PHYSICAL REVIEW VOLUME 187, NUMBER 2 10 NOVEMBER 1969

Pseudopotential Calculation of the Mass Enhancement and Superconducting Transition Temperature of Simple Metals*

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(Received 2 June 1969)

A calculation is presented of the electron-phonon mass-enhancement parameter λ and the superconducting transition temperature T_c for sixteen simple metals plus Ca, Sr, and Ba. Empirical pseudopotentials and phonon spectra are used to calculate the electron-phonon coupling in a one-orthogonalized-plane-wave approximation using a spherical model of the phonons and the Fermi surface. Umklapp processes are explicitly evaluated. Calculated values of λ are compared with values of λ extracted from T_c and with values of the enhancement of the density of states at the Fermi surface as measured by the low-temperature specific heat. Excellent agreement is found for the divalent hexagonal metals, using empirical nonlocal pseudopotentials. Satisfactory agreement is found for the other simple metals. It is predicted that Li and Mg should be superconducting at low temperatures. The calculated results are also compared with a simple model for λ due to McMillan, and the simple model is used to discuss the occurrence of superconductivity in the Periodic Table.

I. INTRODUCTION

ALTHOUGH most of the aims of superconductivity theory have been accomplished by the Bardeen-Cooper-Schrieffer (BCS) theory[1] or more general theories based on BCS, like the Nambu-Gor'kov-Eliashberg theory,[2–4] one of the most basic aims, the calculation and prediction of superconducting transition temperatures T_c, has only begun to be realized. It is widely accepted that the reason for the inavailability of accurate calculations of T_c lies not in any basic failing of superconductivity theory, but rather in the fact that T_c depends sensitively on the normal state properties of materials. In recent years, much has been added to our understanding of these normal state properties, and reliable calculations of T_c can now be attempted. Successful model calculations with a small number of adjustable parameters have been done for several systems where transition temperatures can be varied by varying carrier concentrations. Examples of such calculations are Seiden's work[5] for the lanthanum-selenide system with two adjustable parameters and works by the authors and others for degenerate semiconductor systems using one adjustable parameter.[6,7] The direct calculation of the single number T_c in a metal with no adjustable parameters is more difficult and the results are somewhat less convincing as a test of the theory, but rather good success has been reported by Carbotte and Dynes[8] for Al and Pb.

McMillan[9] has done a detailed study of the dependence of T_c on the electron-phonon coupling in metals. He found a simple model formula for T_c in terms of a few parameters, the most important of which is the electron-phonon mass enhancement λ. Detailed and fairly successful calculations of λ in a few simple metals have now been done by a number of authors.[10–16] The term "simple metal" refers to elements in which the outer (s and p) conduction electrons are far enough removed in energy from d or f levels that these conduction electrons can be treated as nonlocalized nearly free electrons. In these metals the electron-ion interaction can be represented by a pseudopotential,[17] and the pseudowave functions are similar to free-electron plane waves. It is the knowledge of the pseudopotential which has made reliable calculations of λ possible for the simple metals.

In this paper we present pseudopotential calculations of λ and T_c for 16 simple metals plus the alkaline earths, Ca, Sr, and Ba, using Animalu-Heine model potentials,[18] and (whenever possible) empirical pseudopotentials obtained from band-structure calculations fit to Fermi-surface measurements. The theory and a description of the calculations are given in Sec. II. In addition, previous calculations of λ are assembled and discussed in this section. It is argued that a reliable

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* Supported by the National Science Foundation.

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value of λ can be found provided the correct pseudopotential and phonon spectrum are known, even if effects of phonon anisotropy and departure from free-electron behavior of the conduction electrons are ignored.

The calculations are presented and discussed for individual metals in Sec. III. Particularly good success is found for the divalent hexagonal metals Be, Mg, Zn, and Cd, as previously reported by the authors.[19,20] This success is attributed to the availability of extremely accurate empirical nonlocal pseudopotentials in these metals. On the basis of this success we feel it is possible to calculate λ and T_c accurately in simple metals provided the empirical pseudopotentials are known accurately, and the band-structure density of states at the Fermi surface $N(0)$ has been calculated. It appears that the nonlocal form of the empirical pseudopotential is important for obtaining the desired accuracy in these quantities, and in fitting Fermi-surface data to the accuracy of recent experimental work. On the basis of the calculations shown in Sec. III, we predict that Li and Mg should be superconducting at very low temperatures.

In Sec. IV, general trends in the occurrence of superconductivity in the Periodic Table are discussed. In particular, the conclusions of the jellium model[21–23] for simple metals are shown to be roughly correct in the more exact theory. Another example of an interesting regularity first pointed out by McMillan[9] is found in the metals Be, Mg, Zn, and Cd. Finally, in Sec. V we conclude that the theory of T_c for simple metals is now understood, and that the electron-phonon interaction mechanism does a completely adequate job of explaining T_c in these metals.

II. THEORY

A. General Theory

The parameter of fundamental interest to us is λ, the electron-phonon contribution to the electronic mass enhancement at the Fermi surface. In the simple case of a spherically symmetric band structure, the observed mass m^* (as found by cyclotron resonance, de Haas–van Alphen effect, or specific-heat measurements) is related to the band mass m_b (as computed in a band-structure calculation) by

$$m^* = m_b(1+\lambda+\lambda_c)\,. \tag{2.1}$$

The parameter λ_c is the contribution from Coulomb interactions to the electronic mass renormalization; these contributions have been most recently calculated by Rice[16] and appear to be small. Henceforth, we will neglect λ_c on the grounds that its value is small; its magnitude is probably no greater than uncertainties in the value of λ.

Real metals are generally more complicated than the spherical model above. Because of anisotropy and because of Bragg reflection at zone boundaries, cyclotron masses and de Haas–van Alphen masses vary from orbit to orbit, and the renormalization varies from point to point on the Fermi surface. Formula (2.1) then does not define a unique enhancement λ; we must also specify which mass is being considered. In this paper, we will choose m^* to be the specific-heat mass defined as the ratio of the linear coefficient γ of the specific heat to the value γ would have in a free-electron gas of equal density. The proper choice for m_b is then the band-structure density-of-states mass at the Fermi surface, defined as ratio of the calculated density of states at the Fermi surface $N(0)$ to the density of states of the free-electron gas. With this choice λ is an average of the mass enhancements over the Fermi surface and is given by [24]

$$\lambda = N(0)\int dS_{\mathbf{k}}\int dS_{\mathbf{k}'} \times\sum_{\alpha}\frac{|M_\alpha(\mathbf{k}\rightarrow\mathbf{k}')|^2}{\hbar\omega_\alpha(\mathbf{k}-\mathbf{k}')}\Big/\int dS_{\mathbf{k}}\int dS_{\mathbf{k}'}\,. \tag{2.2}$$

The integrals are surface integrals over the Fermi surface, $\omega_\alpha(\mathbf{q})$ is the measured frequency of the phonon of mode α and wave vector $\mathbf{q}$, and $M_\alpha(\mathbf{k}\rightarrow\mathbf{k}')$ is the matrix element for scattering an electron from a Bloch state $|\mathbf{k}\rangle$ to a Bloch state $|\mathbf{k}'\rangle$, both on the Fermi surface, by a phonon of mode α;

$$M_\alpha(\mathbf{k}\rightarrow\mathbf{k}') = \sum_l \delta\mathbf{R}_l{}^\alpha\cdot\langle\mathbf{k}'|\nabla V(\mathbf{r}-\mathbf{R}_l)|\mathbf{k}\rangle\,, \tag{2.3}$$

where $V(\mathbf{r}-\mathbf{R}_l)$ is the electron-ion interaction, the index l runs over the atomic sites $\mathbf{R}_l$, and $\delta\mathbf{R}_l{}^\alpha$ is the displacement of the atom at $\mathbf{R}_l$ arising from phonons of mode α.

Equation (2.2) is exact only if the electron-ion interaction V contains the bare interaction plus the effects of (a) screening by conduction electrons and (b) both Coulomb and phonon vertex corrections. Migdal[25] has shown, however, that phonon vertex corrections contribute nothing to lowest order in the square root of the electron-to-ion-mass ratio $(m/M)^{1/2}$. Furthermore, Heine, Nozieres, and Wilkins[26] have proved that the electron-ion interaction which determines the band structure contains both screening and

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Coulomb vertex corrections in the same fashion as the electron-ion interaction needed for the electron-phonon coupling in (2.3). This means that the correct potential V in Eq. (2.3) is the potential which determines the Fermi surface. Finally, Sham[27] has demonstrated that the matrix element in (2.3) can be computed equally well by using a pseudopotential for V and pseudowave functions for the states $|\mathbf{k}\rangle$, instead of the real potential and the real wave functions. The result of these theorems is that it should be possible to compute λ very accurately [i.e., to lowest order in $(m/M)^{1/2}$] from experimentally accessible quantities, namely, the phonon spectrum and the pseudopotential. Because pseudopotential matrix elements are needed only for states on the Fermi surface, a pseudopotential empirically fitted to Fermi-surface data would seen to be the ideal choice. Pseudopotential theory, however, is not yet at a sufficiently advanced state to identify unambiguously a single pseudopotential to be used incalculating all properties of a given metal. It is to be hoped (but it is not *a priori* certain) that a single truncated pseudopotential, when applied in a consistent way to band-structure and to electron-phonon coupling, is capable of describing both problems. The resultsof the present calculation constitute empirical evidence that a single pseudopotential can be used in this way.

