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Trends in Superconductivity in the Periodic Table

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A unifying scheme is proposed for a conceptual understanding of trends in superconductivity. Physical mechanisms propounded include effects of ionic-core size, *d*-band effects, filled *d*-core repulsion and multi-orthogonalized-plane-wave effects, on either of or both electron-phonon coupling and phonon frequencies.

I. INTRODUCTION

Ever since BCS theory and its refinement in the Nambu-Eliashberg formulation[1] have successfully explained superconductivity in microscopic terms, much effort has been devoted to the effective electron attraction causing the phenomenon and the criteria for its occurrence. It is now commonly believed that the dominant mechanism in metals and alloys is the virtual-phonon exchange. However, the criteria for its dominance over the direct Coulomb repulsion are still a subject of research, depending as it does on often unknown normal-state properties. While this is especially so for transition metals, much more progress has been made for nontransition metals, for which numerical calculations of T_c have been carried out by means of semiempirical physical parameters.[2] However, it is not at all clear in that work as to what are the underlying mechanisms which favor or suppress superconductivity and lead, for example, to the Matthias rules. In the present paper, we suggest a scheme of possible mechanisms, forming an overall coherent picture. The emphasis is on physical mechanisms.

For this purpose, we try to include the electron-phonon interaction self-consistently in the lattice dynamics. Previous discussions have variously emphasized either the role of the interaction directly in the coupling[2] or as it determines the lattice stiffness[3]; we wish to consider both. Clearly, the problem is too difficult to attempt in detail, but we hope a description in simple models carries some elements of truth. We employ jellium as a reference model, into which we introduce modifications in accordance with the type of metal. Special emphasis is made on the role of outer *d* states: as they participate in the electron attraction in transition metals, impede lattice polarization in noble metals, and affect *sp* electron-phonon coupling by hybridization in the pre- and post-transition metals. Furthermore, the effective ionic-core size in the pseudopotential, incorporated into the model, plays a determinant role.

In Sec. II we recall the phonon-induced electron attraction mechanism, and how it appears in the expression for T_c. In Sec. III, we develop modified jellium models, incorporating various features of real metals. In Sec. IV, we review trends in pseudopotential, which seem to be both empirically indicated and theoretically understandable, in particular the effective ionic-core size and the effect of *d* hybridization on pseudopotential strength. Incorporating these trends into the models of Sec. III, we see, in Sec. V, how a picture for T_c trends in metals emerges. We conclude in Sec. VI with a summary. Transition and rare-earth metals are reserved for a subsequent publication.

II. ELECTRON-PHONON INTERACTION AND T_c

The attractive electron interaction leading to superconductivity arises principally through phonon exchange. The criterion for superconductivity depends on the strength of this effect relative to the direct Coulomb repulsion. The effective electron-electron interaction $V_{\text{el-el}}(\vec{k}, \vec{k}', \omega)$, for the transition from momentum states $(\vec{k}, -\vec{k})$ to $(\vec{k}', -\vec{k}')$ with energy difference $\omega = E_{\vec{k}'} - E_{\vec{k}}$ and linear response of medium, is given by

$$V_{\text{el-el}}(\vec{k}, \vec{k}', \omega) = \frac{v(Q)}{\Omega[1+\chi(Q)]} + \sum_{\lambda} \frac{|I_\lambda(\vec{k}, \vec{k}')|^2}{M\Omega(\omega^2 - \omega_{\vec{q}\lambda}^2)}, \qquad (1)$$

where $I_\lambda(\vec{k}, \vec{k}')$ is the electronic matrix element of the change in crystal potential as one atom is moved,

$$I_\lambda(\vec{k}, \vec{k}') = \langle \psi(\vec{k}') \,|\, \vec{\epsilon}_{\vec{q}\lambda} \cdot \vec{\nabla} U \,|\, \Psi(\vec{k}) \rangle ,$$

