Influence of electrons-per-atom ratio and phonon frequencies on the superconducting transition temperature of lead alloys

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The dependence of the superconducting transition temperature T_c of binary and ternary alloys in the Tl-Pb-Bi family on the electron-per-atom ratio ($\mathfrak{z}$) and on the average phonon frequencies has been determined using electron tunneling. These alloys exhibit a variation from weak ($T_c = 2.3$ K) to strong ($T_c = 8.95$ K) coupling behavior as $\mathfrak{z}$ increases from 3 to 4.35. Over a substantial range of this variation the crystal structure remains fcc and it is found that T_c is a monotonic function of $\mathfrak{z}$ in this phase. This is attributed to the increase in electron concentration, rather than to the decrease in phonon frequencies that was inferred from earlier neutron scattering measurements. In fact it is found that, although the electron-phonon coupling strength changes quite substantially throughout this series (λ from 0.8 to 2.1), the phonon spectrum $F(\omega)$ does not vary appreciably and the average phonon energies remain relatively constant. We point out that the "softening" of the lattice observed by neutron scattering has only a small effect on the total phonon spectrum. Our data serve as a critical test for the various calculations of the electron-phonon interaction and superconducting parameters. Good agreement with the extensive free-electron calculations for λ is obtained. The McMillan equation for T_c works well throughout this series with the largest deviations occurring at highest λ, beyond the region considered by McMillan. It is found that the product $N(0)\langle\mathcal{I}^2\rangle$, which is approximately constant for the fcc transition elements, is not constant in this case and we question whether this assumption should be applied indiscriminately. For simple metals McMillan suggested that a better choice of constant would be $\lambda\langle\omega^2\rangle/\Omega_p^2$, where Ω_p is the ionic plasma frequency, and for this alloy series we note that this appears to be more closely obeyed. Hence we derive an alternative "maximum T_c expression" by assuming that the phonon frequencies are fixed but that the electron density can be increased indefinitely. This expression agrees particularly well with experiment at smaller values of λ. Finally, we use the data to test the relationships between λ and the phonon energy renormalization $\Omega^2-\omega^2$ and it is found that quite good agreement can be achieved in this case.

INTRODUCTION

That the superconducting transition temperature of a material depends delicately on the balance between a number of parameters is by now well known. Two of these dependences in their simplest forms are given by the Matthias rule,[1] which links T_c with the average number of valence electrons per atom $\mathfrak{z}$, and the observation by McMillan[2] that T_c in some transition metals depends predominantly on an average phonon frequency. The Matthias rule has proved remarkably useful in predicting the variation of T_c in certain alloy families and in finding new high-T_c superconductors. Alternatively, in a more limited number of cases, the idea of using "soft phonons" in metastable materials has also led to high-T_c materials.[3] That these two parameters, the electron-per-atom ratio and phonon frequencies, are independent is, of course, too simple a picture. For example, if an increase in $\mathfrak{z}$ causes an increase in the number of free electrons, then, especially in a strong-coupling material, this should immediately lead to changes in phonon frequencies as electronic screening of the ion-core changes. This was demonstrated very convincingly by Smith[4] in his neutron-scattering studies of hafnium carbide and tantalum carbide, where he showed the appreciable phonon softening in the material with higher $\mathfrak{z}$. He also pointed out that such softening had been observed[5] in lead when compared to a lead thallium alloy. Since Smith's work in 1970, the dangerous assumption seems to have been made that the observation of softening, maybe in a dispersion curve in only one direction in the lattice, implies a sufficient softening of the total phonon spectrum to give a significantly decreased average phonon frequency and hence an enhanced transition temperature. To prove or disprove this assumption in any given family of elements or alloys requires considerable experimental information, including measurements of specific heat, inelastic neutron scattering in a sufficient number of crystal directions to yield a realistic phonon spectrum, and superconducting tunneling, which gives this spectrum weighted by an electron-phonon coupling strength and hence the electron-phonon coupling parameter λ. There is only one alloy system where most of this information is available, and that is the Tl-Pb-Bi family of binary and ternary alloys. For example, extensive neutron scattering experiments have been performed[5] and, because of the nearly free-electron nature of these alloys, the system has been considered theoretically in some detail.[6,7] Specific-heat measurements have been

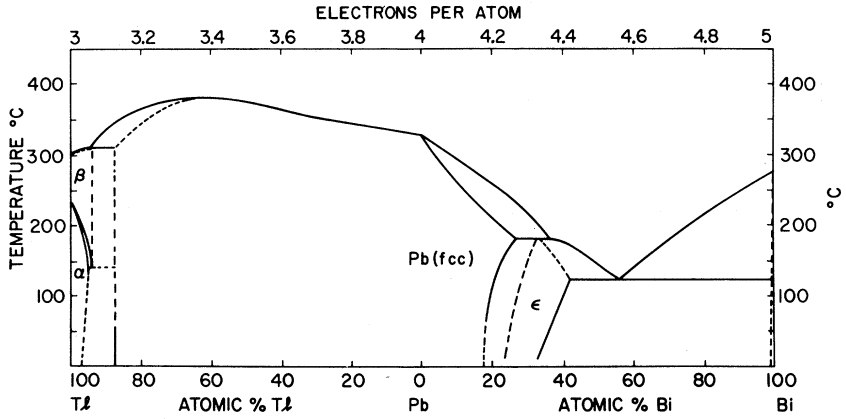

FIG. 1. Composite phase diagram of the PbTl and PbBi system from Ref. 13. Note the large range of solubility in the Pb phase.

carried out[8] in the dilute-alloy regime, and previous tunneling investigations[6,9-12] of some of the alloys indicate the large variation in coupling with alloy concentration. However, a systematic tunneling study of the whole alloy series was not available, and we therefore report in this paper the previous data of Refs. 10 and 11, along with new measurements of seven other alloy concentrations needed to complete the series. This completes the information required for the detailed quantitative theoretical study of superconductivity in this system which will be reported in the following paper.

As shown in Fig. 1, the phase diagram[13] of these alloys indicates that the fcc structure persists from $Pb_{20}Tl_{80}$ to $Pb_{80}Bi_{20}$, a range in ϑ from 3.2 to 4.2. As will be seen shortly, the ϵ phase appears very similar, thus extending the range to 4.35. It is straightforward to prepare films throughout this concentration range by evaporation, and thus the parameter under our experimental control is the electron-per-atom ratio. It is known[14] that T_c varies from 2.3 to almost 9 K throughout this range and that the high-T_c members of this family, although not the highest-T_c superconductors, are among the strongest coupled, in that λ exceeds 2. Thus, as suggested by McMillan,[2] this family of alloys offers a rare opportunity to study the approach to maximum T_c, which he saw occurring either because of saturation of T_c with λ at values >2 or because instability in the lattice induces a crystal transformation.

