Strong-Coupling Effects in the Pressure Dependence of Superconductivity*

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We discuss the effect of hydrostatic pressure on the superconducting properties of the strong-coupling metals Pb and Hg. We solve the Éliashberg gap equations at zero and at finite pressures to obtain the gap Δ_0 in the excitation spectrum at $T=0$ and the critical temperature T_c. The calculations are effected for kernels at zero pressure and repeated with kernels appropriate to a 5% volume decrease. At nonzero pressure the phonon parts of the kernels are rescaled for the upward shift in the phonon frequencies and adjusted for changes in the electron-ion pseudopotential form factor. It is found that Δ_0 and T_c do not scale in the same way under pressure. The gap is relatively more affected, so that the ratio $2\Delta_0/k_BT_c$ tends towards the BCS weak-coupling limit of 3.52 with decreasing volume and, hence, decreasing electron-phonon interaction. In Pb, our results are in good agreement with experiment for both the change in T_c and in the ratio $2\Delta_0/k_BT_c$. In Hg, no experimental results exist at the moment, but we predict similar strong-coupling effects.

I. INTRODUCTION

WHEN the volume of a metal is reduced by application of hydrostatic pressure, the phonon spectrum shifts upwards to higher frequencies as a result of a general stiffening of the lattice. The macroscopic Grüneisen parameters give an indication of the extent of this upward shift. In superconductors it is also observed that associated with the application of pressure there is a considerable decrease in the critical temperature T_c.[1] This indicates a weakening of the electron-phonon interaction with decreasing volume. Interesting systems in this respect are Pb and Hg which exhibit important non-BCS behavior in many of their properties[2] at zero pressure ($P=0$). This is associated with a particularly strong electron-phonon interaction. A convenient measure of the strength of this interaction, as related to superconductivity, appears to be the ratio of the energy gap Δ_0 as measured by tunneling to the critical temperature T_c.[3] BCS theory predicts a value of

$$2\Delta_0/k_BT_c=3.52 \quad (k_B\equiv\text{Boltzmann's constant})$$

which holds well in the weak-coupling limit. For Pb and Hg, this ratio is considerably higher and approximately equal to 4.3 and 4.6, respectively.

Since the actual size of the ratio $2\Delta_0/k_BT_c$ can be taken as a rough measure of the strength of the electron-phonon interaction and since this interaction is reduced on application of hydrostatic pressure, one would expect it to decrease towards 3.52 with decreasing volume. This implies that the gap and T_c will not scale in the same way under stress. The gap must decrease faster than T_c. This effect has been observed experimentally by Franck and Keeler[4] in Pb. From measurements with pressures P up to approximately $3\frac{1}{2}$ kbar they conclude that

$$d\ln\Delta_0/d\ln T_c\cong 2.06.$$

In this paper we show that this strong coupling effect can be understood quantitatively within the Éliashberg[5] formulation of pairing theory. We numerically solve the gap equations at zero and finite temperatures to get Δ_0 and T_c, respectively. The kernels in the Éliashberg gap equations are the phonon-mediated frequency-dependent part $\alpha^2(\omega)F(\omega)$ and the Coulomb repulsions U_c. The repulsive Coulomb part is insensitive to pressure and easily handled. The phonon part is of greater interest. For zero pressure, it is known from inversion of tunneling data.[6] Recently, it has also been possible to calculate it from fundamentals[7,8] from the measured phonon dispersion curves and pseudopotential theory. While the latest calculations of $\alpha^2(\omega)F(\omega)$ in Pb by Carbotte and Dynes[7] are more sophisticated and precise than the earlier work of Swihart, Scalapino and Wada,[9] they still cannot be considered as accurate as the tunneling-derived results. In such first-principle calculations, some model for the lattice dynamics is needed. Carbotte and Dynes take this from a Born–von Kármán force-constant model derived from the measured phonons by inelastic neutron scattering. In Pb, the dispersion curves are highly structured and a convergent force-constant system is difficult to achieve.[10] Nevertheless, such approximate models are useful. They specify completely (if only approximately) the lattice dynamics and in conjunction with pseudopotential theory for the strength of the electron-ion interaction can predict gap values quite close to the

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[2] D. J. Scalapino, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, Inc., New York, 1969).
[3] W. L. McMillan and J. M. Rowell, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, Inc., New York, 1969).
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[7] J. P. Carbotte and R. C. Dynes, Phys. Rev. **172**, 476 (1968).
[8] R. C. Dynes, J. P. Carbotte, D. W. Taylor, and C. K. Campbell, Phys. Rev. **178**, 713 (1969).
[9] J. C. Swihart, D. J. Scalapino, and Y. Wada, Phys. Rev. Letters **14**, 106 (1965).
[10] R. C. Dynes, J. P. Carbotte, and E. J. Woll, Jr., Solid State Commun. **6**, 101 (1968).

observed ones.[7,8] Thus at finite pressure similar calculations can be performed with some confidence using a rescreened pseudopotential form factor and shifted phonons.