Calculations of λ can be tested because there are three independent ways of determining λ. Two have already been mentioned: λ can be calculated directly from Eq. (2.2) or extracted from Eq. (2.1) provided a band-structure density-of-states mass is known. These values of λ depend strongly on the accuracy of the electron-ion potential used. A third method which comes from superconductivity theory gives reliable values of λ independent of the knowledge of the potential. The Eliashberg kernels in the Nambu-Gor'kov integral equations involve a phonon-coupling function $\alpha^2(\omega)F(\omega)$, where $F(\omega)$ is the phonon density of states and $\alpha^2(\omega)$ measures the coupling of electrons to phonons of frequency ω. McMillan and Rowell[28] have devised a technique of inverting the integral equations and extracting α^2F from the measured tunneling density of states. The parameter λ is related to α^2F by

$$\lambda=2\int_0^\infty \frac{d\omega}{\omega}\alpha^2(\omega)F(\omega). \tag{2.4}$$

Thus λ can be computed from tunneling data. Unfortunately this procedure at present is only useful for strong-coupling superconductors where deviations from the BCS tunneling density of states can be observed by present techniques. However, McMillan[9] has also devised an approximate solution of the Nambu-Gor'kov equations, giving the transition temperature T_c as a function of λ and the Coulomb coupling μ:

$$T_c=\frac{\Theta_D}{1.45}\exp\left[-\left(\frac{(1.04)(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right)\right], \tag{2.5}$$

$$\mu^*=\mu/[1+\mu\ln(E_F/\Theta_D)], \tag{2.6a}$$

$$\mu=N(0)\int_0^{2k_F}\frac{qdq}{(2k_F)^2}V_c(q). \tag{2.6b}$$

In these equations, Θ_D is the Debye temperature, E_F is the Fermi energy, and $V_c(q)$ is the fully screened Coulomb interaction between electrons. Equation (2.5) is known as the McMillan equation; it is based on a two-square-well solution of the integral equation, with parameters adjusted to fit more exact calculations of T_c for various coupling constants α^2 and μ^*. McMillan used for $F(\omega)$ a phonon density of states patterned after niobium. This equation yields values of λ when T_c, Θ_D, and μ^* are all known. In practice, μ^* is not usually known, but a rough estimate is adequate because T_c is not too sensitive to μ^*, unless λ is fairly small. For weak-coupling superconductors, values of λ from Eq. (2.5) should be quite reliable. For the strong-coupling superconductors Pb and Hg, however, Eq. (2.5) is not expected to work so well, because T_c becomes sensitive to the exact form of the phonon spectrum. The McMillan equation can also be used to predict T_c if the value of λ is known. We will present some examples of this in Sec. III.

B. Previous Calculations of λ

The earliest calculations of λ were done using screened Coulomb potentials for the electron-phonon coupling and jellium models of the phonon spectrum.[21–23] In addition, umklapp contributions to λ (processes where $\mathbf{k}'-\mathbf{k}$ lies outside the first Brillouin zone) were only roughly estimated. These calculations had some qualitative success in explaining the distribution of superconductivity in the Periodic Table, but little quantitative agreement. Knowledge of the phonon spectrum and electron-ion coupling is now sufficiently improved so that more realistic calculations can be attempted. The minimal requirements for a "realistic" calculation are that the phonon spectrum and electron-ion coupling should conform to experiments insofar as possible, and umklapp contributions should be explicitly evaluated. The present calculation satisfies these criteria in perhaps the simplest and most naive way, by taking an isotropic model of the Fermi surface and the phonon spectrum, free-electron [or single orthogonal plane wave (OPW)] matrix elements, and a Debye sphere for the phonon Brillouin zone. These approximations ignore four effects which would otherwise make the calculation considerably more difficulty:

(i) The actual Fermi surface is distorted away from a sphere near zone boundaries.

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TABLE I. Summary of previous calculations of λ.

Element	Ashcroft and Wilkins[a]	Animalu *et al.*[b]	Pytte[c]	Grimvall[d]	Janak[e] one OPW	Janak[e] two OPW	Trofimenkoff[f] *et al.*	Rice[g]
Li		0.14[h]						
Na	0.18[i]	0.13[h] 0.15[k]		0.19[j]	0.13[h]	0.13[h]	0.12[h]	0.15[j] 0.20[j,l]
K		0.16[h]			0.12[h]	0.12[h]	0.11[h]	0.12[j] 0.11[i]
Rb		0.18[h]						
Cs		0.22[h]						
Mg						0.39[h]		
Zn					0.30[h,m]	0.28[h,m]		
Cd					0.14[h,m]	0.15[h,m]		
Al	0.49[i]		0.46[i]		0.50[h]	0.53[h]	0.46[h]	
Pb	1.12[i]		0.60[n]		1.67[h]	1.55[h]	1.69[h]	

[a] Reference 10.
[b] Reference 11.
[c] Reference 12.
[d] Reference 13.
[e] Reference 14.
[f] Reference 15.
[g] Reference 16.
[h] Using the Animalu-Heine model potential, Ref. 18.
[i] Using an empirical pseudopotential; for Al this is very nearly identical to (*h*).
[j] Using the Ashcroft potential [N. W. Ashcroft, Phys. Letters **23**, 48 (1966)].
[k] Using the empirical phonon spectrum; the remaining numbers in this column use a theoretical phonon spectrum.
[l] Using 13 OPW's. The remaining numbers in this column use a single OPW.
[m] J. F. Janak (private communication). A density-of-states mass m_b $=0.59$ for Zn and 0.54 for Cd has been included to facilitate comparison with the present calculation. The remaining values in these columns use m_b as given by D. Weaire, Ref. 36.
[n] Using the Harrison potential [W. A. Harrison, Phys. Rev. **131**, 2433 (1963)].

(ii) The actual matrix elements involve mixtures of many OPW's, and deviate from the free-electron matrix elements near zone boundaries.

(iii) The phonon frequencies are anisotropic.

(iv) The phonon polarization vectors are not purely longitudinal or transverse except along certain symmetry directions.

A number of previous workers have done realistic calculations of λ, mostly for Na, K, Al, and Pb, using a variety of approaches to include these four effects. Seven such calculations[10–16] are known to the authors, the results of which are summarized in Table I. The most ambitious calculation is that of Ashcroft and Wilkins,[10] which attempts to include all four effects by integrating over the actual distorted Fermi surface using two OPW matrix elements, with a calculated phonon dispersion relation giving $\omega_{q\alpha}$ and $\hat{\epsilon}_{q\alpha}$ fit to symmetry direction neutron scattering data. Pytte[12] has obtained nearly the same value of λ in aluminum by handling effects (i) and (ii) in the same manner as Ashcroft and Wilkins, but ignoring effects (iii) and (iv) in the same fashion as the present calculation. Trofimenkoff *et al.*[15] have also found the same value of λ in Al by ignoring effects (i) and (ii) and including effects (iii) and (iv). Janak[14] has found nearly the same value of λ by ignoring all four effects; also he found very little change in λ when he used two OPW matrix elements to handle effect (ii). These calculations constitute rather good evidence that in Al all four effects can be neglected. The possibility remains that in less free-electron-like metals effects (i) and (ii) may not be entirely negligible. Also there is the possibility that the isotropic phonon approximation may fail in some materials which are less isotropic than Al. However, in the alkali metals, where there is considerable anisotropy in $\omega(q)$ Rice[16] has found that this generates very little anisotropy in λ. We believe that with the possible exceptions of Sn and Ga which have complex structures, phonon anisotropy effects are fairly unimportant. A comparison of Janak's one- and two-OPW calculations shows that the free-electron matrix element approximation has less than a 10% effect on λ not only for free-electron-like metals such as Na, K, Al, and Pb, but also for metals with severely distorted Fermi surfaces like Zn and Cd. This appears to contradict Rice's result that λ for Na is enhanced by 30% when higher OPW's are included. Rice used perturbation theory to include the effects of the 12 (110) reciprocal lattice vectors. When the plane waves $\mathbf{k}$ and $\mathbf{k}'$ mix with higher plane waves $\mathbf{k}+\mathbf{G}$ and $\mathbf{k}'+\mathbf{G}'$, the scattering matrix element involves not only $V(\mathbf{k}'-\mathbf{k})$ but also terms such as $V(\mathbf{k}'+\mathbf{G}'-\mathbf{k}-\mathbf{G})$, where $\mathbf{G}$ and $\mathbf{G}'$ are reciprocal lattice vectors. In the case of a two-OPW calculation the extra plane wave is chosen to lie as near as possible to the Fermi surface, so that the pseudopotential $V(q)$ required for wave vectors q is not much longer than $2k_F$. However, in the Rice type of calculation the pseudopotential is required at wave vectors of the order of $4k_F$ and higher, where it is not determined empirically. Rice's 30% enhancement is highly sensitive to the magnitude of the pseudopotential in the region above $2k_F$. However, the pseudopotential which produces the band structure is effectively truncated at $q\approx 3k_F$. If the same pseudopotential can be used to calculate the electron-phonon coupling, then fewer plane waves than Rice used will actually contribute to λ, and the results should be closer to the one-OPW result.

At least for the simplest metals, the most naive calculations give the same results as the most complex. Therefore it seems worthwhile to try a naive calculation for all the simple metals, using the best available pseudopotentials, and to judge the validity of the approximations by comparison with experiment.

