omega)F_\nu(\omega)$, which can be evaluated in terms of our phonon spectrum model

$$I_\nu\equiv\int_0^\infty\alpha_\nu{}^2(\omega)F_\nu(\omega)\omega d\omega=\alpha_\nu{}^2\omega_1{}^\nu. \tag{8}$$

Therefore,

$$\frac{d\ln\alpha_\nu{}^2}{dP}=\frac{d\ln I_\nu}{dP}-\frac{d\ln\omega_1{}^\nu}{dP}. \tag{9}$$

Our motivation in relating $\alpha_\nu{}^2$ to I_ν is twofold. First, as we shall see below, the pressure dependence of I_ν can be calculated in a reasonably straightforward fashion from pseudopotential theory. Second, from general arguments presented in Sec. V of McMillan's paper, we expect I_ν to be only weakly dependent on pressure, and our calculation in the Appendix bears this out. Thus, since $d\ln\alpha_\nu{}^2/dP$ is determined largely by $d\ln\omega_1{}^\nu/dP$ in Eq. (9), errors introduced by approximations made in our pseudopotential calculation of $d\ln I_\nu/dP$ are of only minor importance to our final result.

Substituting Eqs. (7) and (9) into Eq. (3) gives the main result of this paper

$$\frac{d\ln T_c}{dP}=\frac{d\ln\omega_c}{dP}+\frac{1.23}{(\lambda-0.11)^2}\sum_\nu^3\lambda_\nu\left(\frac{d\ln I_\nu}{dP}-2\frac{d\ln\omega_1{}^\nu}{dP}\right). \tag{10}$$

The least accessible term in this expression is $d\ln I_\nu/dP$. McMillan has noted that I_ν is independent of phonon frequencies and can be expressed in terms of the screened ionic pseudopotential

$$I_\nu=\frac{N(0)}{2M}\int_0^{2k_F}\langle(\boldsymbol{\varepsilon}_{q\nu}\cdot\mathbf{q})^2\rangle_{\rm av}\times|\langle\mathbf{k}_F+\mathbf{q}|w|\mathbf{k}_F\rangle|^2qdq\Big/\int_0^{2k_F}qdq, \tag{11}$$

where $N(0)$ is the electronic density of states per atom

[8] D. J. Scalapino, J. R. Schrieffer, and J. W. Wilkins, Phys. Rev. 148, 263 (1966).
[9] B. N. Brockhouse, T. Arase, G. Caglioti, K. R. Rao, and A. D. B. Woods, Phys. Rev. 128, 1099 (1962).
[10] W. L. McMillan and J. M. Rowell, Phys. Rev. Letters 14, 108 (1965).

TABLE I. Comparison between values of α_ν^2 in meV calculated from experiment and values calculated from various mathematical models.

Phonon mode	Derived from tunneling data[a]	Calculated by SWS[b] using $\beta=60$[c]	This work using $\beta=46.0$	This work using $\beta=60$
Transverse	1.11	1.05	1.28	1.08
Longitudinal	1.34	1.98	1.36	1.49

[a] Reference 10. [b] Reference 3. [c] In units of Ry (a. u. of volume).

at the Fermi surface, M is the ionic mass, k_F is the Fermi wave number, $\epsilon_{q\nu}$ is the phonon polarization unit vector, and $(\epsilon_{q\nu}\cdot\mathbf{q})^2$ is averaged over the angular distribution of $\mathbf{q}$. $\langle\mathbf{k}_F+\mathbf{q}|w|\mathbf{k}_F\rangle$ is the screened electron-ion pseudopotential form factor connecting two points on the Fermi sphere. Calculation of the pressure dependence of I_ν is shown in the Appendix, where we find $d\ln I_t/dP=-0.1\times10^{-6}$ bar^{-1} and $d\ln I_l/dP=1.9\times10^{-6}$ bar^{-1}.