To our knowledge, no extensive data on phonons under pressure are at present available from inelastic neutron scattering. In the absence of this information we shift all phonon frequencies upwards by the same proportion as indicated by the average Grüneisen γ. This procedure is simple but not exact as shown by the tunneling experiments of Franck and Keeler.[11] They find that the average γ in the transverse peak of $\alpha^2(\omega)F(\omega)$ is smaller than that for the main longitudinal peak. Strictly speaking, these results apply only at the relatively low pressures used by Franck and Keeler. It is not obvious that they should remain valid at the pressures that are of interest here—5% volume changes. In any case, by direct calculation we find that such details do not appear to be important in the present context. At worst, one can consider our calculations as representing a model case, similar but perhaps not quite identical to Pb.

From the phonons at finite pressure P and the pseudopotential form factor rescreened to account for the volume decrease we can repeat the calculations of Carbotte and Dynes to get $\alpha^2(\omega)F(\omega)$ at finite P. From these calculations it is found that pseudopotential changes are much less important in Pb than the shifts in the phonon spectrum. Also, changes in the pseudopotential can be included with very little error by a simple multiplicative factor. The size of this factor is determined solely from the form factor, i.e., independent of the lattice dynamics. In simple physical terms this arises because the shape of $\alpha^2(\omega)F(\omega)$ at finite P is to a large extent dominated by that at $P=0$. Further, within the approximation of a uniform shift the changes in the phonons lead to a simple stretching on the frequency axis accompanied by a compression on the vertical axis. These observations are important since they make it possible to go directly from $\alpha^2(\omega)F(\omega)$ at zero pressure to a good estimate of its value at finite P. We can then use tunneling-derived results rather than those obtained from the neutron data. In Pb we have already mentioned that the tunneling $\alpha^2(\omega)F(\omega)$ is likely to be the more accurate. For Hg this is the only source of information on the phonons.

So far we have chosen to emphasize mainly the strong coupling aspects of our calculations. We are, however, at the same time making fundamental calculations of the effect of pressure on T_c.[12] This subject has received much attention in the literature. Recent references are, among others, the paper of Olsen, Andres, and Geballe,[13] of Seiden,[14] and of Hodder.[15] Of these the work of Hodder is perhaps the most closely related to the present discussion[1] McMillan[16] has solved the finite-temperature gap equations for a niobiumlike spectrum with variable coupling strength and frequency range. He then fits an approximate formula for T_c to his numerical solutions. The final form of the formula involves a phonon cutoff ω_c, the Coulomb part U_c, and a constant λ related to the phonon renormalization of the electronic effective mass. Hodder uses the McMillan formula and calculates the effect of pressure on λ from the approximate phonon density of state originally employed by Schrieffer, Scalapino, and Wilkins.[17] Since he does not explicitly solve the gap equations he is unable to discuss separately the gap Δ_0 and T_c as we do. Even for T_c, our work represents a refinement of Hodder's since we avoid any uncertainty there may be associated with the use of McMillan's approximate formula and with the two-Lorentzian form for the phonon spectrum.

In Sec. II the kernels of the Éliashberg gap equations are specified. It is shown how the phonon-mediated part of these kernels can be calculated from the neutron data on the phonons and from the electron-ion pseudopotential form factor. The effect of pressure on these kernels is also discussed. In Sec. III we develop rules for rescaling the zero-pressure results for $\alpha^2(\omega)F(\omega)$, so as to obtain its value at finite pressure. These rules evolve naturally from our calculations of $\alpha^2(\omega)F(\omega)$ from phonon-dispersion curves. Section IV is concerned with the results obtained and discussion. In Sec. V we draw conclusions.

II. KERNELS

The Éliashberg[5] gap equations for superconductivity have been drived in many papers[18] and solved numerically both at finite[9,16] and zero temperature.[3,17] They are now standard and there is no need to write them down; what is involved are two nonlinear coupled integral equations for a frequency-dependent gap function $\Delta(\omega)$ and a renormalization factor $Z(\omega)$. At zero temperature the solution to $\Delta(\Delta_0)=\Delta_0$ with Δ_0 real gives the gap (Δ_0) in the quasiparticle excitation spectrum as measured for instance in a tunneling experiment. The zero-frequency limit of $Z(\omega)$ gives the phonon renormalization of the electronic effective mass at the Fermi surface (FS). At finite temperature the interpretation is no less direct. For details the reader is referred to the recent reviews of Scalapino[2] and of Ambegaokar[19] where the present state of strong coupling

[11] J. P. Franck and W. J. Keeler, Phys. Letters **25A**, 624 (1967).
[12] P. N. Trofimenkoff and J. P. Carbotte, Solid State Commun. **7**, 661 (1969).
[13] J. L. Olsen, K. Andres, and T. H. Geballe, Phys. Letters **26A**, 239 (1968).
[14] P. E. Seiden, Phys. Rev. **179**, 458 (1969).
[15] R. E. Hodder, Phys. Rev. **180**, 530 (1969).
[16] W. L. McMillan, Phys. Rev. **167**, 331 (1968).
[17] J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters **10**, 336 (1963).
[18] J. R. Schrieffer, *Theory of Superconductivity* (W. A. Benjamin, Inc., New York, 1964).
[19] V. Ambegaokar, in *Many-Body Physics*, edited by C. DeWitt and R. Balian (Gordon and Breach, Science Publishers, Inc., New York, 1968).