C. Calculation of λ

The actual integrations involved in evaluating (2.2) are quite difficult. The simplest approximation is to use a completely spherical model in which the Fermi sphere is considered to be undistorted, the states $|\mathbf{k}\rangle$ are single OPW's, and the phonon dispersion relations $\omega_\alpha(\mathbf{q})$ are approximated by spherically symmetric functions $\omega_\alpha(|\mathbf{q}|)$ with a Debye sphere replacing the actual Brillouin zone. One advantage of this model is that the matrix elements of the pseudopotential become simple functions of the magnitude of the momentum transfer $\mathbf{k}'-\mathbf{k}$; thus

$$\langle\mathbf{k}'|\nabla V(r)|\mathbf{k}\rangle = i(\mathbf{k}'-\mathbf{k})V(|\mathbf{k}'-\mathbf{k}|). \qquad (2.7)$$

This result holds both for local and nonlocal pseudopotentials, because the states $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle$ are on the Fermi sphere. The form factors $V(|\mathbf{k}'-\mathbf{k}|)$ are experimentally determined only for $|\mathbf{k}'-\mathbf{k}|=|\mathbf{G}|$, where $\mathbf{G}$ is a low-lying reciprocal-lattice vector. The value of $V(0)$ is rigorously[26] $-\frac{2}{3}E_F$ where E_F is the free-electron Fermi energy. It is convenient to extrapolate between the known values of the form factor by using the shape of the Animalu-Heine model potential.[18]

Within the completely spherical approximation equation (2.2) can be written as

$$\lambda = N(0)\sum_{\mathbf{G}}\sum_{a=1}^{\nu}\sum_{\alpha=1}^{3\nu}\int \frac{d^3q\,|e^{i\mathbf{G}\cdot\tau_a}\hat{\epsilon}_{q\alpha}{}^{a}\cdot(\mathbf{q}+\mathbf{G})V(\mathbf{q}+\mathbf{G})|^2}{16\pi k_F{}^2|\mathbf{q}+\mathbf{G}|M\omega_\alpha{}^2(q)} \times\theta(2k_F-|\mathbf{q}+\mathbf{G}|). \qquad (2.8)$$

The integration goes over the Brillouin zone (replaced by a Debye sphere) and the summations go over reciprocal lattice vectors, atoms at positions $\boldsymbol{\tau}_a$ within the unit cell, and phonon modes α with polarization vectors $\hat{\epsilon}_{q\alpha}{}^a$ at atom a. The number of atoms in a unit cell is ν. The θ function ensures that only scattering on the Fermi sphere is considered.

The majority of the metals under consideration have structures with one atom per unit cell. This simplifies the labor involved in evaluating equation (2.8), because the sum over atomic sites $\boldsymbol{\tau}_a$ drops out and there are only three phonon modes to contend with. The remaining metals are mostly hcp structure, except for Sn and Ga which are complex and quite difficult to treat. At first sight, at least one of our approximations fails badly in hcp metals—the assumption of a Debye sphere in place of the first Brillouin zone, which is quite far from spherical in hcp materials. Furthermore, the phonon spectra of hcp metals looks relatively anisotropic. On closer examination, however, hcp metals should be just as good candidates for a spherical approximation as cubic metals. After all, in real space hcp and fcc structures differ only at second nearest neighbors (or in the stacking order of hexagonal layers). We have attempted to exploit this similarly by treating hcp metals as if they were fcc as far as phonon properties go. This means instead of six modes in a Debye sphere, we take three modes in an extended Debye sphere of twice the volume. Another justification of this is the fact that the optical-phonon modes can be unfolded across the hexagonal face of the Brillouin zone (where optical and acoustic modes are degenerate because the structure factor vanishes) into a Jones zone twice as high as the first Brillouin zone. This extended zone is much more nearly spherical than the first zone is. Then all the isotropic approximations can be made. The spherically averaged phonons give a remarkably good fit to both the acoustic and optical branches. This is illustrated in Fig. 1 for Mg.

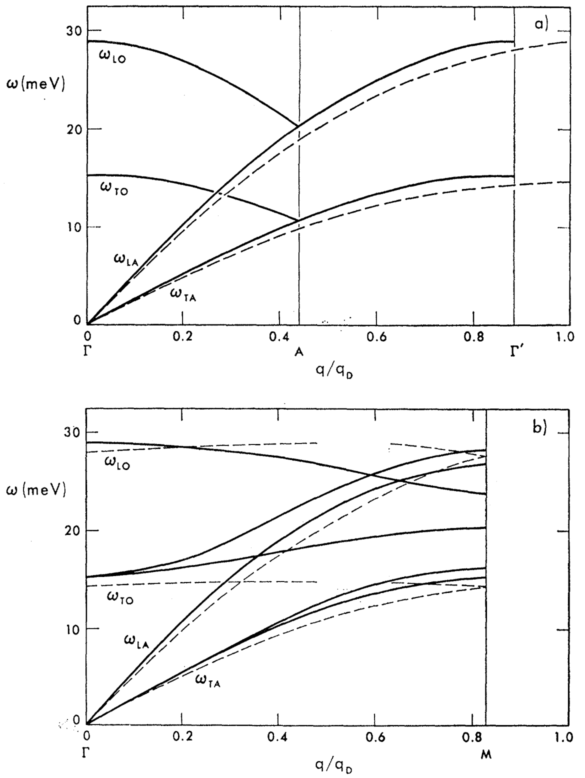

FIG. 1. Phonon dispersion relations $\omega(q)$ in meV for Mg with q measured in units of q_D, the radius of the extended Debye sphere. The solid lines correspond to the neutron scattering measurements of Iyengar *et al.*, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. I, p. 153. The dotted line is the quadratic fit used in the calculations. In (a) the modes along the (0001) direction from Γ to A are shown, with the optical modes unfolded into the second Brillouin zone. In (b) the modes along the $(10\bar{1}0)$ direction from Γ to M are shown. The dotted lines for the optical modes near Γ are found by translating by (0002); for the optical modes near M the translation is $(10\bar{1}0)$.

The same trick is also useful for Sn and Ga as a means of avoiding the difficult task of choosing phonon frequencies and polarization vectors for many phonon

TABLE II. Data used in the calculation of λ and T_c.

	r_s	C_L (10^5 cm/sec)	C_T (10^5 cm/sec)	ω_L (meV)	ω_T (meV)	m^*	Θ_D (°K)	μ^*	m_b
Li	3.24	6.164	2.624	40.0	22.0	2.20	352	0.18	
Na	3.94	3.413	1.486	15.2	8.6	1.26	157	0.16	1.00
K	4.88	2.516	1.113	9.1	4.3	1.24	89.4	0.15	1.00
Rb	5.22	1.629	0.690	5.5	2.76	1.25	54	0.15	1.00
Cs	5.63	1.324	0.566	4.1	2.12	1.43	40	0.14	1.00
Ca	3.27	3.95	2.34	20.1	11.9	1.92	234	0.16	
Sr	3.57	2.67	1.58	12.7	7.5	2.03	147	0.16	
Ba	3.69	2.235	1.325	9.5	5.6	1.40	110.5	0.15	
Be	1.87	13.12	9.21	83.5	56.6	0.37	1390	0.10	0.30
Mg	2.64	6.00	3.23	29.0	14.9	1.33	400	0.15	1.00
Zn	2.29	3.78	2.24	20.8	10.8	0.86	309	0.12	0.59
Cd	2.57	2.98	1.757	16.4	8.4	0.74	209	0.12	0.54
αHg	2.65	1.703	0.944	12.0	5.0	1.88	71.9	0.13	
βHg	2.63	1.703	0.944	12.0	5.0	1.40	94	0.12	
Al	2.07	6.00	3.00	38.9	28.2	1.49	420	0.14	
Ga	2.18	4.4	2.7	28.0	20.4	0.59	324.7	0.11	
In	2.39	2.73	0.935	14.8	6.5	1.39	109	0.12	
Tl	2.47	2.055	0.7216	10.6	4.5	1.14	78.5	0.11	
Sn	2.21	3.546	1.800	16.0	8.0	1.29	195	0.12	
Pb	2.29	2.29	1.007	9.02	6.80	2.01	96.3	0.12	

modes. Within this model, Eq. (2.8) becomes

$$\lambda=N(0)\sum_G\sum_\alpha|S(G)|^2\int d^3q\frac{|\hat{\epsilon}_{q\alpha}\cdot(\mathbf{q}+\mathbf{G})V(\mathbf{q}+\mathbf{G})|^2}{16\pi k_F{}^2|\mathbf{q}+\mathbf{G}|M\omega_\alpha{}^2(q)}\times\theta(2k_F-|\mathbf{q}+\mathbf{G}|)\,, \quad (2.9)$$

where the integration is over the extended Debye sphere and $S(G)$ is the normalized structure factor

$$S(G)=\frac{1}{\nu}\sum_{a=1}^{\nu}e^{i\mathbf{G}\cdot\tau_a}. \quad (2.10)$$

This is the final formula for λ. The polarization vectors are chosen to be purely longitudinal ($\hat{\epsilon}$ parallel to $\mathbf{q}$) or transverse [$\hat{\epsilon}$ perpendicular to $\mathbf{q}$, with $(\hat{\epsilon}\cdot\mathbf{G})^2$ averaged over orientations of $\hat{\epsilon}$ perpendicular to $\mathbf{q}$]. The term with $\mathbf{G}=0$ then arises only from longitudinal phonons. This is called the normal or N contribution to λ. The remainder is the umklapp or U contribution, and is usually much larger than the N contribution (except in the alkalis where the Fermi surface is small).