$v(Q)/\Omega$ is the direct Coulomb repulsion $4\pi e^2/\Omega Q^2$ screened by the linear static function of the electron gas, $1+\chi(Q)$, which also screens the ionic potential in U; Q and q are, respectively, the momentum transfer and reduced momentum transfer in the first zone, in the extended zone scheme for the electron states; M and Ω are the ionic mass and atomic volume, respectively; and $\vec{\epsilon}_{\vec{q}\lambda}$ is the lattice polarization vector. For scattering close to the Fermi surface, ω is far smaller than Fermi energy E_F and so the electron gas responds to the disturbance adiabatically. Thus, the direct screened Coulomb repulsion is instantaneous. The ions, attracted by the electronic disturbance, follow in phase when the induced frequency ω is below the natural frequency $\omega_{\vec{q}\lambda}$ of the phonons. Electrons, adiabatically following the ions, are thereby effectively attracted by the electronic disturbance. For a macroscopic disturbance $Q = q \ll k_F$, ω is the Doppler frequency $\vec{q} \cdot \vec{v}_F$ of electrons moving with velocity $\vec{v}_F$ in the density fluctuation of wavevector $\vec{q}$. In general, one has a retarded interaction in which an electron disturbance induces a positive charge of ions to form around it in time ω_D^{-1} (ω_D is the Debye frequency). The high-frequency components $\omega > \omega_D$, which are out of phase with the disturbance, have by then destructively interfered. The cloud then attracts further electrons until, under destructive interference of all components, it is finally dissipated away. Short wave vector components $q \ll q_D$ are attractive in a smaller range of $\omega < \omega_{q\lambda}$, they cannot exceed the Coulomb repulsion term in magnitude at small ω (Sec. III C) and, moreover, smaller phase space is available. Therefore, the attraction is mainly mediated by high-q phonons. The interaction remains short range on account of the weak dispersion at high $\omega_{q\lambda}$.

The theory of superconductivity, incorporating the time dependence of the attractive interaction, was developed by Nambu and Eliashberg[1] and Morel and Anderson,[4] using Green's functions. A good fit to a numerical solution of their energy-gap equations by McMillan,[3] for an isotropic superconductor (see below) is given by

$$T_c = \frac{\Theta_D}{1.45} \exp\left[-\left(\frac{1.04\,(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right)\right] \tag{2}$$

in terms of λ, the average electron-phonon renormalization of electron mass,

$$\lambda = \int \frac{dS_k}{v_F} \int \frac{dS'_k}{v'_F} \sum_\lambda \frac{|I_\lambda(k, k')|^2}{M\omega_{q\lambda}^2} \bigg/ \int \frac{dS_k}{v_F} \tag{3}$$

and Coulomb pseudopotential μ^*,

$$\mu^* = \frac{\mu}{1 + \mu \ln E_F/\omega_D} , \tag{4a}$$

$$\mu = \int_0^{2k_F} \frac{dQ\, Q}{(2\pi)^2 v_F} \frac{v(Q)}{1 + \chi(Q)} . \tag{4b}$$

λ and μ are, respectively, the phonon-exchange term and the direct Coulomb term in $V_{\text{el-el}}(k, k', \omega = 0)$, with k and k' integrated over the Fermi surface; in μ, a Fermi sphere is taken. The parameter λ gives the enhancement of electron mass due to the wake of phonons induced by the electron traveling at constant momentum ($\omega = 0$), averaged over the Fermi surface (in the normal state at $T = 0$). In general, the Coulomb renormalization of propagators and vertices are included in λ and μ. In the weak-coupling limit $\lambda \ll 1$, the formula (2) becomes

$$T_c = \frac{\Theta_D}{1.45} e^{-1.04/(\lambda - \mu^*)} ,$$

provided λ is greater than μ^*, which is the condition for a nonzero solution for the gap equation. The Coulomb repulsion μ is less effective than the phonon-induced attraction λ on account of its instantaneous nature, and is reduced to μ^*. The origin of the factor $(1+\lambda)$ in the exponent of Eq. (2), is the electron-phonon renormalization of electron propagators, i.e., $(1+\lambda)^{-1}$, since the weight of pure electron component $|\Psi_k\rangle$ in the wave function, with phonon wake included, corrects the matrix elements and Fermi velocities. The electron-phonon renormalization of vertices is known to be negligible. The correction $0.62\lambda\mu^*$ to $\lambda - \mu^*$ comes from the effect of the instantaneous Coulomb repulsion on the time correlation between the attracting electrons. The McMillan formula becomes less reliable, however, for strong-coupling superconductors $\lambda > 1$, where the result is sensitive to the shape of the phonon spectrum. In this respect the solution for $\Delta(\omega)$, the energy gap for quasiparticles of energy ω, yields the phonon spectrum experimentally for strong-coupling superconductors, $\Delta(\omega)$ being observable, then, in the density of states in quasiparticle tunneling. For a pure crystal, Δ is anisotropic in $\vec{k}$ space but, in practice, specimens are sufficiently dirty for single Bloch states $|\Psi\vec{k}\rangle$ to have lifetime $\tau \ll \Delta^{-1}$. As long as $\tau \gg E_F^{-1}$, it is sufficient to average all quantities over constant energy surfaces, as in the McMillan formula above. The determining parameters are λ and μ^*; the Debye temperature Θ_D is of secondary importance.