From our tunneling studies of this system, we obtain the transition temperature T_c, the superconducting energy gap Δ_0, the phonon density of states $F(\omega)$ weighted by the electron-phonon coupling parameter $\alpha^2(\omega)$, and Coulomb pseudopotential μ^*. We first compare our measured T_c with that calculated from McMillan's T_c equation using our λ, μ^*, and average phonon frequency $\langle\omega\rangle$. It is found that, except perhaps in the very-strong-coupling limit, agreement between measured and calculated values is quite good. In his paper, McMillan found, rather suprisingly, the empirical fact that $N(0)\mathcal{I}^2$ for five transition metals is relatively constant [where $N(0)$ is the density of states at the Fermi surface and $\mathcal{I}$ an average of the electron-ion matrix elements], with a variation of only 50% compared to almost a factor of 10 change in $N(0)$ and $\mathcal{I}^2$. Assuming $N(0)\mathcal{I}^2$ to be constant, he then predicted a variation of T_c with λ. In the Tl-Pb-Bi alloys, we shall show that the average phonon frequencies vary only slightly, although T_c varies by a factor of almost 4. We find that $N(0)\mathcal{I}^2$ is not constant, varying by a factor of ~2.5, and thus the maximum T_c expression is not valid in this case. We suggest instead that the extreme alternative is to assume that only changes in $N(0)$ affect λ, the phonon frequencies being fixed. Based on this precept, we find a dependence of T_c on λ which agrees more convincingly with the measurements, especially at small λ. Finally, we examine recent work,[15,16] including that described in the subsequent paper,[17] in which attempts are made to relate the coupling strength λ to the interaction-broadened linewidth of phonons γ.

EXPERIMENTAL

The measurements to be described here, both of the tunneling characteristics and T_c, were performed on thin-film tunnel junctions evaporated onto glass substrates. These junctions were of the configuration aluminum-aluminum oxide alloy, of area typically 0.25 mm^2, having aluminum and alloy film thicknesses about 2000 Å and normal-state resistances between 10 and 500 Ω. The films were evaporated in a vacuum in the 10^{-6}- or 10^{-7}-Torr range, and the aluminum film was oxidized by exposure to air. The Pb-Bi alloys were easy to prepare, the premade alloy being evaporated from a single heated tungsten basket. However, the vapor pressures of Tl and Pb are sufficiently different that this method could not be used, and the source

alloy was therefore cut into many small chips (at least 100), which were then "flashed" consecutively from a heated boat. The production and testing criteria for such junctions, which have been described in detail previously,[6,10,11,18,19] were applied in this work. In particular, the single most useful indication of junction quality appears to be the ratio of the conductance of the junction at zero voltage in the normal state to that in the superconducting state (at ~ 1 K), which was at least 10^3 in all the junctions studied here. The reproducibility of the results obtained from tunneling measurements has been investigated most thoroughly in Ref. 19, which deals with a study of superconducting tin. As most of the alloys discussed here have a T_c above that of tin, the accuracy of the alloy measurements is improved over that obtained for the tin junctions.

The transition temperature of the alloy film was determined using the technique described previously,[20,21] in which the opening of the superconducting energy gap is signaled by a break in the temperature dependence of the zero-bias conductance of the junction. The temperature measurement was made using a calibrated germanium thermometer. The sharpness of the break gave an estimate of the width of the transition, typically 0.05 K. The absence of any further breaks at lower temperatures indicated that single-phase alloy films had been prepared at each concentration,[21] while agreement of the value of T_c with previous measurements for bulk alloys showed that the films had the expected concentration. At the lowest temperatures (0.92 K for the alloys, 0.3 K for Tl) the energy gaps were determined using the cusp in the I-V characteristic to locate $\Delta_{alloy} - \Delta_{Al}$ and using the construction of Ref. 18 to find $\Delta_{alloy} + \Delta_{Al}$. Two samples (a total of ten junctions) were made at each alloy concentration, and the energy gaps were reproducible to within about 0.02 mV. The rise in current at $\Delta_{alloy} + \Delta_{Al}$ was very abrupt in these alloy junctions, again indicating that a single-phase film had been formed.[21]

The derivative measurements (dI/dV and d^2I/dV^2 versus V) were also measured at 0.92 K for the alloys, 0.3 K for Tl. The second derivative was measured as the harmonic 1000-Hz signal generated from a 500-Hz modulation whose amplitude was ~ 100 μV. The signal, as a function of voltage, was recorded on paper tape, and a plot of this data for each alloy is shown in Figs. 2 and 3. It is immediately obvious that, although these second-derivative plots do show interesting changes in the positions of some critical points as a function of alloying, the gross structure due to the transverse and longitudinal phonon peaks remains almost fixed in energy. The first derivative was measured as dV/dI, with the junctions in both the superconducting (S) and normal (N) states, the latter being produced by warming the junction above T_c of the alloy. The critical fields of the alloys were too high to allow the use of our available magnetic fields to quench the superconductivity. After recording these two derivatives for the junction on the paper tape, the normalized conductance $[(dI/dV)_S/(dI/dV)_N]$ was obtained. To isolate the density of states of the alloy, the contribution of the superconducting aluminum on the other side of the junction was removed, assuming a BCS density of states with an appropriate gap in the aluminum. Particularly in the lower-T_c alloys, the density of states exhibits strong-coupling effects as only small deviations from a BCS density of states, and to show these effects in detail we calculate the ratio of the alloy density of states to a BCS density with the same gap. As these ratios vary in strength by roughly 10 from the