The pseudopotential can also be used to calculate the electron-phonon part of the electrical resistivity $\rho(T)$, using an expression given by many authors[29]; for convenience we will call it the Ziman-Baym theory. Within our spherical model, ρ is given by Eq. (2.9) except that a factor

$$\frac{2\pi m\beta}{ne^2\hbar}\,\frac{\hbar^2\omega_\alpha{}^2(q)}{(1-e^{-\beta\hbar\omega_\alpha(q)})(e^{\beta\hbar\omega_\alpha(q)}-1)}(1-\cos\theta) \quad (2.11)$$

must be included in the integral, where n is the electron density, $\beta=1/k_BT$, and θ is the angle between $\mathbf{k}$ and $\mathbf{k}'$. The factor $1-\cos\theta$ weights the large momentum transfer scattering more heavily than the small-angle scattering, and further enhances the U contribution over the N contribution.

The data used in the calculations are given in Table II. For convenience, a quadratic fit to the phonon dispersion curves was used, fitted to the measured sound velocity C_L and C_T for longitudinal and transverse modes, respectively, and to representative frequencies ω_L and ω_T at the radius of the extended Debye sphere $q=q_D$. The constants C_L and C_T were chosen whenever possible by taking $T=0$ elastic const and averaging the inverse square of the velocity for each mode on the various symmetry directions. Since the two transverse modes enter Eq. (2.9) in an identical way, their frequencies were averaged together to get one representative doubly degenerate mode. The constants ω_L and ω_T were chosen, whenever possible, to be the most representative maximum frequency of the mode as measured by neutron scattering. In metals where neutron data are unavailable we used frequencies of peaks in the superconducting tunneling density of states whenever possible. In the absence of either type of information, ω_L was set equal to Θ_D and ω_T was given by $(C_T/C_L)\Theta_D$, except for Cs where reference was made to theoretical calculations.[30] In Ca and Sr where only C_L and Θ_D were available, the value of (C_T/C_L) found in Ba was used. Finally, in Cd ω_L and ω_T were chosen by taking the values for Zn and scaling them by $(C_{\mathrm{Cd}}/C_{\mathrm{Zn}})$ for each mode.

The quadratic fit to the phonon spectrum is shown in Fig. 1 for Mg. This form was chosen because it gives a rather good fit to the phonons in a variety of materials. The added errors from the quadratic model lie within the roughly 10% uncertainty already present because of the isotropic approximation. The convenience

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[29] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1963), Chap. 9; G. Baym, Phys. Rev. **135**, A1691 (1964). For an application of these theories in simple metals using pseudopotentials see R. C. Dynes and J. P. Carbotte, *ibid.* **175**, 913 (1968).

[30] P. S. Ho, Phys. Rev. **169**, 523 (1968); A. O. E. Animalu, F. Bonsignori, and V. Bortolani, Nuovo Cimento **44B**, 159 (1966).

TABLE III. Calculated values of λ, T_c, and ρ using various pseudopotentials. The experimental values of the electrical resistivity at 295°K are given by Meadan[a]; residual resistivities have been subtracted.

Element	pseudopotential	λ(McMillan)	λ(calc)	T_c(expt) (°K)	T_c(calc) (°K)	ρ_{295}(expt) ($10^{-6}\ \Omega$ cm)	ρ_{295}(calc) ($10^{-6}\ \Omega$ cm)
Li	HA[b]		0.56	<0.08	1.5	9.32	15.0
	Harrison[c]		0.53		1.1		9.8
	Goddard[d]		0.37		0.015		6.1
Na	HA[b]		0.15			4.75	2.7
	Lee,[e] Ho[f]		0.19				3.9
	Darby[g]		0.23				4.7
K	HA[b]		0.14			7.19	4.1
	Lee,[h] Ho[f]		0.14				4.0
Rb	HA[b]		0.14			12.5	5.0
Cs	HA[b]		0.12			20.0	5.0
Ca	HA[b]		0.22			3.6	2.5
	Animalu[i]		0.28		5×10^{-5}		4.5
Sr	Animalu[i]		0.19			21.5	2.9
Ba	HA[b]		0.14			39.0	3.4
	Animalu[i]		0.14				3.5
Be	HA[b]	0.23	0.10	0.026		3.25	0.30
	Tripp[j]		0.26		0.15		1.07
Mg	HA[b]		0.35	<0.017	0.08	4.30	3.1
	Kimball[k]		0.31		0.009		2.3
Zn	HA[b]	0.38	0.27	0.875	0.013	5.92	1.5
	Stark[l]		0.42		0.9		3.2
Cd	HA[b]	0.38	0.10	0.56		7.27	0.4
	Stark[l]		0.40		0.5		3.5
αHg	HA[b]	1.0(1.6)[m]	0.84	4.153	2.5	95.9[n]	7.1
	Brandt[o]		0.97		3.4		8.0
	Bogle[p]		0.98		3.4		8.2
βHg	HA[b]		0.69	3.949	2.1		5.9
	Brandt[o]		0.79		3.0		6.3
	Bogle[p]		0.80		3.1		6.6
Al	HA[b]	0.38	0.53	1.196	3.0	2.74	2.1
	Ashcroft[q]		0.52		2.6		2.0
Ga	HA[b]	0.40	0.25	1.091	0.006	14.85	1.2
	Reed V_{12}[r]		0.29		0.05		1.0
	Reed V_5[r]		0.22		0.0003		0.8
	Inglesfield V_6[s]		0.23		0.0009		1.0
	Inglesfield V_7[s]		0.23		0.0005		0.9
In	HA[b]	0.69	0.89	3.404	4.6	8.75	5.8
	Cohen[t]		1.16		7.2		6.7
	Ashcroft V_1[u]		0.88		4.4		4.7
	Ashcroft V_2[u]		0.84		4.0		7.6
Tl	HA[b]	0.71	1.07	2.39	4.8	16.4	7.0
Sn	HA[b]	0.60	0.78	3.722	6.2	11.0	3.3
	Weisz[v]		0.99		10.2		3.2
Pb	HA[b]	1.12(1.3)[m]	1.34	7.193	7.6	21.0	5.9
	Anderson[w]		1.32		7.5		5.6

[a] G. T. Meaden, *Electrical Resistance of Metals* (Plenum Press, Inc., New York, 1965).

[b] Heine-Animalu model potential, Ref. 18.

[c] W. A. Harrison, Ref. 38.

[d] Reference 39.

[e] M. J. G. Lee, Proc. Roy. Soc. (London) **A295**, 440 (1966).

[f] P. S. Ho, Ref. 30. We have used only the value of q_0 determined in this calculation, where $v(q_0)=0$.

[g] This is the potential Darby extracted from liquid-metal data which was used by N. W. Ashcroft and J. W. Wilkins, Ref. 10; J. F. Janak, (private communication).

[h] Reference 35.

[i] Reference 42.

[j] Reference 31.

[k] Reference 32.

[l] Reference 33.

[m] The values in parentheses are derived by inverting the tunneling data.

[n] For liquid mercury, whereas the calculated values assume mercury is still solid.

[o] G. B. Brandt and J. A. Rayne, Phys. Rev. **148**, 644 (1966).

[p] T. E. Bogle, J. B. Coon, and C. G. Grenier, Phys. Rev. **177**, 112 (1969).

[q] N. W. Ashcroft, Phil. Mag. **8**, 2055 (1963).

[r] W. A. Reed and V. Heine, Bull. Am. Phys. Soc. **13**, 364 (1968); W. A. Reed (private communication).

[s] J. E. Inglesfield, J. Phys. C, **1**, 1337 (1968).

[t] Reference 47.

[u] Reference 46.

[v] Reference 45.

[w] J. R. Anderson and A. V. Gold, Phys. Rev. **139**, A1459 (1965).

of this choice outweighs the added precision of using individually fitted dispersion relations. In the case of pseudopotentials, however, it would be a mistake to sacrifice accuracy for convenience. The calculated value of λ is quite sensitive to the details of the pseudopotential, particularly in the region near $2k_F$, where the pseudopotential passes through zero. Thus in our computer calculations, we supplied as data the pseudopotential tabulated at increments of 0.1 in $q/2k_F$.

The final ingredient in a calculation of λ is the density of states at the Fermi surface $N(0)$ (or, equivalently, the mass m_b), which should be taken from a band-structure calculation, i.e., not renormalized by phonons. Currently available values of m_b vary widely and are quite sensitive to the type of band calculation and to the form of the potential used. For example, a nonlocal pseudopotential will give a different value from that found with a local pseudopotential. At the present time, there is probably more certainty in the value of $1+\lambda$ (although perhaps not in λ itself) than there is in m_b in most cases. This suggests that m_b should be estimated using m^* and $1+\lambda$. We have been somewhat arbitrary in our choice of values of m_b. In a few cases, namely, Be, Mg, Zn, and Cd, we have used values of m_b obtained in nonlocal pseudopotential band-structure calculations.[31–33] For the alkali metals Na, K, Rb, and Cs (but not Li) we have chosen the value $m_b=1$. These values are shown in Table II. For the remaining metals we have first calculated a value of λ denoted by λ_0 using $m_b=1$. We then chose a scale factor m_b in a self-consistent way such that

$$\lambda \equiv m_b\lambda_0 = m^*/m_b - 1\,, \tag{2.12}$$

where the value of m^* is shown in Table II. The value of m_b found by this method depends on the calculated value of λ_0 and thus on the particular choice of the pseudopotential; therefore the numbers are not shown in Table II. The results of our calculations are shown in Table III, and discussed in Sec. III.