III. RESULTS AND DISCUSSION

The pressure dependence of the phonon density of states in Pb can be obtained from the recent experimental work of Franck and Keeler. Their data are particularly appropriate to this discussion, since they used the same experimental apparatus to measure pressure-induced shifts in both the phonon spectrum[11] and in T_c[12] of Pb films. Thus, any systematic error that may have occurred in their determination of the pressure will cancel in all terms of Eq. (10), except the term $d\ln I_\nu/dP$ which is small to begin with. Franck and Keeler's phonon results are $d\ln\omega^t/dP=(5.3\pm0.7)\times10^{-6}$ bar^{-1} and $d\ln\omega^l/dP=(7.0\pm0.7)\times10^{-6}$ bar^{-1}. As pointed out by these authors,[11] these data imply values of the temperature-dependent Grüneisen parameter which are in excellent agreement with those derived from thermal-expansion and heat-capacity data by White.[13] The term $d\ln\omega_c/dP$ in Eq. (10) is evaluated by assuming that the relative shift in ω_c is given by the relative shift in the longitudinal peak. Equation (10) then predicts a pressure-induced shift in the transition temperature of $d\ln T_c/dP=-5.0\times10^{-6}$ bar^{-1}. This is to be compared to Franck and Keeler's experimental value of $(-4.9\pm0.2)\times10^{-6}$ bar^{-1}. Experimentally determined values of $d\ln T_c/dP$ for bulk Pb are $(-5.27\pm0.10)\times10^{-6}$ bar^{-1} as measured by Garfinkel and Mapother[14] and $(-5.37\pm0.17)\times10^{-6}$ bar^{-1} as measured by Smith and Chu.[15]

More recently, Zavaritskii, Itskevich, and Voronovskii[16] have published additional tunneling data on the pressure dependence of the phonon peaks of Pb. They found $d\ln\omega^t/dP=(10.1\pm1.4)\times10^{-6}$ bar^{-1}, $d\ln\omega^l/dP=(7.05\pm0.7)\times10^{-6}$ bar^{-1}, and $d\ln\omega_c/dP=(7.1\pm1.4)\times10^{-6}$ bar^{-1}. The large discrepancy between their value of $d\ln\omega^t/dP$ and that found by Franck and Keeler is not understood. Furthermore, Zavaritskii's data imply a low-temperature Grüneisen parameter[16] which is larger by a factor of 2 than that calculated from thermal-expansion data.[13,17] Using Zavaritskii's results in Eq. (10), we find $d\ln T_c/dP=-12.9\times10^{-6}$ bar^{-1}, in poor agreement with experiment.

We note that, in addition to its use in evaluating the pressure dependence of T_c, Eq. (8) can be used to obtain an independent theoretical estimate of α_ν^2. For this purpose the "band structure" value[18] of $N(0)$, obtained from the electronic heat-capacity coefficient, is used in the calculation of I_ν in the Appendix. We find $\alpha_t^2=1.28$ meV and $\alpha_l^2=1.36$ meV. These results are to be compared to those calculated[10] from experimental tunneling data noted earlier: $\alpha_t^2=1.11$ meV and $\alpha_l^2=1.34$ meV.

Perhaps it is worthwhile to comment on the differences between our results and previous values of $\alpha_t^2=1.05$ meV and $\alpha_l^2=1.98$ meV calculated by Scalapino, Wada, and Swihart[3] (SWS). These authors also employed the pseudopotential approach, but in a somewhat different scheme in which they calculated $\alpha_\nu^2(\omega)$ as a function of ω. The results quoted are this function evaluated at the frequencies of the respective peaks in the phonon spectrum. A particularly significant difference between the calculations is that SWS used a value of $\beta=60$ Ry (a. u. of volume) in the point-ion model of the bare ion pseudopotential [see Eq. (A7)]. This was determined from early calculations by Harrison[19] of the pseudopotential form factors for Pb. Our value of $\beta=46.0$ Ry (a.u. of volume) was also obtained by Harrison,[20] but by curve fitting to later and more detailed calculations by Animalu and Heine.[21] In order to investigate the sensitivity of our results to this parameter, we recalculated α_ν^2 using $\beta=60$ Ry (a.u. of volume) obtaining $\alpha_t^2=1.08$ meV and $\alpha_l^2=1.49$ meV. The different results are summarized in Table I.

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APPENDIX: PRESSURE DEPENDENCE OF I_ν

We derive here the pressure dependence of I_ν principally from consideration of the ionic pseudopotential.[22]

[11] J. P. Franck and W. J. Keeler, Phys. Letters **25A**, 624 (1967).
[12] J. P. Franck and W. J. Keeler, Phys. Rev. Letters **20**, 379 (1968).
[13] G. K. White, Phil. Mag. **7**, 271 (1962).
[14] M. Garfinkel and D. E. Mapother, Phys. Rev. **122**, 459 (1961).
[15] T. F. Smith and C. W. Chu, Phys. Rev. **159**, 353 (1967).
[16] N. V. Zavaritskii, E. S. Itskevich, and A. N. Voronovskii, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu **7**, 271 (1968) [English transl.: Soviet Phys.—JETP Letters **7**, 211 (1968)].
[17] J. G. Collins and G. K. White, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1964), Vol. 4.
[18] See Sec. IV of Ref. 4 for a discussion of this parameter.
[19] W. A. Harrison, Rev. Mod. Phys. **36**, 256 (1964).
[20] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966), p. 57.
[21] A. O. E. Animalu and V. Heine, Phil. Mag. **12**, 1249 (1965).
[22] In this section we rely heavily on Ref. 20, Chap. 2.