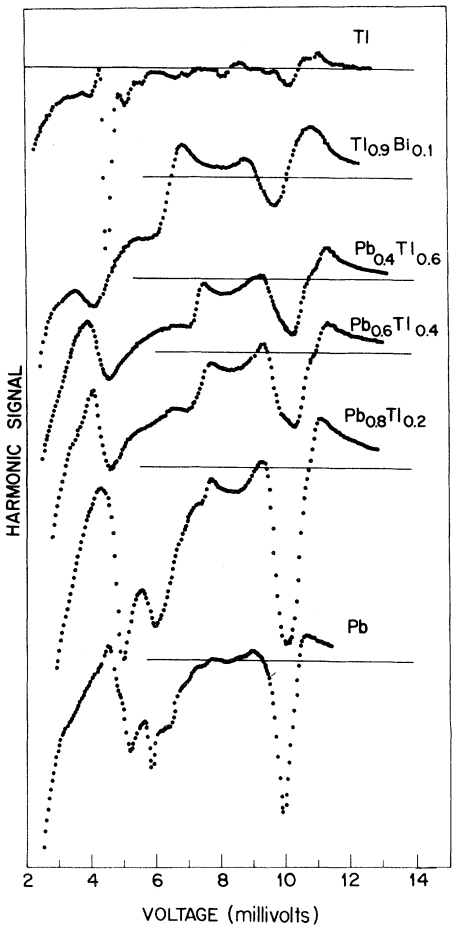

FIG. 2. Harmonic signal vs voltage for the PbTl alloys. This is approximately the second derivative d^2I/dV^2 of the tunneling characteristic. Zero signal for each concentration is marked by the horizontal lines. To obtain the energy of a critical point in these plots, $\Delta_{alloy} + \Delta_{Al}$ must be subtracted from the voltage scale. Δ_{alloy} is given in Table I, $\Delta_{Al} = 0.15$ meV.

lowest-T_c to the highest-T_c alloys, the plots are presented in three separate figures (Figs. 4–6). These figures rather dramatically illustrate the increase in coupling strength as one moves across this alloy series. The McMillan program[18] was used to numerically invert the Eliashberg-gap equations to give the gap parameter $\Delta(\omega)$, the renormalization functions $Z_n(\omega)$ and $Z_s(\omega)$, the spectral function $\alpha^2(\omega)F(\omega)$, and the Coulomb pseudopotential μ^*.[28]

The concentrations of the alloys studied in this work, along with some of the parameters derived from the tunneling experiments, are listed in Table I. At the lowest $\bar{s}$ of 3, Tl is, of course, not fcc, and its hcp structure is reflected in the different shape of $\alpha^2(\omega)F(\omega)$, as will be shown below. The

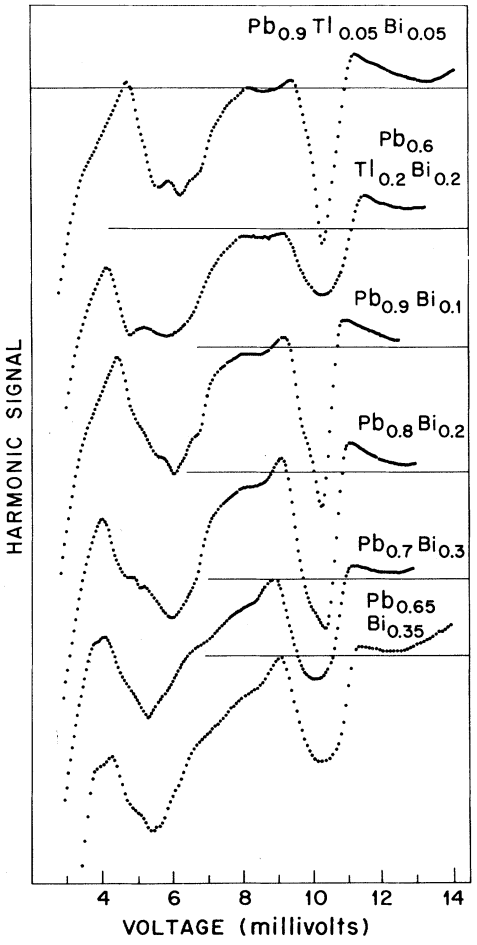

FIG. 3. Harmonic signal vs voltage for the ternary and PbBi alloys. This is approximately the second derivative d^2I/dV^2 of the tunneling characteristic. Zero signal for each concentration is marked by the horizontal lines. To obtain the energy of a critical point in these plots, $\Delta_{alloy}+\Delta_{Al}$ must be subtracted from the voltage scale. Δ_{alloy} is given in Table I, $\Delta_{Al}=0.15$ meV.

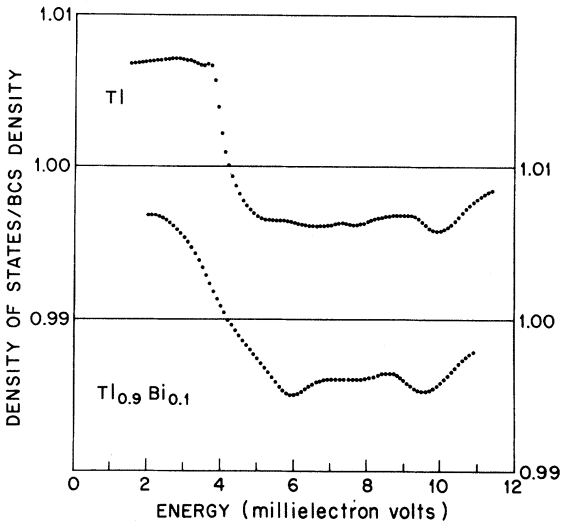

FIG. 4. Densities of states of Tl (left scale) and $Tl_{0.9}Bi_{0.1}$ (right scale), divided by the BCS densities of states for superconductors with the same energy gaps, as a function of energy. The energy scale is measured from the gap edge.

alloy $Tl_{80}Pb_{20}$, which should, according to the phase diagram of Fig. 1, be stable, was found to be difficult to make as a single phase, and instead we substituted $Tl_{90}Bi_{10}$ (an equivalent $\bar{s}$ of 3.2), for which neutron-scattering results are available. Above a Bi concentration of 20% the Pb-Bi alloys are also

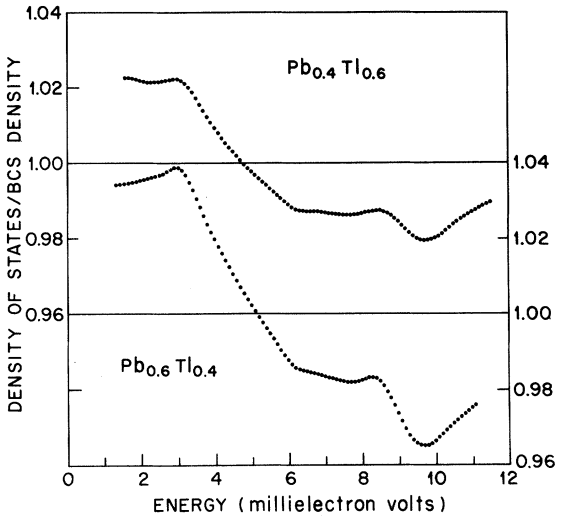

FIG. 5. Densities of states of $Pb_{0.4}Tl_{0.6}$ (left scale) and $Pb_{0.6}Tl_{0.4}$ (right scale), divided by the BCS densities of states for superconductors with the same energy gaps, as a function of energy. The energy scale is measured from the gap edge. Note change in vertical scale from Fig. 4.