D. Calculation of T_c

Using the experimental value of Θ_D, the calculated value of λ, and some assumed value of μ^*, the transition temperature can be calculated from Eq. (2.5), the McMillan equation. McMillan[9] assumed a value $\mu^*=0.1$ when he extracted λ from T_c for the simple metals. For the purpose of estimating T_c in metals not yet seen to be superconducting, it is important to have a more accurate value of μ^*; Eq. (2.5) is very sensitive to μ^* in cases where λ and T_c are small. Inspection of Eq. (2.6) and (2.7) suggests that considerable variation may occur in μ^* from metal to metal, both because of variations in m_b (from 0.3 in Be to nearly 2.0 in Li) and because of variations[34] in $\ln(E_F/\omega_L)$ (from 5.0 in Li to 7.0 in Pb). It is difficult to get reliable first principles values of μ because of the lack of a consistent and convergent scheme for calculating Coulomb interactions for real metals which have values of the electron-gas parameter r_s between 2 and 6. However, values of μ^* have been extracted from experiments for a few metals, either using the isotope shift or the inversion of tunneling data. The isotope shift yields a value $\mu^*=0.12$ in Zn. If μ is evaluated within the random phase approximation (RPA) with the correct value of m_b, the result for Zn is $\mu^*=0.10$. Since r_s does not vary much for most of the metals, it seems reasonable that the RPA should give values of μ that scale properly from metal to metal, even if the absolute magnitude is wrong. Therefore, we have computed μ^* by taking RPA values for μ and scaling these values of μ by a constant amount, such that μ^* in Zn agrees with the isotope-effect measurement. The values of μ^* we obtained are given in Table II. The resulting transition temperatures are listed in Table III, and are discussed individually in the next section.

III. DISCUSSION OF RESULTS

Calculated values of the mass enhancement λ, the superconducting transition temperature T_c, and the electrical resistivity at 295°K ρ_{295} are shown in Table III, and compared with experimental results and with the values McMillan[9] found for λ. The over-all agreement is fairly good for λ and worse for ρ. Our theoretical estimates of ρ from the Ziman-Baym theory are usually smaller than the experimental values. More complete calculations of $\rho(T)$ by Dynes and Carbotte[29] have shown that the Ziman-Baym theory agrees well with experiment for $T \ll \Theta_D$, but that at temperatures $T \sim \Theta_D$, the measured resistivities are higher than predicted. This partly arises from neglecting the change of phonon frequencies and lattice constants with temperature, which serve to increase ρ. However, additional discrepancies appear to be present, which have been ascribed[29] to multiphonon and anharmonic effects. In our calculations the disagreement is most pronounced for the metals with low values of Θ_D or melting temperature. For example, in the case of the alkali metals, experimental values exceed theoretical values by 30 or 40% in Li and Na, and the discrepancy increases monotonically as atomic number increases (and Θ_D decreases) up to Cs where the discrepancy is 400%. There is no reason to believe that this reflects a corresponding weakness in the theoretical values of λ. As far as transition temperatures are concerned, the theoretical values are surprisingly good on the whole, especially considering the sensitivity of the dependence of T_c on μ^* and λ, and the inherent uncertainties of the calculation. For an over-all estimate of the uncertainties, we assign a 10% uncertainty in λ arising from the spherical approximation for the phonons, and another 10% uncertainty arising from the free-electron approximation used for the Fermi surface and the matrix elements. These estimates come from the analysis of previous calculations as discussed in Sec. II B, and are probably overestimates. In many cases, particularly Be, Zn, and Cd, the variations induced in λ by using different pseudopotentials far exceeds this 20% over-all uncertainty. Thus the first requirement for a reliable calculation of λ is a reliable pseudopotential. On the other hand, in the hexagonal divalent metals where we believe the pseudopotentials are most reliable, the evidence suggests that the theoretical values of λ are reliable to considerably better than 20%. In the following sections the calculations are discussed individually for various groups of metals.

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[31] J. H. Tripp, W. L. Gordon, P. M. Everett, and R. W. Stark, Phys. Letters **26A**, 98 (1967).

[32] J. C. Kimball, R. W. Stark, and F. M. Mueller, Phys. Rev. **162**, 600 (1967).

[33] R. W. Stark and L. M. Falicov, Phys. Rev. Letters **19**, 795 (1967).

[34] We have used ω_L in place of Θ_D in Eq. (2.6). This has a very small effect on μ^*.

A. Alkali Metals

These are the simplest of all the metals in that the Fermi surface is very close to the free-electron sphere, and the free-electron approximation for matrix elements should be most reliable. Consequently, they have received the most theoretical attention. On the other hand, the simplicity of these metals constitutes something of a drawback in that it is nearly impossible to obtain experimentally more than one Fourier coefficient of the pseudopotential from Fermi-surface measurements. Furthermore, this form factor occurs at a reciprocal lattice vector $G=2.28k_F$, and thus it is difficult to know the behavior of $V(q)$ for $q<2k_F$. In the case of K, Lee and Falicov[35] have found that a highly nonlocal pseudopotential gives the best fit to the Fermi surface. The magnitude of this pseudopotential is not too different from that of the Animalu-Heine model potential.

For the band mass, a value $m_b\approx 1.0$ seems quite likely for Na and K. There are two effects which cause deviations from the value of 1.0, first the nonlocality of the pseudopotential, and second the influence of band gaps on $\epsilon(k)$ at the Fermi surface. (A third effect, the reduction in area of the surface because of zone boundaries, is not present for the alkalis.) Weaire[36] has studied the first effect using the Animalu-Heine model potential, and finds the corrections are small. Ham[37] has done more complete calculations using the quantum-defect method. His results show m_b is nearly 1.0 for Na and K; however, his results for Rb and Cs seem too large (larger than m^* in Cs). We have somewhat arbitrarily used a value $m_b=1.0$ for Na, K, Rb, and Cs. We have made no attempt to compare calculated values of λ with the observed masses, because of the uncertainty in m_b. Rice[16] has shown that Coulomb renormalization is larger (on the order of 0.05) in the alkalis (where $r_s>3.0$) than in other metals. He finds good agreement with the experimental value of m^* in Na and K by assuming $m_b=1.0$, and including both Coulomb and phonon renormalization.

None of the alkalis is presently believed to be superconducting, so the only test on our calculated values of λ is by comparison with previous calculations. The only previous calculation for the whole series of alkalis is that of Animalu *et al.*,[11] who find λ rising with increasing atomic number. Our calculated values on the other hand decrease with increasing atomic number. The basic source of this discrepancy is probably the choice of phonon spectra. Animalu *et al.* used theoretical phonon spectra computed from the Animalu-Heine model potential, with no adjustments made to fit experimental data. Several other calculations of λ have been made for Na and K, and these are in fairly good agreement with the present calculation. These results are shown in Table I. Also Rice[16] has calculated various moments of the scattering function which he denotes as g_l^{ep}, where g_0^{ep} is the same as $\lambda/(1+\lambda)$. We have also computed these moments, and the results are compared with those of Rice in Table IV.

TABLE IV. The first three moments of the electron-phonon scattering function $g^{ep}(\mathbf{k},\mathbf{k}')$ as defined by T. M. Rice in Ref. 16. The zeroth moment g_0^{ep} corresponds to $\lambda/(1+\lambda)$.

Element	Pseudo-potential[a]	Author[b]	g_0^{ep}	g_1^{ep}	g_2^{ep}
Li	HA		0.36	−0.17	0.17
	Harrison		0.35	−0.006	0.10
	Goddard		0.27	0.03	0.10
Na	HA		0.13	0.06	0.014
	Lee, Ho		0.16	0.06	−0.004
	Darby		0.19	0.07	−0.002
	Ashcroft[c]	Rice	0.13	0.05	−0.001
	Ashcroft[d]	Rice	0.17	0.06	0.01
K	HA		0.12	0.06	0.014
	Lee, Ho		0.12	0.06	0.012
	Ashcroft[c]	Rice	0.11	0.05	−0.001
	Lee[c]	Rice	0.10	0.04	0.001
Rb	HA		0.12	0.07	0.016
Cs	HA		0.11	0.06	0.018

[a] The references for the pseudopotentials are given in Table I and III.
[b] Present calculation unless otherwise noted.
[c] One OPW calculation.
[d] Thirteen OPW calculation.