theory is amply described. Of greatest interest to us here are the kernels in the gap equations. They involve a number $N(0)U_c$ characteristic of the basic Coulomb repulsions between electron pairs at the Fermi surface and the frequency-dependent product function $\alpha^2(\omega)F(\omega)$ describing the phonon-mediated part of the pairing interaction. Approximate formulas for $N(0)U_c$ are known. It can be written as

$$N(0)U_c=\frac{N(0)V_c}{1+N(0)V_c\ln(E_F/\omega_c)}, \tag{1}$$

where $N(0)$ is the single spin density of electron states at the FS and V_c is the FS average of the screened Coulomb potential. The argument of the logarithm in (1) is the ratio of the Fermi energy E_F to a phonon cutoff ω_c usually taken to be of the order of five times the maximum phonon energy. In the Fermi-Thomas approximation,

$$N(0)V_c=\frac{k_s^2}{8k_F^2}\ln\left(\frac{k_s^2+4k_F^2}{k_s^2}\right), \tag{2}$$

where k_s is the Fermi-Thomas screening parameter. It is straightforward from (1) and (2) to verify that $N(0)U_c$ varies, under volume change, more slowly than $1/k_F$. This variation is of no consequence for our calculations. While formula (1) is not exact, we can assume that it gives a reliable measure of the pressure variation of this parameter which we can then take as constant.

The phonon part of the kernels can be written as

$$\alpha^2(\omega)F(\omega)=\sum_\lambda\int_{s_F}d^2p\int_{s_{F'}}d^2p'\frac{|g_{\mathbf{p},\mathbf{p}';\lambda}|^2}{(2\pi)^3v_F}\times\delta[\omega-\omega(\mathbf{p}-\mathbf{p}',\lambda)]\Big/\int_{s_F}d^2p, \tag{3}$$

where v_F is the Fermi velocity. The two integrals over $\mathbf{p}$ and $\mathbf{p}'$ are to be performed on the FS. They describe all scatterings of electrons from an arbitrary initial state $|\mathbf{p}\rangle$ to a final state $|\mathbf{p}'\rangle$. The scattering with momentum transfer $\mathbf{p}-\mathbf{p}'$ is through the phonon field and $g_{p,p';\lambda}$ is the electron-phonon coupling constant. The index λ denotes the polarization branch—one longitudinal and two transverse. The phonon frequency $\omega(\mathbf{p}-\mathbf{p}';\lambda)$ corresponds to the mode in the first Brillouin zone (FBZ) which is defined by the reduced part of $\mathbf{p}-\mathbf{p}'$. In general, umklapp processes are involved.

Using pseudopotential theory[7] for the electron-ion interaction the coupling $g_{\mathbf{p},\mathbf{p}';\lambda}$ can be related to the electron-ion form factor $\langle\mathbf{p}'|\omega|\mathbf{p}\rangle$ for scattering from $|\mathbf{p}\rangle$ to $|\mathbf{p}'\rangle$ on the FS. It is

$$g_{\mathbf{p},\mathbf{p}';\lambda}=-i[2\omega(\mathbf{p}-\mathbf{p}';\lambda)MN]^{-1/2}\times(\mathbf{p}-\mathbf{p}')\cdot\boldsymbol{\varepsilon}(\mathbf{p}-\mathbf{p}';\lambda)\langle\mathbf{p}'|w|\mathbf{p}\rangle, \tag{4}$$

where M is the ion mass, N is the number of ions per unit volume and $\boldsymbol{\varepsilon}(\mathbf{p}-\mathbf{p}',\lambda)$ is the polarization vector associated with the phonon frequency $\omega(\mathbf{p}-\mathbf{p}';\lambda)$. The pseudopotential form factor is as described by Harrison.[20]

A considerable simplification results if we assume the FS to be spherical and take $\langle\mathbf{p}'|w|\mathbf{p}\rangle$ to depend only on the momentum transfer $\mathbf{p}-\mathbf{p}'$ (local approximation).[20] The two surface integrals in (3) reduce to a three-dimensional integral over $\mathbf{q}\equiv\mathbf{p}-\mathbf{p}'$, and we can write

$$\alpha^2(\omega)F(\omega)=\frac{1}{N}\sum_\lambda\int_{<2k_F}\frac{d^3q}{(2\pi)^3}L_\lambda(\mathbf{q})\delta[\omega-\omega(\mathbf{q};\lambda)], \tag{5}$$

with the integral over q extending throughout a sphere of radius $2k_F$ and $L_\lambda(\mathbf{q})$ given by

$$L_\lambda(\mathbf{q})=\frac{1}{4}\frac{m}{M}\frac{|\mathbf{q}\cdot\epsilon(\mathbf{q};\lambda)|^2}{k_Fq\omega(\mathbf{q};\lambda)}|w(\mathbf{q})|^2, \tag{6}$$

where $w(\mathbf{q})$ is the local pseudopotential form factor.