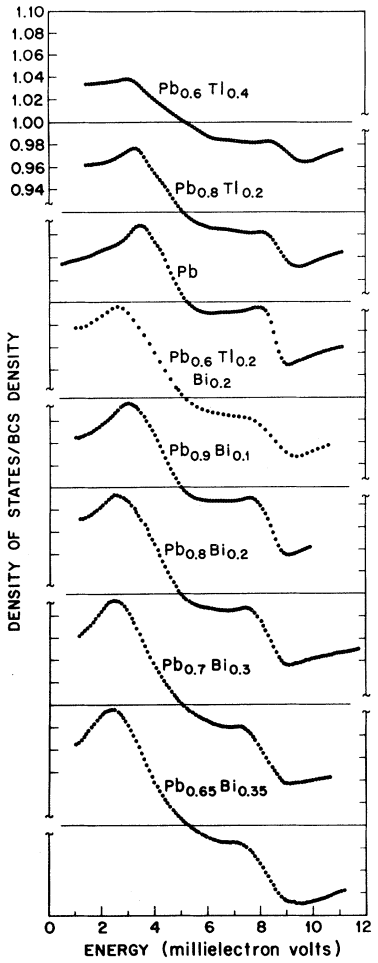

FIG. 6. Densities of states of the higher T_c alloys of the Tl-Pb-Bi series, divided by the BCS densities of states for superconductors with the same energy gaps, as a function of energy. The energy scale is measured from the gap edge, the vertical scale is 0.02 per division in all cases, and the horizontal lines indicate where the ratio of densities is unity for each alloy.

not fcc, but the variation of superconducting properties and phonon spectra seems sufficiently smooth to warrant inclusion of the $Pb_{70}Bi_{30}$ and $Pb_{65}Bi_{35}$ alloys. Above 40% Bi, both the T_c measurements and tunneling characteristics indicated mixed phase formation, and so no measurements above 35% Bi are reported here.

RESULTS

The measured critical temperatures in this Tl-Pb-Bi alloy family are shown in Fig. 7 as a function of the valence-electron concentration. These measurements are, within experimental errors, in agreement with the results of other investigators[14] who studied bulk alloys, with the possible exception of $Pb_{35}Bi_{65}$, where we observe a T_c of 8.95 K, which is higher than that reported previously. It is clear from Fig. 7 that there is a strong increase in T_c with increasing $\mathfrak{z}$ in this alloy series. This result and the reason for it have been noted previously[6] and will be reiterated shortly. It is apparent that by changing the electron concentration one can go from a relatively weakly coupled material with $T_c = 2.3$ K and $2\Delta/kT_c = 3.58$ to a very strongly coupled system with $T_c = 8.95$ K and $2\Delta/kT_c = 4.78$. In the hope of extrapolating these results to higher $\mathfrak{z}$ values, we attempted to form the metastable phases recently observed[22] at the higher Bi concentration of $Pb_{45}Bi_{55}$. Attempts to form this phase by evaporation onto cold substrates at 77 and 4.2 K always resulted in transitions lower than 8.5 K and/or mixed phases. The phonon spectra of these films resembled those of amorphous lead evaporated at 4.2 K or $Pb_{65}Bi_{35}$ evaporated at 77 K. In view of these low T_c values, whether or not one of these new phases was formed seemed uninteresting in the context of the present experiment. The mixed phase nature, or the drastic change in the shape of $\alpha^2(\omega)F(\omega)$ obtained, justified exclusion of these data from this series.

TABLE I. Parameters obtained from tunneling measurements.

Alloy	$\langle\omega\rangle$ (meV)	$\bar{\omega}$ (meV)	$\langle\omega^2\rangle$ (meV^2)	λ	Δ_0 (meV)	μ^*	T_c (K)
Tl	5.03	6.08	30.6	0.795	0.366	0.135	2.36
$Tl_{0.9}Bi_{0.1}$	4.77	5.87	28.0	0.78	0.354	0.119	2.30
$Pb_{0.4}Tl_{0.6}$	4.79	5.89	28.2	1.15	0.805	0.113	4.60
$Pb_{0.6}Tl_{0.4}$	4.87	5.86	28.6	1.38	1.08	0.126	5.90
$Pb_{0.8}Tl_{0.2}$	4.84	5.75	27.8	1.53	1.28	0.122	6.80
Pb	5.20	5.94	30.8	1.55	1.40	0.131	7.20
$Pb_{0.9}Tl_{0.05}Bi_{0.05}$	5.00	5.74	28.7	1.56	1.42	0.105	7.20
$Pb_{0.6}Tl_{0.2}Bi_{0.2}$	4.56	5.40	24.6	1.81	1.50	0.137	7.26
$Pb_{0.9}Bi_{0.1}$	4.80	5.63	27.0	1.66	1.54	0.095	7.65
$Pb_{0.8}Bi_{0.2}$	4.44	5.36	23.8	1.88	1.61	0.111	7.95
$Pb_{0.7}Bi_{0.3}$	4.48	5.28	23.7	2.01	1.77	0.110	8.45
$Pb_{0.65}Bi_{0.35}$	4.31	5.24	22.6	2.13	1.84	0.111	8.95

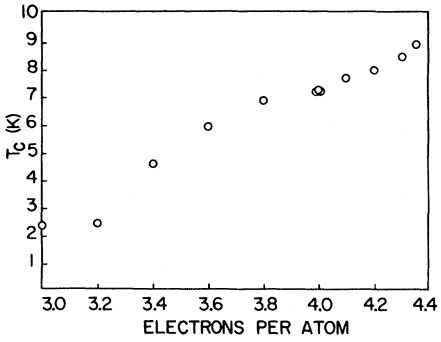

FIG. 7. Measured critical temperatures T_c as a function of electron-to-atom ratio.