The results for Li are anomalous. Both the Animalu-Heine potential and the Harrison[38] potential have exceptionally large positive values near $q=2k_F$. The Animalu-Heine potential has an additional anomaly at $q=0$ where its magnitude is smaller than $\frac{2}{3}E_F$. This is reflected in the large negative value of g_1^{ep} in Table IV; also the resistivity (in Table III), which is closely related to $g_0^{ep}-g_1^{ep}$, comes out anomalously big. The resistivity is also too large using the Harrison potential. Goddard[39] has calculated a pseudopotential for Li from first principles, which passes through zero at the same point q_0 as the Animalu-Heine potential, but takes smaller positive values near $q=2k_F$. When this potential is further reduced to take account of conduction electron screening (using a static Lindhard dielectric function), a more reasonable value of the resistivity is found. All three of these potentials predict that Li is a superconductor. It is interesting to note that Fröhlich[40] found an anomalously large electron-phonon coupling in Li in his pre-BCS theory arguments relating superconductivity to electrical resistivity. Lithium is presently believed [41] to remain normal down to 0.08°K. It would be interesting to test Li for superconductivity at lower temperatures. It is not possible to make unambigous theoretical estimate of T_c for Li at the present time because of the uncertainty in our knowledge of its properties. In particular, there is no reliable empirical pseudopotential. Furthermore, our most conservative value of λ, a value of 0.37 using the

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[35] M. J. G. Lee and L. M. Falicov, Proc. Roy. Soc. (London) **A304**, 319 (1968).
[36] D. Weaire, Proc. Phys. Soc. (London) **92**, 956 (1967).
[37] F. S. Ham, Phys. Rev. **128**, 82 (1962); **128**, 2524 (1962).
[38] W. A. Harrison, Phys. Rev. **131**, 2433 (1963).
[39] W. A. Goddard, III, Phys. Rev. **174**, 659 (1968).
[40] H. Fröhlich, Phys. Rev. **79**, 845 (1950).
[41] B. B. Goodman, Nature **167**, 111 (1951).

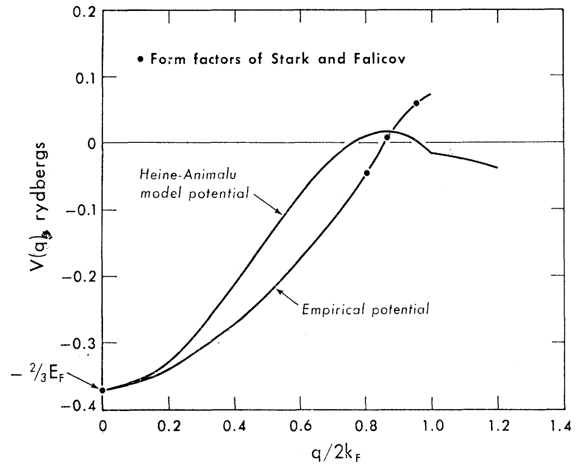

FIG. 2. Pseudopotentials used for Cd.

Goddard potential, assumes a band mass $m_b = 1.61$ (which follows from $m^* = 2.20$). To be more conservative, (i.e., generous in allowing for uncertainty in m^*), a value $m_b = 1.0$ reduces λ to 0.23 and T_c becomes effectively zero ($<10^{-12}$ °K) because of the anomalously large Coulomb coupling.

It would appear that for a wide range of reasonable choices of the pseudopotential and m_b, the conclusion remains that Li alone among the alkalis, is probably superconducting at a theoretically attainable temperature. For the other alkalis, T_c is certainly either nonexistent or negligibly small.

B. Alkali Earths Ca, Sr, and Ba

These are the most complex of the metals under consideration in the sense that their conduction electrons have a fair amount of d-like character, making them relatively unsuitable candidates for free-electron approximations. Furthermore, experimental knowledge of the band structure is meager, and of the phonons is practically nonexistent. However, the position of these metals in the Periodic Table makes them obvious candidates for undiscovered superconductors, so it is interesting to try to make reasonable estimates for λ. The best data are for Ba where room-temperature elastic constants are known. Model potentials of Animalu[42] and of Heine and Animalu[18] both seriously underestimate the resistivity and give $\lambda = 0.14$. The recent discovery[43] of superconductivity in Ba under pressure might tend to indicate a larger value of λ at zero pressure. The most serious problem in computing λ is probably the lack of an empirical pseudopotential.

In Ca and Sr there are apparently no measured elastic constants. The sound velocity can be computed from room-temperature thermodynamic data. The Animalu potential[42] gives T_c for Ca around 10^{-4} °K, but overestimates the resistivity. The Animalu-Heine potential gives a reasonable resistivity, and gives $\lambda = 0.22$, and no superconductivity. The situation in Sr is similar to that in Ba. Once again there is no empirical potential. These results seem to rule out superconductivity in Ca at zero pressure, but are inadequate to allow any statement for Sr and Ba.

TABLE V. Empirical values of the mass enhancement in Be, Mg, Zn, and Cd compared with theoretical values using empirical nonlocal pseudopotentials.

Pseudopotential	Be Tripp *et al.*[a]	Mg Kimball *et al.*[b]	Zn Stark and Falicov[c]	Cd Stark and Falicov[c]
Band mass m_b	0.30	1.00	0.59	0.54
Specific-heat mass m^*	0.37	1.33	0.86	0.74
Emprical mass enhancement λ	0.25	0.33	0.43	0.36
McMillan value of λ	0.23	...	0.38	0.38
Calculated value of λ	0.26	0.31	0.42	0.40

[a] Reference 31. [b] Reference 32. [c] Reference 33.

C. Hexagonal Divalent Metals Be, Mg, Zn, and Cd

These metals are the most suitable candidates for studying the electron-phonon coupling, partly because the phonon spectra are known (except in Cd), but mainly because the Fermi surfaces have been studied in great detail. Band-structure calculations fitted to the Fermi surface have been done using both local and nonlocal types of pseudopotentials. The local potentials cannot fit all the data to the available accuracy, and nonlocal potentials are now available[31–33] which do give an accurate fit. Furthermore, band masses m_b have been calculated using these nonlocal potentials. These are listed in Table V along with the specific-heat masses m^* and the enhancement factors λ derived from Eq. (2.1). Also shown in Table V are the values of λ which McMillan found from T_c and the values of λ computed from the empirical nonlocal potentials. All three values of λ are in remarkably good agreement and are well within the uncertainties of the various calculations. This is perhaps the most unambiguous evidence yet assembled for the essential correctness of the theories involved: the same value of λ explains both the specific heat and the transition temperature, and a pseudopotential model of the electron-phonon interaction gives the correct value of λ. Furthermore, the appropriate pseudopotential for calculating λ is the pseudopotential derived from a band-structure calculation of the Fermi surface. This answers the questions raised in Sec. II A about the uniqueness of the empirical pseudopotential. The calculated value of λ is quite sensitive to the magnitude of the pseudopotential near $q = 2k_F$, as can be seen by comparing values of λ computed with the empirical potentials with values of λ computed with the Animalu-Heine potential. The difference is most dramatic in Cd where there is a factor of 4

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[42] A. O. E. Animalu, Proc. Roy. Soc. (London) **294**, 376 (1966).

[43] J. Wittig and B. T. Matthias, Phys. Rev. Letters **22**, 634 (1969).

change. The pseudopotentials used for Cd are shown in Fig. 2. The use of nonlocal pseudopotentials seems indicated both for fitting accurately the details of the Fermi surface, and for giving accurate values of the Fermi-surface density-of-states mass m_b.

Several predictions can be made on the basis of these calculations. One interesting point is that Be, Zn, and Cd all have strong pseudopotentials and therefore strong electron-phonon coupling. However, the strong pseudopotential in a divalent material has the effect of reducing the Fermi-surface area considerably, almost filling up the conduction band and approaching a semiconducting state. This can be seen by examining the calculated electronic density of states as a function of energy, as shown in Fig. 1 of Ref. 19. There is a sharp dip in the density of states right at the Fermi energy. Thus alloys of Zn or Cd with atoms of higher or lower valence would have higher densities of states at the Fermi surface within the rigid-band model. Simple calculations assuming that phonons are unaffected show that dilute alloys (1–5%) of either valence-1 metals such as Cu or valence-3 metals such as Ga in Zn and Cd would have higher transition temperatures than the pure elements.

Magnesium is anomalous from this point of view. It has a weak pseudopotential and thus a weak electron-phonon coupling. However, the Fermi surface is free-electron-like, with a density of states unchanged from the free-electron value. Thus λ for Mg is moderately large, large enough, in fact, to expect it to be superconducting. However, because of a large density of states, the Coulomb coupling μ^* is also large. The effects compete, but do not cancel entirely, and Mg should definitely be superconducting at some theoretically attainable temperature.[20] Because of the accuracy of the experimental knowledge of Mg, it is possible to assign fairly narrow limits to λ and μ^*. Unfortunately, the range in temperature is rather large because T_c is so sensitive to λ and μ^* for weak-coupling superconductors. This is shown in Fig. 3, where isotherms of T_c versus λ and μ^* are constructed from Eq. (2.5). We have chosen $\lambda = 0.33 \pm 0.03$ in line with the mass enhancement value; the theoretical values of λ are 0.31 from the nonlocal empirical potential[32] and 0.35 from the Animalu-Heine potential which agrees with a rather accurate local pseudopotential.[32] A value of $\mu^* = 0.16$ is chosen rather than $\mu^* = 0.15$ as shown in Table II. The justification for this is that the effective value of μ^* in Zn (the reference material) is depressed by an additional amount over a free-electron metal like Mg owing to the increase of the Coulomb repulsion away from the Fermi surface as the density of states rises. The expected value of T_c as shown in Fig. 3 is 0.012°K, a presently attainable temperature, and not far below the lowest temperature at which Mg has been already tested. However, values of T_c as low as 0.001°K are consistent with the uncertainties in the calculations.