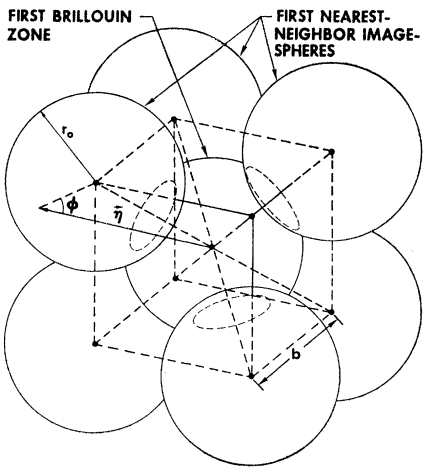

FIG. 1. Model of $\boldsymbol{\eta}$ space showing first Brillouin zone and six of the first nearest-neighbor image spheres.

Since k_F appears as a natural pressure-dependent variable in Eq. (11), we begin by relating $d\ln I_\nu/dP$ to changes in this parameter. Expressing k_F in terms of the volume of a unit cell Ω_0

$$k_F=(3\pi^2Z/\Omega_0)^{1/3}, \tag{A1}$$

we obtain

$$\frac{d\ln I_\nu}{dP}=-\frac{1}{B}\frac{d\ln I_\nu}{d\ln\Omega_0}=\frac{1}{3B}\frac{k_F}{I_\nu}\frac{dI_\nu}{dk_F}, \tag{A2}$$

where B is the bulk modulus. For the purpose of evaluating the pressure dependence of I_ν, we assume that the electronic density of states is given by its free-electron value

$$N(0)=3Zm/2\hbar^2k_F{}^2, \tag{A3}$$

where Z is the valence, and m is the electronic mass. Introducing this approximation and a change of the variable of integration ($\boldsymbol{\eta}=\mathbf{q}/k_F$) into Eq. (11) we obtain

$$I_\nu=\frac{3Zm}{8M\hbar^2}\int_0^2\langle(\boldsymbol{\varepsilon}_{\eta\nu}\cdot\boldsymbol{\eta})^2\rangle_{\rm av}|\langle\mathbf{k}_F+\mathbf{q}|w|\mathbf{k}_F\rangle|^2\eta d\eta. \tag{A4}$$

Within the approximations to be given below, $\langle(\boldsymbol{\varepsilon}_{\kappa\nu}\cdot\boldsymbol{\eta})^2\rangle_{\rm av}$ is purely a geometric factor, independent of the scale of the atomic lattice. We therefore expect

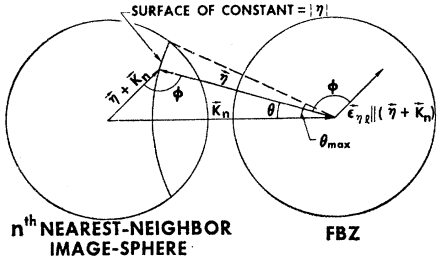

FIG. 2. Relationship between the parameters used in the calculation of $\langle\sin^2\varphi\rangle_{\rm av}$.

$\langle(\boldsymbol{\varepsilon}_{\kappa\nu}\cdot\boldsymbol{\eta})^2\rangle_{\rm av}$ to remain constant under changes in pressure.

To evaluate the pseudopotential contribution to (A4), we assume that the self-consistent screening of the ion by the electron field is carried only to first order, such that the form factor can be written as a simple ratio

$$\langle\mathbf{k}_F+\mathbf{q}|w|\mathbf{k}_F\rangle=\langle\mathbf{k}_F+\mathbf{q}|w_0|\mathbf{k}_F\rangle/\epsilon_q, \tag{A5}$$

where $\langle\mathbf{k}_F+\mathbf{q}|w_0|\mathbf{k}_F\rangle$ is the bare ion pseudopotential, and ϵ_q is the static Hartree dielectric function

$$\epsilon_q=1+\frac{2me^2}{\pi\hbar^2\eta^2k_F}\left(\frac{4-\eta^2}{4\eta}\ln\left|\frac{2+\eta}{2-\eta}\right|+1\right)$$
$$\equiv 1+f(\eta)/k_F. \tag{A6}$$