The most useful parameter obtained from these superconducting tunneling measurements is the spectral function $\alpha^2(\omega)F(\omega)$,[23] defined in the free electron approximation by[6]

$$\alpha^2(\omega)F(\omega) = \frac{1}{N}\sum_{\alpha}\int_{<2k_F}\frac{d^3Q}{(2\pi)^3}L_{\alpha}(\vec{Q})\delta(\omega-\omega'_{Q,\alpha}), \quad (1)$$

where $\omega_{Q\alpha}$ is the phonon dispersion relation for the α branch, the integration is over a sphere of radius $2k_F$ (maximum Q transfer of an electron to a phonon), and $L_{\alpha}(\vec{Q})$ is an electron-phonon coupling kernel defined by

$$L_{\alpha}(\vec{Q}) = \frac{1}{4}\frac{m}{M}\frac{\vec{Q}\cdot\hat{\epsilon}_{Q\alpha}}{\hbar^2 k_F |Q|\omega_{Q\alpha}}\left|(v(\vec{Q}))\right|^2. \quad (2)$$

Here $\hat{\epsilon}$ is the phonon polarization vector and $v(\vec{Q})$ is the electron-ion pseudopotential form factor[24] for scattering from one point $(\vec{k})$ to another $(\vec{k}+\vec{Q})$ on the Fermi surface, m is the electron mass, and M the ion mass. The term inside the integral of Eq. (1) simply describes the scattering strength of the αth branch phonon at the point $\vec{Q}$. This is then summed over all available $\vec{Q}$ and the branches α. It is clear then that increasing the electron concentration by alloying increases k_F and E_F if no violent changes in band structure occur, and, if the phonon spectrum remains relatively unchanged, the increase in available phase space for scattering results in an increase in $\alpha^2(\omega)$ and hence in T_c. This expectation is realized experimentally in these Tl-Pb-Bi alloys, as illustrated in the results of Fig. 8. Here the measured $\alpha^2(\omega)F(\omega)$ is plotted for the materials studied in this alloy series. With increasing carrier concentration, there is an overall increase in the strength of the spectral function. With the possible exception of the hcp Tl, the shapes of this function throughout the series and the positions of the longitudinal and transverse phonon modes are surprisingly constant. This result might initially be surprising in view of the softening of the Pb lattice when compared to the $Pb_{40}Tl_{60}$ lattice, as observed by neutron scattering along the [001] direction.[5] However, as will be discussed in more detail in the following paper, this softening results in very little overall change in the phonon spectrum in these alloys.

Previous comparisons of the various distributions obtained by tunneling in these alloys have been made with $F(\omega)$ calculated using the neutron-scattering measurements and a Born–von Karman force-constant analysis,[6,10,11] and, except where this analysis is thought to be suspect,[25] the agreement between $\alpha^2(\omega)F(\omega)$ and $F(\omega)$ measured by these two techniques is quite good. Hence it is now generally accepted that tunneling measurements provide a faithful representation of the phonon density of states; that is, $\alpha^2(\omega)$ is a smoothly varying function with very little fine structure. The smearing of the van Hove critical points in $\alpha^2(\omega)F(\omega)$, evident in the high-impurity-concentration alloys and especially in the isoelectronic series $Pb_{1-2x}Bi_xTl_x$, has been noted previously[11,26] and ascribed to the finite lifetime smearing of the phonons due to the disordered nature of the alloys.

A quantitative measure of the electron-phonon coupling strength is given by the parameter λ introduced by McMillan as

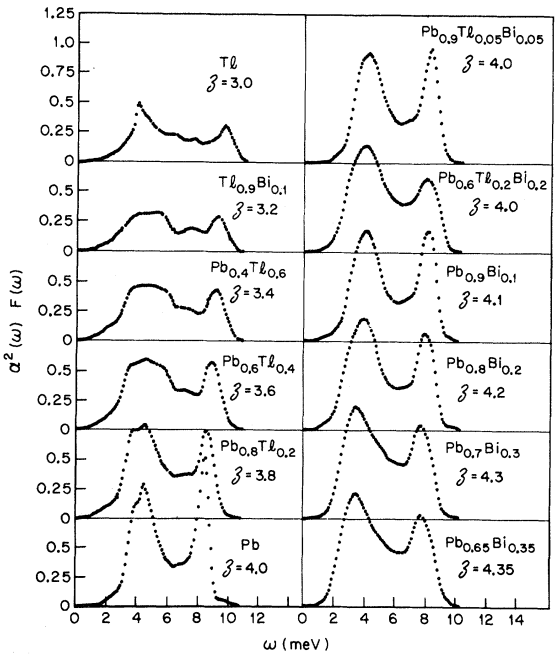

FIG. 8. Derived spectral functions $\alpha^2(\omega)F(\omega)$ for the various materials studied in this series. Reading down the first column and then the second, one sees the effect of increasing electron/atom ratio.

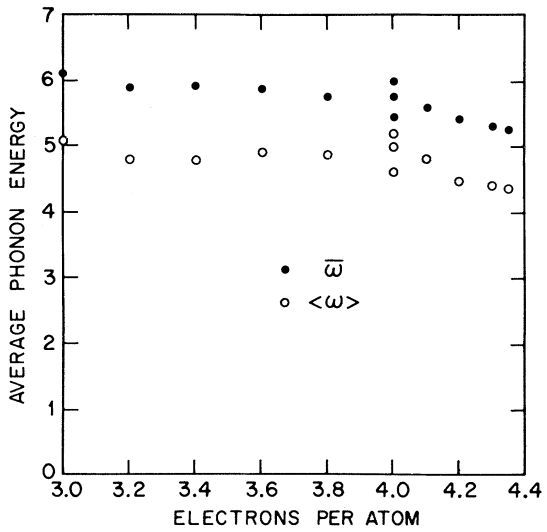

FIG. 9. Average phonon energies $\bar{\omega}$ and $\langle\omega\rangle$ as a function of $\mathfrak{z}$. See text for definitions of these averages.

$$\lambda = 2\int_0^\infty \frac{\alpha^2(\omega)F(\omega)d\omega}{\omega}\,. \tag{3}$$

In order to compare the relative weightings of the various alloy spectra it is convenient to define various averages over the spectral function, namely,[2]

$$\langle\omega\rangle = \int_0^\infty \alpha^2(\omega)F(\omega)d\omega \Big/ \int_0^\infty \frac{\alpha^2(\omega)F(\omega)}{\omega}\,d\omega\,, \tag{4}$$

$$\bar{\omega} = \int_0^\infty \omega\alpha^2(\omega)F(\omega)d\omega \Big/ \int_0^\infty \alpha^2(\omega)F(\omega)d\omega\,, \tag{5}$$

$$\langle\omega^2\rangle = \bar{\omega}\langle\omega\rangle = \int_0^\infty \omega\alpha^2(\omega)F(\omega)d\omega \Big/ \int_0^\infty \frac{\alpha^2(\omega)F(\omega)}{\omega}d\omega. \tag{6}$$

The values of these parameters, as well as the Coulomb pseudopotential μ^*, energy gap Δ_0, and T_c, are listed in Table I. A plot of $\langle\omega\rangle$ and $\bar{\omega}$ versus Z is shown in Fig. 9, where in a more quantitative fashion it is apparent that the phonon spectrum, or either of the weighted averages over the spectrum, is not changing markedly, although the superconducting properties such as T_c or Δ_0 vary appreciably. Upon inspection of Eqs. (1) and (2), this then implies, as previously asserted, that the stronger electron-phonon coupling at high $\mathfrak{z}$ is due primarily to the increase in the phase space available for electron-phonon scattering.