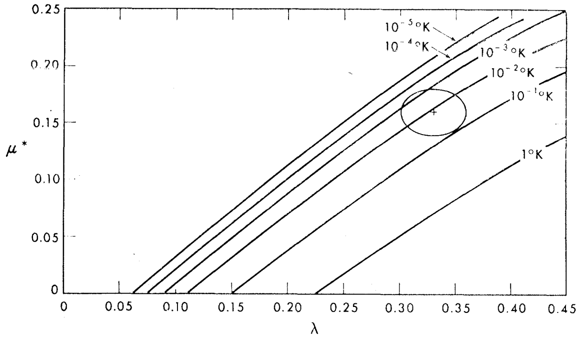

FIG. 3. Isotherms of T_c for Mg as a function of μ^* and λ. The probable ranges of λ and μ^* are within the oval centered about x.

It seems worthwhile to investigate Mg for superconductivity, both by direct measurement, and by the indirect proximity effect method.

D. Other Polyvalent Metals

The remaining simple metals are Hg, Al, Ga, In, Tl, Sn, and Pb. These are all superconductors with a variety of crystal structures and wide variations in the current status of experimental knowledge. For many of these metals, the Fermi-surface data are precise enough to warrant a nonlocal pseudopotential band-structure calculation, but unfortunately none have been reported yet. Probably the simplest of these metals are Al and Pb, which have fcc structures, well-known phonon spectra, and rather free-electron-like Fermi surfaces. The computed values of λ for Al and Pb shown in Table III are in good agreement with both McMillan's value and with previous calculations (Table I). In both Al and Pb the empirical potentials are very similar to the Animalu-Heine model potentials, and give the same regults for λ. For Al, the calculated values of λ are somewhat high, as is the case with previous calculations. However, if instead of $\mu^* = 0.10$ (McMillan's choice), a value $\mu^* = 0.14$ is used, the McMillan value of λ would be raised to 0.46, in better agreement with the calculations.

The most complex of the polyvalent metals, at least in terms of crystal structure, are Sn and Ga. Here it may be expected that the simple spherical extended zone approximation to the phonons may fail. In particular for Ga the calculated value of λ is too small. The phonon spectrum of Ga has recently been measured by Reichardt *et al.*[44] by neutron scattering. A number of optic modes occur which are softer than any modes that can be obtained from our model, and these modes also hybridize with the acoustic modes, depressing their frequencies as well. A realistic calculation for Ga would be tedious, but the answer would certainly be larger than our value. For Sn the spherical extended zone model also gives a poor fit to the phonons, and

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[44] W. Reichardt, R. M. Nicklow, G. Dolling, and H. G. Smith, Bull. Am. Phys. Soc. 14, 378 (1969); and (private communication).

overestimates the frequencies of several modes. It is therefore surprising that both Weisz's empirical potential[45] and the Animalu-Heine model potential give values of λ which are too large. The calculated resistivities on the other hand seem somewhat small. Perhaps this is a clue that the pseudopotential needs improvement; it is difficult to see how a more realistic model of the phonons could both lower λ and raise the resistivity.

The remaining metals are Hg, In, and Tl. The calculated value of λ in In agrees fairly well with experiment for the Animalu-Heine and Ashcroft-Lawrence potentials,[46] but is too high when the Cohen-Bergstresser potential[47] derived from InSb is used. The calculated values of λ for Hg are in fair agreement with McMillan's value of 1.0, but not with the more reliable estimate[9] of 1.6. In Tl the Animalu-Heine potential gives a value of λ somewhat too large. In both Hg and Tl, the spherical phonon spectrum could possibly be at fault; neutron scattering measurements of the phonon spectra are not yet available to check this. More likely, however, a more reliable pseudopotential is what is needed.

IV. OBSERVATIONS

Shortly after the BCS theory, Pines[21] discussed a number of regularities in the occurrence of superconductivity in the Periodic Table, most of which had been previously pointed out by Matthias.[48] Two regularities in particular apply to the simple metals:

(i) Superconductivity is enhanced as the valence Z is increased in a row of the Periodic Table.

(ii) Superconductivity is enhanced for fixed valence Z as r_s increases (this generally occurs as atomic number A increases in a given column).

The earliest comprehensive theoretical treatments of transition temperatures were estimates of the BCS coupling $N_{\uparrow}(0)V$ within the jellium model by Pines,[21] by Morel,[22] and by Morel and Anderson.[23] [$N_{\uparrow}(0)$is the density of states for a single spin orientation, half as large as $N(0)$.] In these calculations, Fermi-Thomas screening of point-ion potentials was assumed, and only longitudinal phonons were included, using a Debye spectrum with the Bohm-Pines velocity of sound. Pines calculated the quantity $\lambda-\mu$, and shortly afterwards Morel and Anderson improved the theory by noting that μ should be changed to μ^*. In spite of the shortcomings of the calculations, Pines succeeded in giving a fairly satisfactory explanation of the regularities (i) and (ii). The present calculation is the most comprehensive survey since that time for the simple metals. In terms of numerical agreement with experiment, much has been gained by using empirical pseudopotentials and phonon spectra. However, the simplicity of earlier calculations had the advantage of providing a simple scheme for explaining the empirical rules (i) and (ii). It is not nearly so obvious where these regularities originate in the present calculation, but it seems worthwhile to attempt to uncover these origins insofar as is possible.

McMillan[9] noted that λ as given in Eqs. (2.2) or (2.9) can be approximated by a simple model

$$\lambda\cong\frac{1.51m_b}{r_s}\frac{\langle v^2\rangle}{(\langle\omega^2\rangle/\Omega_p{}^2)}, \tag{4.1}$$

where $\langle v^2\rangle$ is an appropriate dimensionless average of the pseudopotential $V(q)$ squared:

$$\langle v^2\rangle=\int_0^{2k_F}V^2(q)q^3dq\bigg/\int_0^{2k_F}V^2(0)q^3dq \tag{4.2}$$

and is a measure of the strength of the pseudopotential as it affects λ. The quantity Ω_p is the ionic plasma frequency and $\langle\omega^2\rangle^{1/2}$ is an average over-all phonon frequency for which McMillan suggests using the average of longitudinal and transverse peaks in the phonon density of states. The ratio $\langle\omega^2\rangle/\Omega_p{}^2$ is a measure of the amount by which electronic screening reduces the phonon frequencies from their "bare" values. In the jellium model this is given simply by a dielectric function, and a measure of the screening is

$$\langle\omega^2\rangle/\Omega_p{}^2\approx\tfrac{1}{2}q_D{}^2/k_s{}^2=(1/8r_s)(3\pi^2/Z)^{2/3}, \tag{4.3}$$

where k_s is the Fermi-Thomas screening wave vector. The potential strength $\langle v^2\rangle$ is a simple function of r_s in the jellium model, and can be approximated by $0.075r_s$ in the region $2<r_s<5$. The actual behavior is shown in Fig. 4. Combining these results we see that λ should scale as $r_sZ^{2/3}$ in the jellium picture.

McMillan has also written Eq. (4.1) in a slightly different fashion

$$\lambda\cong N_{\uparrow}(0)\langle I^2\rangle/M\langle\omega^2\rangle, \tag{4.4}$$

where $\langle I^2\rangle$ is the average of $[qV(q)]^2$ over the Fermi surface, and is related to $\langle v^2\rangle$ by

$$\langle I^2\rangle=2k_F{}^2(\tfrac{2}{3}E_F)^2\langle v^2\rangle. \tag{4.5}$$

We have computed the various parameters in Eqs. (4.1) and (4.4) using the choice

$$\langle\omega^2\rangle^{1/2}=\tfrac{1}{2}(\omega_L+\omega_T). \tag{4.6}$$

The results are shown in Table VI, using the empirical nonlocal pseudopotential for Be, Mg, Zn, and Cd, and Animalu-Heine potentials for several other metals. The resulting values of λ are generally too small by about 50%, and the agreement could be improved by choosing a somewhat smaller value of $\langle\omega^2\rangle$. Apart from this effect, there are still significant differences between

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[45] G. Weisz, Phys. Rev. **149**, 504 (1966).

[46] N. W. Ashcroft and W. E. Lawrence, Phys. Rev. **175**, 938 (1968).

[47] M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).

[48] B. Matthias, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1957), Vol. 2.

TABLE VI. Values of various parameters entering the simplified calculation of λ. The pseudopotentials mentioned in row 1 are identified in Table III.