For the unscreened pseudopotential we use the point-ion model in which the ionic forces are represented by a Coulomb attraction outside a δ-function hard core:

$$\langle\mathbf{k}_F+\mathbf{q}|w_0|\mathbf{k}_F\rangle=\frac{k_F{}^3}{3\pi^2z}\left(\frac{-4\pi Ze^2}{\eta^2k_F{}^2}+\beta\right). \tag{A7}$$

We take the value $\beta=46.0$ Ry (a.u. of volume) for the strength of the core repulsion for Pb. This result was obtained by Harrison by fitting the point-ion model to more detailed calculations of the form factor by Animalu and Heine.[21] From this work Harrison also deduced that β is relatively insensitive to changes in ionic density. We therefore take β to be independent of pressure.

I_ν can now be written explicitly in terms of k_F by using Eqs. (A5)–(A7) in (A4):

$$I_\nu=\frac{mk_F{}^4}{24\pi^4M\hbar^2Z}\int_0^2\frac{(-4\pi e^2/\eta^2+k_F{}^2\beta)^2}{[k_F+f(\eta)]^2}\langle(\boldsymbol{\varepsilon}_{\eta\nu}\cdot\boldsymbol{\eta})^2\rangle_{\rm av}\eta d\eta. \tag{A8}$$

Thus,

$$\frac{dI_\nu}{dk_F}=\frac{mk_F{}^3}{12\pi^4M\hbar^2Z}\int_0^2\frac{[k_F+2f(\eta)](-4\pi Ze^2/\eta^2+k_F{}^2\beta)^2+2k_F{}^2\beta[k_F+f(\eta)](-4\pi Ze^2/\eta^2+k_F{}^2\beta)}{[k_F+f(\eta)]^3}\langle(\boldsymbol{\varepsilon}_{\eta\nu}\cdot\boldsymbol{\eta})^2\rangle_{\rm av}\eta d\eta. \tag{A9}$$

These integrals can be numerically integrated quite easily on a computer if, for every value of $|\boldsymbol{\eta}|$, we are able to evaluate $\langle(\boldsymbol{\varepsilon}_{\eta\nu}\cdot\boldsymbol{\eta})^2\rangle_{\rm av}$. From the orthonormal properties of $\boldsymbol{\varepsilon}_{\eta\nu}$ we note that if φ is the angle between

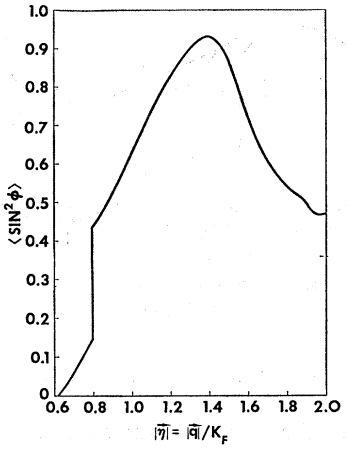

FIG. 3. $\sin^2\varphi$ averaged over the $|\boldsymbol{\eta}|$ = constant surface as a function of $|\boldsymbol{\eta}|$. The contribution from below the discontinuity at $|\boldsymbol{\eta}| = (\frac{1}{2})^{1/3}$ is due to overlap of first nearest-neighbor image spheres into the FBZ. The discontinuity itself is due to a change in normalization upon leaving the FBZ.

$\boldsymbol{\varepsilon}_{\eta l}$ and $\boldsymbol{\eta}$, then

$$\langle(\boldsymbol{\varepsilon}_{\eta l}\cdot\boldsymbol{\eta})^2\rangle_{\rm av}\equiv\tfrac{1}{2}[\langle(\boldsymbol{\varepsilon}_{\eta l_1}\cdot\boldsymbol{\eta})^2\rangle_{\rm av}+\langle(\boldsymbol{\varepsilon}_{\eta l_2}\cdot\boldsymbol{\eta})^2\rangle_{\rm av}]$$
$$=\tfrac{1}{2}\eta^2\langle\sin^2\varphi\rangle_{\rm av}, \qquad \text{(A10)}$$

$$\langle(\boldsymbol{\varepsilon}_{\eta l}\cdot\boldsymbol{\eta})^2\rangle_{\rm av}=\eta^2(1-\langle\sin^2\varphi\rangle_{\rm av}), \qquad \text{(A11)}$$

and our problem is reduced to one of evaluating $\langle\sin^2\varphi\rangle_{\rm av}$.