Carbotte and Dynes have recently evaluated Eq. (5) directly from the lattice dynamics in some simple metals and used the resulting $\alpha^2(\omega)F(\omega)$ to discuss superconducting properties with some success. Since then the work has been extended to the Tl-Pb-Bi alloy series by Dynes, Carbotte, Taylor, and Campbell[8] giving added confidence in the method. The pseudopotential form factor can be taken from the work of Heine and Abarenkov.[21] The phonons are measured by the inelastic neutron scattering technique. Select phonon frequencies are determined usually in the high-symmetry directions. The experimental dispersion curves are analyzed on the basis of a Born–von Kármán force-constant model. For a specific number of nearest-neighbor shells the spring constants between ions are adjusted to get the best possible least-squares fit to the neutron data. The system of force constants so obtained specifies equally well the dynamical matrix at any point in the FBZ. The renormalized phonon frequencies and polarization vectors at q are simply the eigenvalues and eigenvectors of the dynamical matrix at q. Gilat and Raubenheimer[22] have developed sampling techniques and computer programs that can generate an accurate frequency distribution from the force constants. By repeated diagonalization of the dynamical matrix they can calculate quite accurately the function

$$F(\omega)=\frac{1}{N}\sum_\lambda\int\frac{d^3q}{(2\pi)^3}\delta(\omega-\omega(\mathbf{q},\lambda)), \tag{7}$$

with q extending over the FBZ. Carbotte and Dynes

[20] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).
[21] V. Heine and I. Abarenkov, Phil. Mag. **9**, 451 (1964).
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have generalized this program to calculate instead $\alpha^2(\omega)F(\omega)$. Besides the force constants, the only additional input is $w(\mathbf{q})$ for q in the range 0 to $2k_F$. We want to repeat these calculations for metals under pressure.

III. EFFECT OF PRESSURE ON $\alpha^2(\omega)F(\omega)$

To our knowledge no extensive inelastic neutron scattering data exist for metals under hydrostatic pressure. Some indirect information is always available from the Grüneisen constant for the material. These are related to the shifts in the long-wavelength part of the dispersion curves. In Pb, superconducting tunneling provides additional information. Franck and Keeler[11] quote average γ's for both the main transverse and longitudinal peaks in the lead-phonon spectrum. For the low-energy peak they find $\gamma_T=2.6$, in good agreement with the usual Grüneisen γ and a value of $\gamma_L=3.4$ for the high-energy longitudinal peak. These results are obtained with the application of relatively modest pressures and may not apply directly to a 5% volume change which we consider. To begin, we use a constant frequency independent Grüneisen γ. Later we return to the more complicated shifting suggested by Franck and Keeler's work.

We can proceed in two ways. We can take the neutron results of Brockhouse *et al.*[10] for the phonons at atmospheric pressure and rescale them with an average γ to obtain dispersion curves appropriate to a 5% volume decrease. A Born–von Kármán force-constant fit can be made to these new curves and used as inputs to the computer program of Carbotte and Dynes. The phonon-dispersion curves in Pb are, however, very structured and show distinct Kohn kinks, so that they are difficult to fit accurately with a limited number of nearest-neighbor shells. Uncertainties in the spring-constant system then become important and the method is less good. For this reason and also for simplicity it is better to use the atmospheric value of the force constants, calculate the phonons, and rescale the frequencies internally. This ignores all changes in the polarization vectors under pressure. This is not likely to be an important limitation. Detailed scans of the FBZ show that in cubic systems the polarization vectors are very nearly completely transverse or completely longitudinal everywhere in the zone. They are not likely to be altered provided the symmetry is not changed, i.e., a phase transition to a new crystal structure does not occur.

The pseudopotential form factor also is affected by volume compressions. It can be written as a bare form factor $v^0(\mathbf{q})$—characteristic of the ion core and taken approximately independent of energy—which must then be screened because of the conduction electrons. Assuming $v^0(\mathbf{q})$ to be a weak perturbation, we can screen in linear-response theory and get

$$w(\mathbf{q})=v^0(\mathbf{q})/\epsilon(\mathbf{q})\Omega^0, \tag{8}$$

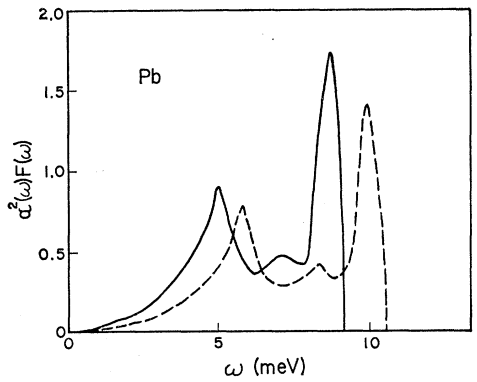

FIG. 1. $\alpha^2(\omega)F(\omega)$ in Pb calculated for volume changes of 0% (solid) and 5% (dashed).

where $\epsilon(\mathbf{q})$ is the dielectric function for the electron gas and Ω^0 the volume per ion. Under pressure $v^0(\mathbf{q})$ is unaffected and only Ω^0 and the dielectric function $\epsilon(\mathbf{q})$ is affected. But these are determined only from the electron gas density, i.e., k_F value. This change is easily incorporated.