Pseudopotential	Be Tripp	Mg Kimball	Zn Stark	Cd Stark	Al HA	In HA	Tl HA	Sn HA	Pb HA
$N_\uparrow(0)$[states/eV atom]	0.031	0.208	0.093	0.107	0.187	0.189	0.151	0.212	0.270
$\langle I^2\rangle[(\text{eV}/\text{Å})^2]$	41.2	3.1	10.2	9.5	11.2	6.8	7.5	8.4	8.6
$N_\uparrow(0)\langle I^2\rangle(eV/\text{Å}^2)$	1.29	0.65	0.95	1.01	2.09	1.28	1.14	1.78	2.32
$(M/m)\langle\omega^2\rangle(\text{Ry}^2)$	0.44	0.12	0.16	0.17	0.30	0.13	0.12	0.17	0.13
$N_\uparrow(0)\langle I^2\rangle/M\langle\omega^2\rangle=\lambda$ (approximate)	0.12	0.23	0.24	0.24	0.29	0.41	0.41	0.43	0.75
λ (exact calculation)	0.26	0.31	0.42	0.40	0.53	0.89	1.07	0.78	1.34
$\langle v^2\rangle$	0.059	0.036	0.050	0.093	0.030	0.043	0.058	0.033	0.042
m_b	0.30	1.00	0.59	0.54	0.97	0.74	0.55	0.73	0.86
$\langle\omega^2\rangle/\Omega_p{}^2$	0.118	0.088	0.080	0.121	0.074	0.049	0.048	0.038	0.032
$r_sZ^{2/3}\langle\omega^2\rangle/\Omega_p{}^2$	0.35	0.37	0.29	0.50	0.32	0.24	0.25	0.21	0.18

values of λ predicted by Eqs. (2.9) and (4.4). These differences reflect mainly the details of the pseudopotential, which are washed out in the average in Eq. (4.2). However, we have found that Eq. (2.9) predicts values of λ that are independent of the crystal structure, provided m_b and the phonon spectrum do not change. This helps to justify the simple form, Eq. (4.4), which should be adequate at least for discussing general trends. The following observations can be made:

(a) The jellium model tends to overestimate the coupling strength and the phonon frequencies rather badly, but these effects cancel to some extent in calculations of λ.

(b) The scaling of the phonon frequencies predicted by the jellium model, Eq. (4.3), is roughly obeyed. This can be seen from the last row of Table VI where values of $r_sZ^{2/3}\langle\omega^2\rangle/\Omega_p{}^2$ are shown. Variations of a factor of 3 still occur, but there is greater regularity in this quantity than there is in $\langle\omega^2\rangle/\Omega_p{}^2$ which is also shown in the Table. The remaining irregularities would be considerably reduced if $Z^{5/3}$ were used instead of $Z^{2/3}$. (However, the alkalis deviate in that $\langle\omega^2\rangle/\Omega_p{}^2$ scales like r_s instead of like $1/r_s$.) The remaining variations in $\langle\omega^2\rangle/\Omega_p{}^2$ seem random, and probably reflect the rather complex fashion in which phonon frequencies depend on the pseudopotential and the crystal structure.

(c) The situation with the pseudopotential strengths $\langle v^2\rangle$ is somewhat more random. In Fig. 4 values of $\langle v^2\rangle$ for various metals are plotted against the value of r_s, and compared with the value in the jellium model. Animalu-Heine potentials are used for all except the divalent hexagonal metals Be, Mg, Zn, and Cd. A roughly linear increase of $\langle v^2\rangle$ with r_s can be detected within the trivalent and quadrivalent metals. However, for the divalent metals where the potentials are most reliable, there is no perceptible order. In the monovalent alkalis, an inverse relationship appears between $\langle v^2\rangle$ and r_s; this same inversion was noted above for the behavior of $\langle\omega^2\rangle/\Omega_p{}^2$.

(d) The net result is that the empirical rules appear to be explained for metals of valence 3 and 4, with the jellium model providing the correct explanation except that empirically λ should scale as $r_sZ^{5/3}$ instead of $r_sZ^{2/3}$. In the alkalis we find λ *decreasing* with r_s. This contradicts both the empirical rules and the Animalu calculation[11] based on theoretical phonon spectra. We have no explanation for this phenomenon. Finally, no regularities emerge for the divalent metals. Matthias[48] also noted this phenomenon. For completeness it should be noted that the empirical rule (ii) was not intended to apply to the alkalis. The regularity applying to the alkalis is the observation that monovalent metals are not superconductors. However, the present calculation indicates that this regularity should be broken in the case of Li.

McMillan[9] noted another regularity among the bcc transition metals V, Nb, Ta, Mo, and W. He found that the parameter $N_\uparrow(0)\langle I^2\rangle$ was very close to a constant value of ~6 eV Å^{-2} in these metals, although the parameters $N_\uparrow(0)$ and $\langle I^2\rangle$ individually varied by nearly an order of magnitude. The fairly wide variation of λ in this group of metals is then entirely dominated by the term $M\langle\omega^2\rangle$, which measures the lattice stiffness. This same regularity occurs for the computed values of $N_\uparrow(0)\langle I^2\rangle$ in the divalent hexagonal metals Be, Mg, Zn, and Cd, when empirical nonlocal pseudopotentials are used. These results are shown in Table VI. Once again $N_\uparrow(0)$ and $\langle I^2\rangle$ vary individually by an order of magnitude. The regularity is not quite as striking here as it is

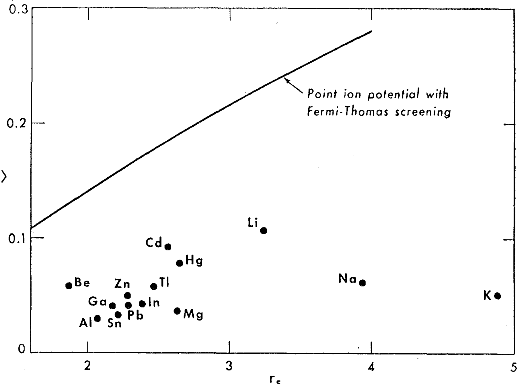

FIG. 4. Dimensionless parameter $\langle v^2\rangle$ plotted against r_s. The value of $\langle v^2\rangle$ is calculated using empirical nonlocal pseudopotentials for Be, Mg, Zn, and Cd, and using the Animalu-Heine potential for various other metals. The solid line is the value for a point ion potential with Fermi-Thomas screening.

for McMillan's bcc transition metals; the scatter of values of $N(0)\langle I^2\rangle$ is somewhat larger, and the range of values of λ spanned is not so wide. However, it is possible to offer some qualitative explanations for this phenomenon in the simple metals, as opposed to the transition metals where it is as yet entirely unexplained. It is easier to discuss this effect in terms of dimensionless parameters

$$N_{\uparrow}(0)\langle I^2\rangle = \text{const}\times Zm_b\langle v^2\rangle/r_s^4. \tag{4.7}$$

The divalent metals have just enough electrons to fill up their Brillouin zone and condense into an insulating state. They would do just this if the potential $\langle v^2\rangle$ were large enough. Magnesium has the weakest pseudopotential of the four metals (and the smallest value of $\langle v^2\rangle$), and its Fermi surface is quite free-electron-like. The value of λ is moderately small, partly because of the weak pseudopotential. The other divalent metals have stronger pseudopotentials, and the Fermi surface distortion is quite sensitive to the potential. The most important effect is that the area of the Fermi surface is reduced to 50% or less of the free-electron area, and the density of states as measured by m_b is correspondingly reduced. This has the effect of keeping λ relatively small, in spite of large electron-phonon matrix elements. Thus a strong pseudopotential can inhibit superconductivity as much as enhance it, and the net effect will clearly act to prevent large variations in $N_{\uparrow}(0)\langle I^2\rangle$. Why it should be so close to constant is still not clear.

V. CONCLUSION

For most of the simple metals we have had good success in computing λ and T_c. This adds further weight to the already existing body of evidence that electron-phonon properties of simple metals can be calculated accurately from empirical pseudopotentials, and that the superconducting properties can be calculated from the electron-phonon interaction and the screened Coulomb interaction, with no other interactions necessary. The assumptions of phonon and Fermi surface isotropy appear to be empirically justified. The evidence points to the conclusion that a single empirical pseudopotential can accurately describe both the Fermi surface of a metal and the electron-phonon coupling.

General trends in superconductivity can be partly explained by a jellium model, because this model happens to predict roughly correct behavior for the pseudopotential strength and the phonon frequencies as a function of valence Z and density r_s for many metals. However, the exceptions, such as the divalent hexagonal metals, are widespread, and no metal except possibly metallic H, behaves much like jellium. The details of the pseudopotential change λ from its jellium value in three ways. First through decreasing the coupling strength $\langle v^2\rangle$, second by changing the density-of-states mass m_b, and third by producing variations in phonon spectra.

It would be very interesting to know the superconducting properties of the predicted high-pressure metallic phase of H. According to the jellium model, the coupling λ should be quite small because both Z and r_s are small. However, Ashcroft[49] has suggested that the phonon frequencies may be considerably lower than the jellium prediction, and metallic H may be superconducting at quite high temperatures. This result seems plausible on the basis of simple arguments like those of Sec. IV. The jellium model should be fairly good for predicting the coupling strength $\langle v^2\rangle$, and this quantity will be large at nearly all densities. The phonon spectrum of an assumed stable metallic H lattice would certainly contain modes softer than the jellium prediction. There is no reason to expect the mass m_b to be small. Thus, λ should be at least moderately large and T_c may be very high because of the large Debye temperature.

Finally, we would urge that Mg and Li be tested for superconductivity at low temperatures. The discovery of superconductivity in these materials would be a rather convincing demonstration that the theory of the transition temperature had come of age. The discovery of superconductivity in Li would be particularly interesting in that it would remove the dictum that monovalent metals are not superconducting, and add weight to the suggestion that H may be a superconductor at high temperatures and pressures.

ACKNOWLEDGMENTS

We would like to acknowledge useful conversations with L. M. Falicov, N. W. Ashcroft, J. F. Janak, and T. M. Rice. We are indebted to W. Reichardt for sending us his measured phonon spectra of Ga and In.

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[49] N. W. Ashcroft, Phys. Rev. Letters 21, 1748 (1968).