DISCUSSION

As noted in the Introduction, this alloy system, because of its relative simplicity and the availability of extensive experimental data, should serve as a useful critical test of the theoretical models used to describe the electron-phonon interaction and superconductivity. To understand in detail this interaction in more complicated systems, such as transition metals, $A15$ compounds, or transition-metal carbides, a complete understanding of this simpler s-p metal system is first necessary. For several of these alloys $\alpha^2(\omega)F(\omega)$ has previously been calculated[6,7] from Eq. (1) using a Born–von Karman force-constant analysis fitted to existing inelastic-neutron-scattering data and a local form of the Heine-Abarenkov pseudopotential form factor $v(Q)$. This was essentially a first-principles calculation in the free-electron approximation within the framework of pseudopotential theory. The resultant coupling strengths λ, compared with those obtained from this tunneling work, are shown in Fig. 10, satisfactory agreement being achieved. Most of the differences can probably be ascribed to band-structure effects (deviations from the free-electron picture). In fact, if we renormalize the calculation of λ for Pb by the ratio of the band-structure mass to the free-electron mass, the agreement becomes even better. The measured and calculated values of Fig. 10 indicate that in this simple metal system, where pseudopotential and free-electron theory can be applied and the dispersion curves are well known, an adequate description of the electron-phonon interaction is possible. On the other hand, it is difficult to imagine extending these calculations to more complicated systems, the already extensive calculations would become even more demanding for nonspherical Fermi surfaces, and the treatments of d bands in transition metals and the electron-ion interaction is a complex problem.

Realizing that first-principles calculations of the superconducting properties of transition metals are far in the future, McMillan took an alternative approach.[2] Assuming a model $\alpha^2(\omega)F(\omega)$ similar to that of Nb, he made a numerical solution of the Eliashberg-gap equations at T_c and derived an ex-

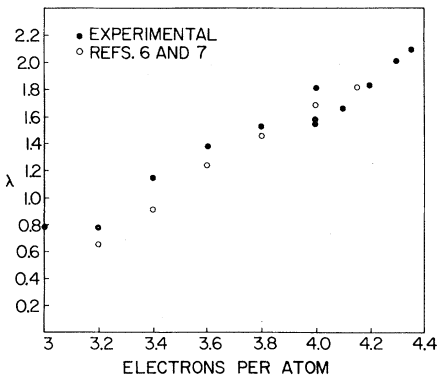

FIG. 10. Values of λ as a function of $\mathfrak{z}$. Solid circles are experimental values, open circles are those calculated from Refs. 6 and 7.

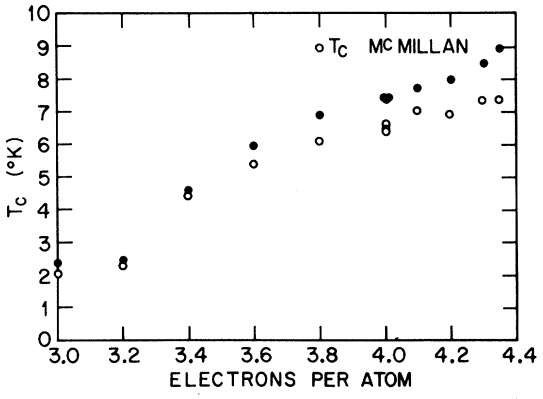

FIG. 11. T_c as a function of Z. Solid circles are experimental values, open circles are those calculated from the McMillan equation [Eq. (7) in text].

pression for T_c in terms of $\langle\omega\rangle$, λ, and μ^* given by

$$T_c = \frac{\langle\omega\rangle}{1.20} \exp\left(\frac{-1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right). \quad (7)$$

It was subsequently shown[27] that this expression yields T_c values in good agreement with those measured experimentally, even for materials such as Hg or Sn which have phonon spectra very different from that of Nb. We compare the T_c calculated from Eq. (7) with our measured values in this alloy series as a function of ϑ in Fig. 11. Again the agreement is satisfactory, the maximum deviation occurring at the highest T_c, i.e., highest coupling strengths. This deviation, increasing with T_c or λ, is possibly due to the fact that for very-strong-coupling materials the phonon-induced structure in the energy-dependent gap parameter $\Delta(\omega)$ become comparable to, or larger than, the gap edge value Δ_0, and the approximations employed by McMillan could start to break down. It is observed that the discrepancies are most substantial for values of λ above 1.5, these values being larger than the maximum values used by McMillan in his solution. Hence this breakdown of the T_c expression at these high λ's is not too surprising.

McMillan also showed that λ could be written

$$\lambda = N(0)\langle\vartheta^2\rangle / M\langle\omega^2\rangle,$$

where $\vartheta = \vec{Q}\cdot\hat{\epsilon}_{Q\alpha}v(Q)$, and the average is over all scatterings from any point on the Fermi surface to any other point on the surface. $N(0)$ is the density of states at the Fermi surface and M is the atomic mass. Using experimentally measured values for λ, $N(0)$, and $\langle\omega^2\rangle$, McMillan noticed with some surprise that, although $N(0)$ and ϑ^2 varied by an order of magnitude for the transition metals V, Nb, Ta, Mo, and W, the product $N(0)\vartheta^2$ was constant to within approximately 50%. Applying this observation to Eq. (7), i.e., $\lambda = c/M\langle\omega^2\rangle$, it became clear that T_c has a maximum as a function of λ, as an attempt to increase λ by decreasing $\langle\omega^2\rangle$ will increase the exponential term in (7) but decrease the prefactor $\langle\omega\rangle$. By a simple calculation McMillan showed that the critical temperature was maximized at $\lambda \sim 2$, with further increase of λ resulting in a slow decrease of T_c. McMillan derived an expression for the variation in T_c within a given family of materials which is useful for comparison with our data,