In Fig. 1 we compare $\alpha^2(\omega)F(\omega)$ for a volume decrease of 5% with the zero-pressure results of Carbotte and Dynes. The average Grüneisen γ used was 2.85 and the pseudopotential was the Heine-Abarenkov form tabulated in Harrison properly rescreened according to (8). We note the shift to higher frequencies and the general lowering of $\alpha^2(\omega)F(\omega)$ on the vertical scale. Both these effects tend to reduce the effectiveness of $\alpha^2(\omega)F(\omega)$ in causing superconductivity. The decrease on the vertical axis can be traced in part to the frequency factor in the denominator of (6). Changes in the pseudopotential form factor have the opposite effect. They tend to shift the curve up a little without appreciably changing its over-all shape. These changes are, however, much smaller than the corresponding changes due to the phonons. Careful comparison of the two distributions in Fig. 1 in fact, shows that for all practical purposes one can be obtained from the other by a simple rescaling of the two axes. This can be understood quite readily from Eqs. (5) and (6). It is convenient to think of all momenta as measured in units of $2\pi/a$ where a is the lattice parameter. No change then occurs under pressure except for the pseudopotential and the frequency denominator in (6) as well as the phonon frequency in the δ function of (5). The pseudopotential change is as we have already discussed not large and for the moment can be left out. For a given relative volume change $-\Delta V/V$, $\omega(\mathbf{q};\lambda)$ gets multiplied by β given by

$$\beta=1-(\Delta V/V)\gamma,$$

and noting that

$$\delta[\beta\omega-\beta\omega(\mathbf{q};\lambda)]=(1/\beta)\delta[\omega-\omega(\mathbf{q};\lambda)],$$

we conclude that $\alpha^2(\omega)F(\omega)$ at finite P is related to its

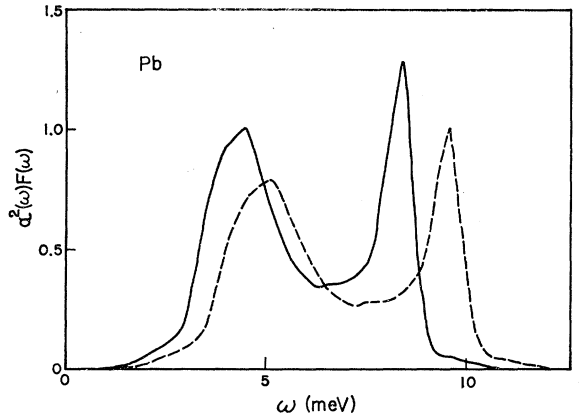

FIG. 2. Solid curve is $\alpha^2(\omega)F(\omega)$ in Pb (after McMillan and Rowell, Ref. 3). The dashed curve is the McMillan-Rowell curve rescaled to correspond to a 5% volume decrease.

value at $P=0$ by

$$\alpha^2(\beta\omega)F(\beta\omega)=(1/\beta^2)\alpha_0^2(\omega)F_0(\omega). \tag{9}$$

To include, at least approximately, the small pseudopotential changes we can follow the procedure of McMillan.[16] We note that the first moment of $\alpha^2(\omega)F(\omega)$ is independent of the lattice dynamics and determined completely by the pseudopotential form factor

$$\int_0^\infty \omega\alpha^2(\omega)F(\omega)d\omega\alpha\int_0^{2k_F}\frac{1}{k_FN}|w(\mathbf{q})|^2q^3dq, \tag{10}$$

which is obtained directly from (5) and (6) using the closure relation on the polarization vectors

$$\sum_\lambda \epsilon_\alpha(\mathbf{q};\lambda)\epsilon_\beta^*(\mathbf{q};\lambda)=\delta_{\alpha\beta}. \tag{11}$$

Since, as we have already stated, the main effect on $\alpha^2(\omega)F(\omega)$ of pseudopotential shifts is to multiply it by some small factor rather than change its shape, we can account for the effect by simply multiplying (9) by a further constant factor B defined by the ratio

$$B=\left[\int_0^{2k_F}|w(\mathbf{q})|^2q^3dq\right]_{(\Delta V/V=5\%)}\Bigg/\left[\int_0^{2k_F}|w(\mathbf{q})|^2q^3dq\right]_{(P=0)}. \tag{12}$$

Thus, we are lead to the approximate relation

$$\alpha^2(\beta\omega)F(\beta\omega)=(B/\beta^2)\alpha_0^2(\omega)F_0(\omega). \tag{13}$$

As implied this relation appears to be almost exact.