To calculate $\langle\sin^2\varphi\rangle_{\rm av}$ we make two major simplifications. First, we assume that $\boldsymbol{\varepsilon}_{\eta l}$ lies in a direction parallel to $\boldsymbol{\eta}$ reduced to the first Brillouin zone (FBZ). That is to say that only longitudinal phonons couple to electrons via normal scattering processes. Then φ becomes simply the angle between $\boldsymbol{\eta}$ and $(\boldsymbol{\eta}+\mathbf{K})$, where $\mathbf{K}$ is the reciprocal lattice vector necessary to reduce $\boldsymbol{\eta}$ to the FBZ. Since Pb is a fcc structure in real space, its lattice in reciprocal space is bcc, and $\mathbf{K}$ must be some translation vector of this structure. The length b of one edge of the unit cell in reciprocal space is determined in reduced units by noting that the volume of the cell, which contains four electronic states per atom, is equal to that of the Fermi sea of Pb, which has a valence of $Z=4$. Thus $b=(\frac{4}{3}\pi)^{1/3}$ in units of $q/k_{\rm F}$. As our second approximation, we replace the FBZ by a sphere of equivalent volume in phase space. Since the FBZ occupies half of the unit cell, the radius of this sphere is just $r_0=(\frac{1}{2})^{1/3}$ in reduced units.

These simplifications provide a simple model which determines the mechanics of the calculation. We envision in $\boldsymbol{\eta}$ space a set of slightly overlapping spheres of radius r_0 centered on the lattice points of a bcc lattice as shown in Fig. 1. One of these points is taken as the origin, and the sphere centered on it is the FBZ. All other spheres are labeled as nth nearest-neighbor image-spheres (each is an image of the FBZ translated by the reciprocal lattice vector connecting the origin to its center). For $\boldsymbol{\eta}$ falling within a given image sphere, φ is simply the angle between $\boldsymbol{\eta}$ measured from the origin and $\boldsymbol{\eta}$ measured from the center of that sphere, as shown in Fig. 2.

The average of $\sin^2\varphi$, for some value of $|\boldsymbol{\eta}|$, is taken over those portions of a spherical surface of radius $|\boldsymbol{\eta}|$ which lie within image spheres

$$\langle\sin^2\varphi\rangle_{\rm av}=\frac{\sum_n N_n\int\sin^2\varphi\,d\Omega_n}{\sum_n N_n\int d\Omega_n}, \qquad \text{(A12)}$$

where N_n is the number of nth nearest-neighbor lattice points in the bcc structure, and $d\Omega_n$ is an element of the solid angle bounded by the intersection of the surface of constant $|\boldsymbol{\eta}|$ with an nth nearest-neighbor image sphere. This approximation amounts to counting twice those points in $\boldsymbol{\eta}$ space enclosed by two spheres (the overlap) and neglecting points not enclosed by any sphere.

Using only simple geometric relationships, we find

$$\int\sin^2\varphi\,d\Omega_n$$
$$=2\pi K_n^2\int_0^{\theta_{\max}}\frac{\sin^2\theta\,d\theta}{K_n^2+\eta^2-2K_n\eta\cos\theta}$$
$$=\frac{\pi}{2K_n\eta^2}\Big\{(K_n^2-\eta^2)^2\ln\frac{|K_n-\eta|}{r_0}$$
$$+\tfrac{1}{4}[(K_n+\eta)^2+2(K_n^2+\eta^2)-r_0^2]$$
$$\times[r_0^2-(K_n-\eta)^2]\Big\}, \qquad \text{(A13)}$$

$$\int d\Omega_n=2\pi\int_0^{\theta_{\max}}\sin\theta\,d\theta=\frac{\pi}{2K_n\eta}[r_0^2-(K_n-\eta)^2], \qquad \text{(A14)}$$

where K_n is the length of the nth nearest-neighbor reciprocal lattice vector. Using these forms, $\langle\sin^2\varphi\rangle_{\rm av}$ is readily evaluated, and the results are plotted as a function of $|\boldsymbol{\eta}|$ in Fig. 3.

Equations (A8) and (A9) can now be integrated numerically for substitution into (A2). Using White's value of the bulk modulus ($B=4.88\times10^5$ bar) calculated from elastic-constant data, we find $d\ln I_l/dP=-0.1\times10^{-6}$ bar^{-1} and $d\ln I_l/dP=1.9\times10^{-6}$ bar^{-1}.