$$T_c/T_c(\max) = \sqrt{2/\lambda}\, e^{1/2-1/\lambda}. \quad (8)$$

By assuming that the T_c(max) in the Tl-Pb-Bi alloys is 8.95 K, the experimentally measured values of T_c may be compared with this T_c expression in Fig. 12 (solid line). The general shape of the T_c expression of Eq. (8) is not confirmed. Specifically, there appears to be no real indication that T_c saturates to its maximum value with increasing λ. On the other hand, as suggested by McMillan, at these very high values of λ the system does become unstable. This can be seen (Fig. 1) by attempting to increase λ further by increasing the Bi concentration, which results in a system of mixed crystal phases with reduced T_c. The root of the disagreement between Eq. (8) and our data in Fig. 12 can be traced back to the assumption that $\lambda\langle\omega^2\rangle M$ is constant. As the average ion mass is approximately constant in these alloys, we may plot $\lambda\langle\omega^2\rangle$ vs ϑ in Fig. 13, and we observe that there is a strong variation of almost 2.5 throughout this series. Hence it appears that, even in this simple case, one cannot assume that $N(0)\vartheta^2$ is constant, and the use of this relation for other classes of materials should be limited to those where there is some in-

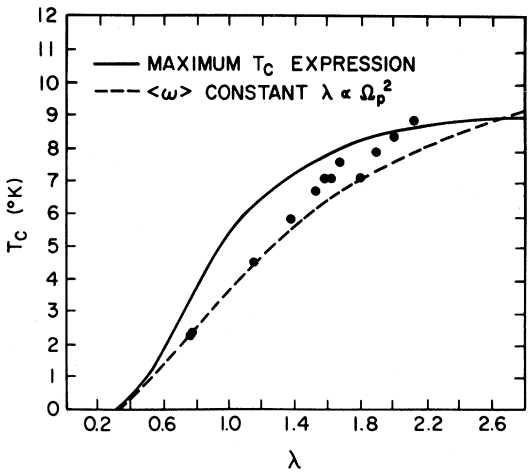

FIG. 12. Experimental T_c's as a function of λ compared with the maximum T_c expressions. The solid line is McMillan's expression for maximum T_c assuming $\lambda\langle\omega^2\rangle$ is constant. Dashed line is calculated assuming the phonon frequencies constant and that λ varies as Ω_p^2.

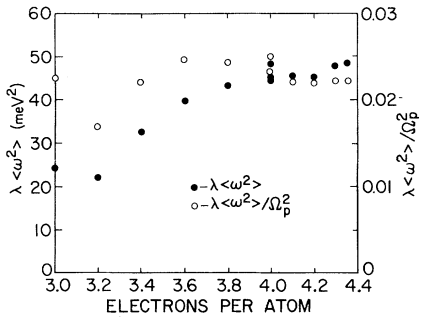

FIG. 13. $\lambda\langle\omega^2\rangle$ (closed circles) and $\lambda\langle\omega^2\rangle/\Omega_p^2$ (open circles) as a function of $\mathfrak{z}$. It is clear that $\lambda\langle\omega^2\rangle/\Omega_p^2$ is much more constant throughout this series.

dependent evidence that it is applicable. McMillan did suggest that in the simple polyvalent metals (a class in which this series belongs) a more correct relation between λ and $\langle\omega^2\rangle$ should be that $\lambda = c'(\langle\omega^2\rangle/\Omega_p^2)^{-1}$, where Ω_p is the ionic plasma frequency. Plotting $\lambda\langle\omega^2\rangle/\Omega_p^2$ in Fig. 13, it is seen that the value of this parameter does indeed remain closer to a constant than does $\lambda\langle\omega^2\rangle$.

The fact that Fig. 13 shows $\lambda\langle\omega^2\rangle/\Omega_p^2$ is approximately constant, and the knowledge that $\langle\omega^2\rangle$ changes little throughout this alloy series, implies that λ is proportional to Ω_p^2. This is a restatement of our claim that changes in λ are determined primarily by the increase in $N(0)$ or $\mathfrak{z}$ as $\Omega_p^2 = 4\pi Z^2 e^2/M$ per atomic volume. Hence we come to the following conclusion: Given that McMillan derived a maximum T_c expression on the assumption that λ can be increased indefinitely by decreasing the average phonon frequencies, then an alternative maximum T_c expression can be derived by assuming that $N(0)$ can be increased to infinity. Of course these two expressions represent the limiting behavior of $\lambda \propto 1/\langle\omega^2\rangle$ or $\lambda \propto \Omega_p^2$, and we do not expect them to apply exactly in any family of materials, but it seems likely that the new expression will be a closer approximation to the Tl-Pb-Bi T_c behavior. We derive this expression by returning to Eq. (7) and substituting for λ as $0.0225\Omega_p^2/\langle\omega^2\rangle = \lambda$. The result is

$$T_c = \frac{\langle\omega\rangle}{1.20}\exp\frac{-1.04(1+0.0225\Omega_p^2/\langle\omega^2\rangle)}{0.0225\Omega_p^2/\langle\omega^2\rangle - \mu^* - 0.014\mu^*\Omega_p^2/\langle\omega^2\rangle}.$$

If we now fix $\langle\omega\rangle$ at a value typical of these lead alloys, namely, 4.5 meV, and put $\mu^* = 0.1$, we may plot T_c versus λ again on Fig. 12 (dashed line). Agreement with experiment is particularly good at low λ, where, from Fig. 9, we know $\langle\omega\rangle$ is essentially constant. In any given sytem, one would expect results somewhere between these two extreme limits.

An interesting consequence of this alternate form for T_c is that we have a new maximum T_c as $\mathfrak{z} \to \infty$, given by

$$T_c = (\langle\omega\rangle/1.2)e^{-1.11},$$

where we have again assumed $\mu^* = 0.1$. In these Pb alloys, this is 14.4 K, but again it is clear that a crystal phase change occurs before this limit can be reached.