Formula (13) is important here not only because of its simplicity but also because it allows us to go quite directly from the zero-pressure tunneling derived value of $\alpha_0^2(\omega)F_0(\omega)$ to a good estimate of its value at finite P. The value of β can be worked out from the Grüneisen constant and B is easily calculated from Harrison's tabulation of the Heine-Abarenkov pseudopotential which must further be rescreened at finite P. In Hg, only tunneling results exist on the phonons. In Pb the Born–von Kármán force-constant model with a practical number of force constants does not give a very good representation[10] of the frequency distribution,[7] and tunneling derived results are at the moment thought to be more accurate, although they do not lead to very different gap values. Finally, we note that Eq. (13) is easily generalized to account for a different shift of the phonons in the longitudinal and transverse peaks of Fig. 1.

IV. RESULTS AND DISCUSSION

First we solve the zero-temperature Éliashberg gap equations to determine the gap Δ_0 in the ground-state excitation spectrum as measured for instance in a tunneling experiment or in optical absorption. For the $P=0$ spectrum of Fig. 1 we adjusted the Coulomb part $N(0)U_c$ so as to reproduce the measured gap

$$\Delta_0=1.35\text{ meV}.$$

This should remove much of the uncertainty in U_c even at finite pressure. We expect no important change in this quantity for a 5% volume change and keep it constant. For the shifted spectrum of Fig. 1, we obtain a gap value of

$$(\Delta_0)_{5\%}=1.01\text{ meV}.$$

These numbers are mainly for reference. We want next to compare them with the equivalent results obtained by rescaling the McMillan-Rowell "inversion" value for $\alpha^2(\omega)F(\omega)$ at $P=0$ according to prescription (13). We expect this form to be somewhat better.

For a 5% volume change we find, by direct evaluation of the right-hand side in (12) from the tables in Harrison of the Heine-Abarenkov form factors, a value $B=1.035$. This is less than a 4% change. In contrast, for a average Grüneisen $\gamma=2.85$, the multiplicative factor β shifting the phonons is $\beta=1.143$, considerably more important. From this information and the value at $P=0$ of $\alpha_0^2(\omega)F_0(\omega)$ given by McMillan and Rowell we have con-

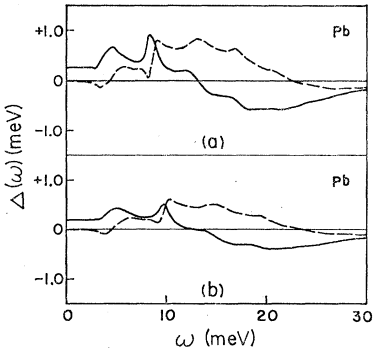

FIG. 3. (a) $\Delta_1(\omega)$ (solid) and $\Delta_2(\omega)$ (dashed) for $P=0$ and T near T_c in Pb. (b) $\Delta_1(\omega)$ (solid) and $\Delta_2(\omega)$ (dashed) for a 5% volume decrease and T near T_c in Pb.

structed Fig. 2, in which we compare the zero-pressure results with those for a 5% volume decrease. We have calculated the zero-temperature gap for both these spectrum using the suggested value of 0.13 for the Coulomb part $N(0)U_c$. For $P=0$, we obtained

$$\Delta_0=1.346 \text{ meV},$$

which is a good check on our computations. At 5% volume decrease it is

$$(\Delta_0)_{5\%}=1.04 \text{ meV},$$

which compares favorably with the value obtained using the Carbotte-Dynes spectrum. We expect, however, the Rowell-McMillan spectrum to be more accurate than the neutron derived one so that we prefer it in all further work. Our first-principle calculations have served mainly to establish the validity of our Eq. (13).

It is important to compare our Fig. 2 with the recent work of Franck, Keeler, and Wu.[23] They have inverted tunneling data obtained at a pressure of 3445 bar to recover the phonon part $\alpha^2(\omega)F(\omega)$ at that pressure. Their zero-pressure inversion is in good agreement with our Fig. 2. At finite pressure, the comparison is not so direct and unambiguous. A pressure of 3445 bar induces much more modest shifts than a 5% volume change. On the frequency scale the same general shift to higher frequencies is observed although, as previously discussed, tunneling results give more shift in the longitudinal peak at 8–9 meV than in the transverse peak at 4–5 meV. We have used the same average Grüneisen γ throughout with value slightly larger than Franck and Keeler's γ_T and less than their γ_L. More significant are the changes on the vertical scale. We find a definite decrease with increasing pressure by an amount $\sim B/\beta^2$. It is difficult to say whether or not this is observed in the tunneling results. The van Hove singularity observed on top the main transverse part of the spectrum does not appear to show this decrease. It is such a sharp peak, however, that such a statement is not very meaningful. The same inconclusive situation is found when considering the logitudinal peak maximum. On the other hand, the minimum between the two main peaks in the spectrum does show a trend towards lower values. The evidence is, however, not conclusive.

Before discussing our finite-temperature work and results, we want to make one more point. It is easy to modify our Eq. (13) to account for a different shift of the transverse phonons than of the longitudinal ones. We have actually done such a calculation using the data of Franck and Keeler ($\gamma_T=2.6$, $\gamma_L=3.4$) and found that the resulting gap value is not significantly different from that obtained from an average shift with $\gamma=2.85$. This indicates that our rescaling procedure,

[23] J. P. Franck, W. J. Keeler, and T. M. Wu, Solid State Commun. 7, 483 (1969).

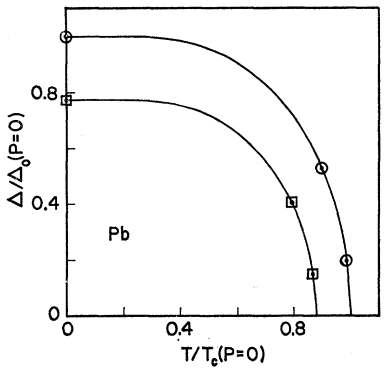

FIG. 4. Variation of the gap with temperature in Pb. The curves are BCS; the points are our calculations for volume charges of 0% (circled) and 5% (boxed).

while not exact in detail, is nevertheless adequate for the present work.

To get critical temperatures T_c we solve the finite-temperature version of the gap equations. The frequency- and temperature-dependent gap $\Delta(\omega,T)$ is obtained by iteration of the basic equations. The temperature dependence of the "gap edge" is obtained from

$$\Delta_0(T)=\mathrm{Re}\Delta(\Delta_0(T),T)$$

for two temperatures below T_c but sufficiently close to it that $\Delta_0(T)$ is a rapidly decreasing function of temperature in this region and so that one can easily extrapolate from these two points to get the temperature at which it vanishes. This gives the critical temperature. This method was previously employed by Scalapino, Wada, and Swihart[24] and by Wu.[25]

A solution for the real and imaginary part of the gap

$$\Delta(\omega,T)=\Delta_1(\omega,T)+i\Delta_2(\omega,T)$$

is shown as a function of frequency in Fig. 3(a). The plot is for a temperature near T_c and for $P=0$. It compares well with a similar figure given by Scalapino, Wada, and Swihart.[24] In Fig. 4 we show the temperature variation of the gap $\Delta_0(T)$. The two points near T_c are those obtained by solution of the gap equations as is the point at zero temperature. The solid curve is a BCS form for $\Delta_0(T)$. It can be used to help us extrapolate our numerical data to the $\Delta_0(T_c)=0$ situation and hence obtain T_c. Our last point on the curve is sufficiently close to the critical temperature that an extrapolation is hardly needed. For the McMillan-Rowell spectrum we obtain at $P=0$ a ratio

$$2\Delta_0/k_BT_c=4.27,$$

which is in close agreement with the measured value of 4.3. This is, however, not new and can be considered as a check on our numerical work.

[24] D. J. Scalapino, Y. Wada, and J. C. Swihart, Phys. Rev. Letters 14, 102 (1965).

[25] T. M. Wu, Phys. Rev. Letters 19, 508 (1967).

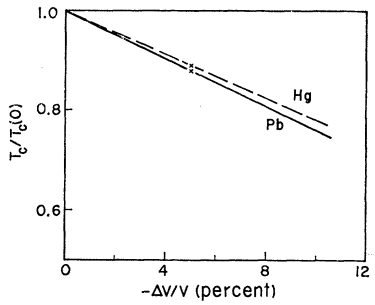

FIG. 5. Variation of the critical temperature with volume change in Pb and Hg. The solid line is the experimental results of Smith and Chu, Ref. 1, in Pb.

For comparison we have plotted in Fig. 3(b) $\Delta_1(\omega,T)$ and $\Delta_2(\omega,T)$ as a function of frequency for a volume change of 5% and a temperature near T_c. We see that the shift in $\alpha^2(\omega)F(\omega)$ is faithfully reproduced in the solutions of the gap equations. In Fig. 4 we show the temperature variation of $\Delta_0(T)$ derived from such solutions. We note that a BCS temperature variation fits well to our limited data. At 5% volume decrease the BCS ratio is

$$(2\Delta_0/k_BT_c)_{5\%}=3.75,$$

which is much closer than the $P=0$ result to the weak coupling limit of 3.52.

The gap Δ_0 and T_c scale differently under pressure so that the BCS ratio decreases towards the weak coupling value. To compare with the experimental results of Franck and Keeler[4] it is interesting to work out from our data the value of

$$d\ln\Delta_0/d\ln T_c.$$

It varies somewhat with pressure. At $P=0$ we find the value 1.92. At a 5% volume decrease it is 2.18. Both these values are in close agreement with the experimental result 2.06. Strong coupling theory can quantitatively account for the effect observed by Franck and Keeler.