Recently, attempts have been made[15-17] to relate the coupling strength λ to the linewidth γ of the phonon as broadened by the electron-phonon interaction. It was shown that a rigorous definition of λ is given by

$$\lambda = \sum_{Q,\alpha}^{1\text{st BZ}} \frac{2\gamma_{Q\alpha}}{\pi N(0)\hbar\omega_{Q\alpha}^2}. \tag{9}$$

This linewidth is the imaginary part of the phonon self-energy and is related via a Kramers-Kronig relation to the real part. The real part, in turn, is related to the energy shift $\Omega_{Q\alpha}^2 - \omega_{Q\alpha}^2$ observed between the "bare" frequencies of the lattice $\Omega_{Q\alpha}^2$ and the real (measured) values $\omega_{Q\alpha}^2$. Substituting the relationship between γ and $\Omega_{Q\alpha}^2 - \omega_{Q\alpha}^2$, the final relation is derived as

$$\lambda = \bar{f}\sum_{Q,\alpha}^{1\text{st BZ}} \frac{\Omega_{Q\alpha}^2 - \omega_{Q\alpha}^2}{\omega_{Q\alpha}^2}, \tag{10}$$

where $\bar{f}$ is a q-space average of the proportionality term $f(Q)$ relating γ and $\Omega_{Q\alpha}^2 - \omega_{Q\alpha}^2$. The details of the derivation of this formula and extensive discussions of its implications are given in the following paper. Because there is no extrinsic reference in this relationship to the electronic properties, it is hoped that this formula can be extended to more complicated materials where pseudopotential calculations of the type displayed in Fig. 10 are much more difficult. It is hoped that the electronic properties, and the electron-phonon interaction strengths, are "measured" in the difference $\Omega_{Q\alpha}^2 - \omega_{Q\alpha}^2$, and hence a careful determination of the real phonon frequencies will be sufficient. With this approach there are problems associated with the determination of $\Omega_{Q\alpha}$, the "bare" frequencies, and these problems are discussed in the following paper. Nevertheless, using this relation, one can, from inelastic-neutron-scattering data, make estimates of λ. These estimates, for two choices of $\bar{f}$, are shown in Fig. 14, and it is seen that quite good agreement between the calculations and experiment is achieved. In fact, for an arbitrary choice of $\bar{f} = \text{const.} = 0.023$, the agreement is excellent. This approach, however, does not yet exclude utilization of the electronic properties in the calculation of $\Omega_{Q\alpha}^2$, and some work on this problem remains to be done.

CONCLUSIONS

We have performed extensive tunneling measurements on the alloy system Tl-Pb-Bi, where the

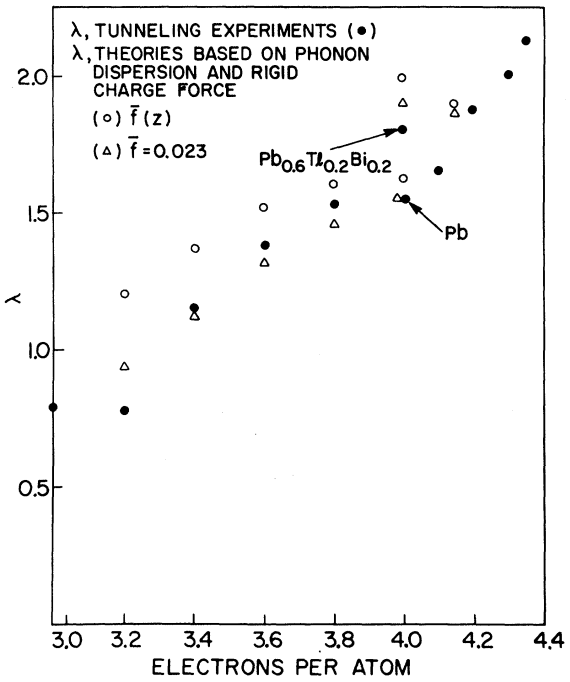

FIG. 14. Experimental (closed circles) and calculated (open circles and triangles) values of λ for this series. The values were calculated from Eq. (10) for two different choices of the parameter $\bar{f}$. The details of this calculation are described in the following paper.

electron concentration $\mathfrak{z}$ has been varied from 3 to 4.35. Over a substantial range of this variation the crystal structure remains fcc. Via the tunneling measurements, we obtain T_c and the various parameters describing the superconducting properties of these materials. It is found that T_c is a monotonic function of $\mathfrak{z}$ in the fcc phase, and this is attributable to the increase in electron concentration. In addition, it is found that, although the electron-phonon coupling strength changes quite substantially throughout this series, the phonon spectrum $F(\omega)$ does not vary appreciably, and the average phonon energies $\langle\omega\rangle$ or $\bar{\omega}$ remain relatively constant.

The data obtained from these measurements serve as a critical test for the various calculations of the electron-phonon interaction and superconducting parameters. Good agreement with the extensive free-electron calculations for λ is obtained.[5,9] The McMillan equation[10] for T_c works well throughout this series with the largest deviations occurring at highest λ, beyond the region considered by McMillan. It is found, though, that the product $N(0)\langle\mathcal{I}^2\rangle$, which is approximately constant for the fcc transition elements, is not constant in this case and we question whether this assumption should be applied indiscriminately. For simple metals, however, McMillan did suggest that a more favorable relation would be $\lambda\langle\omega^2\rangle/\Omega_p^2 = \text{const.}$ and for this alloy series we notice that this appears to be more closely obeyed. Hence we derive an alternative "maximum-T_c expression" by assuming that the electron density can be increased indefinitely. This expression agrees particularly well with experiment at smaller values of λ. Finally, we use the data to test the relationships between λ and the phonon energy renormalization $\Omega^2 - \omega^2$. It is found that quite good agreement can be achieved in this case, and it is hoped that a relationship of this type can be extended to the transition metals.

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[28]For those who require the detailed numerical results, we should mention that "A Tabulation of the Electron-Phonon Interaction in Superconducting Metals and Alloys. Part I" by J. M. Rowell, W. L. McMillan, and R. C. Dynes, is available from the authors. For Pb, In, Sn, Hg, Tl, Ta, $Pb_{0.6}Tl_{0.4}$, $Pb_{0.4}Tl_{0.6}$, $Pb_{0.6}Tl_{0.2}Bi_{0.2}$, and $Pb_{0.9}Bi_{0.1}$, this gives plots of d^2I/dV^2 versus V and $\alpha^2(\omega)F(\omega)$ and tables of the density of states divided by the BCS density, the gap parameter $\Delta(\omega)$, and renormalization function $Z_N(\omega)$. A similar tabulation of results for the other alloy concentrations studied in this paper, and the InTl alloys of Ref. 21, is almost complete. The entire collection will be submitted for publication in J. Phys. Chem. Ref. Data.