In Fig. 5 we have plotted the variation of T_c with volume which we obtain and compare it with the experiments of Smith and Chu.[1] The black line is a straight line through the experimental results. The agreement with theory is excellent so that our calculations also account accurately for the observed value of $d\ln T_c/dV$. Before turning to a discussion of our calculations in Hg a number of comments are in order. McMillan[16] has also solved the gap equations to obtain the critical temperature for a Nb-like spectrum which he rescales according to coupling strength as well as frequency range. The actual shape of $\alpha^2(\omega)F(\omega)$ used was $F(\omega)$ for *Nb* as revealed by inelastic neutron scattering[26] and a constant α^2. This was an appropriate choice since McMillan's main interest was in the BCC transition metals. He fits his numerical results to an analytic form which has now become extensively used. The McMillan formula for T_c is given in terms of the Debye temperature θ which fixes the range of the spectrum on the frequency scale, the parameter

$$\lambda=2\int\frac{\alpha^2(\omega)F(\omega)d\omega}{\omega}, \tag{14}$$

which fixes the strength of the electron-phonon interaction and finally the Coulomb-repulsion parameter $N(0)U_c\equiv\mu^*$. The formula is

$$T_c=\frac{\theta}{1.45}\exp\left(-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right). \tag{15}$$

It is interesting to use (15) to calculate the ratio $T_c(5\%)/T_c(0)$ which we have found to be 0.88 for our detailed calculations. In (15) we consider μ^* fixed at 0.13 and scale the Debye temperature with a $\gamma=2.85$. The change in λ with pressure is calculated from the two spectra of Fig. 2 and Eq. (14). We find $\lambda(0)=2.53$ and $\lambda(5\%)=2.21$. Substituting these numbers into the McMillan formula gives 0.87 for the ratio of the two temperatures which is very close to our value of 0.88. The small difference is safely assigned to the approximate nature of the McMillan result. It shows, however, that it can be used with confidence to discuss the effect of pressure on T_c for metals with a phonon spectrum similar to that of Nb. Hodder has, in fact, recently used this formula to discuss the effect of pressure on the critical temperature in Pb. His work is closely related to ours, although our results should be somewhat more accurate since we have avoided some of the approximations used by Hodder.

We now present results for Hg. The phonon spectrum is known from tunneling experiments and the BCS ratio is even greater than in Pb. Strong coupling effects should be even more pronounced. In Fig. 6 we have plotted $\alpha^2(\omega)F(\omega)$ for a 5% volume decrease and for $P=0$. The Gruneisen γ used was $\gamma=3.0$ as suggested by Olsen, Andres, and Geballe.[13] A constant γ may be more valid in this case than for Pb because the strong peak at low frequency is quite important. At $P=0$, $N(0)U_c$ is adjusted to 0.09 so as to get the measured gap value $\Delta_0=0.825$ meV at $T=0$. The ratio obtained for

$$2\Delta_0/k_BT_c=4.62$$

as compared with 4.6 from experiment. Swihart, Scalapino, and Wada obtained 4.8 from a relatively crude representation of the spectrum in Hg. At 5% volume decrease, we get

$$(\Delta_0)_{5\%}=0.675\text{ meV}$$

and

$$(2\Delta_0/k_BT_c)_{5\%}=4.25,$$

[26] Y. Nakagawa and A. D. B. Woods, Phys. Rev. Letters 11, 271 (1963).

which is still almost as large as that found in Pb, indicating that we are well in the strong coupling regime in this case even for a 5% volume change. To our knowledge there does not exist any experimental data against which these numbers can be compared. We are then making a prediction in this case, although the results are, of course, completely consistent with the situation in Pb. In Fig. 5 we have plotted our Hg results along side the Pb data. We see that the volume variation of T_c should be nearly the same in Hg as in Pb.

V. CONCLUSIONS

We have performed a detailed calculation of the phonon part $\alpha^2(\omega)F(\omega)$ for Pb under a 5% volume change using the method outlined by Carbotte and Dynes. It is found that the resulting distribution can be approximated very well by a simple rescaling of the zero-pressure distribution. This rescaling can be carried through just as easily on the zero-pressure tunneling-derived value for $\alpha^2(\omega)F(\omega)$, so that such data can be used to obtain finite-pressure results.

The decrease in the critical temperature observed in Pb with volume decrease can be understood quantitatively from the calculated shifts in the phonon kernel of the Éliashberg gap equations. Also these same equations correctly predict the measured decrease in the BCS ratio under pressure. That is, the zero-temperature gap Δ_0 is found to decrease somewhat more rapidly than the critical temperature. Superconducting Hg also behaves in a similar fashion. While a 5% volume decrease in Pb reduces $2\Delta_0/k_BT_c$ to a value of 3.75, close to the weak coupling limit of 3.52, the same decrease in Hg gives a value of 4.25, still well within the strong coupling regime. At present, there exist no experiments in Hg against which these predictions can be tested quantitatively.

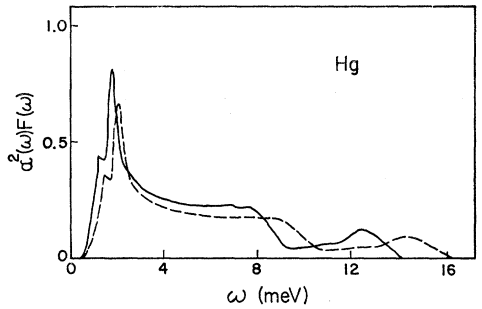

FIG. 6. Solid curve is $\alpha^2(\omega)F(\omega)$ in Hg (after McMillan and Rowell, Ref. 3). The dashed curve is the McMillan-Rowell curve rescaled to correspond to a 5% volume decrease.

ACKNOWLEDGMENTS

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