III. MODELS

The account of trends in superconductivity will be developed in models that include the electron-phonon interaction self-consistently in the lattice dynamics. The reference model is jellium, with suitable modifications introduced as appropriate.

A. Jellium

The ions form a positive continuum, in which the electron gas is immersed. Slowly vibrating ions are adiabatically followed and screened by the responding electron gas, so that the ionic plasma frequency $\omega_M^2 = 4\pi e^2 Z^2/M\Omega$ is reduced to $\omega_q^2 = \omega_M^2/[1+\chi(q)]$, where $\chi(q)$ is the static susceptibility of the electron gas. There is no resistance to shear, and so no transverse vibrations. The direct Coulomb interaction between electrons $v(q)$ is modified by the linear dielectric function of the medium $\epsilon(q, \omega)$, viz.,

$$\epsilon(q, \omega) = 1 + \chi(q, \omega) - \omega_M^2/\omega^2 ,$$

to give an effective electron-electron interaction

$$V_{\mathrm{el\text{-}el}}(q,\omega)=\frac{v(q)}{\Omega\epsilon(q,\omega)}=\frac{v(q)}{\Omega(1+\chi(q)}\times\left(1+\frac{\omega_M^2}{1+\chi(q)}\,\frac{1}{\omega^2-\omega_q^2}\right). \tag{5}$$

The second term in the large parentheses of Eq. (5) is the phonon-exchange term. It is seen that the electron-phonon coupling is given by the Coulomb interaction screened by the electron gas, i.e.,

$$I(k,k+q)=\vec{\epsilon}\cdot\vec{q}\,(4\pi e^2Z/q^2)[1+\chi(q)]^{-1}\,. \tag{5$'$}$$

Alternatively, one may derive Eq. (5) by substituting (5′) into the second term of Eq. (1). In the static limit, $V_{\mathrm{el\text{-}el}}$ is zero for all q, so that under purely Coulombic forces, the positive continuous background adjusts to neutralize any disturbance over even the smallest distances (perfect screening). This condition gives [Eqs. (3) and (4b)]

$$\lambda=\mu=\frac{1}{(2\pi)^2v_F}\int_0^{2k_F}dq\,q\,\frac{v(q)}{1+\chi(q)}\,.$$

B. Point-Ion Lattice

Let us first consider the ionic lattice in a fixed unresponding background. The lattice is stable against compression and shear. The transverse-phonon frequencies, $s_\perp(q)$ in units of ω_M, pass linearly to zero with q, i.e., in the limit of no distortion, and the frequencies of compression waves are lowered in the structure as follows[5,6]:

$$\omega_M^2\rightarrow\omega_M^2\left(1-\sum_\perp s_\perp^2(q)\right). \tag{6}$$

Let us now return to the physical case in which the electron gas responds adiabatically to the lattice vibrations. It is instructive to compare the phonon frequencies to the jellium phonon frequency, written with the electronic contribution separated out:

$$\omega_q^2=\omega_M^2-\omega_M^2\chi(q)/[1+\chi(q)]\ \text{(jellium)}\,. \tag{7}$$

Equation (7) is modified by the lattice to Eqs. (9), with $F=1$. Likewise, $V_{\mathrm{el\text{-}el}}(Q,\omega)$, Eq. (5) becomes Eq. (10) for N scattering, $\vec{Q}=\vec{q}$, and Eq. (11) for U scattering, $\vec{Q}=\vec{q}+\vec{\tau}$. The model would be applicable to metallic H, see Sec. V A 1.

C. Pseudopotential Effects

Electron-ion pseudopotentials $W(Q)$ are introduced into the model through a form factor $F(Q)$. Section IV is devoted to the behavior of $W(Q)$ in various metals. It will be shown that

$$\frac{-4\pi e^2Z}{Q^2[1+\chi(Q)]}\rightarrow\frac{-4\pi e^2Z}{Q^2[1+\chi(Q)]}F(Q)=W(Q)\,. \tag{8}$$

$F(Q)$ equals unity at zero Q, Eq. (19), drops as Q increases, passes through zero at Q_0, and is finally zero at large Q. Trends in Q_0 and the behavior of $F(Q)$ at $Q\gtrsim Q_0$, where the ionic cores are sampled, will be considered in Sec. IV.

The jellium phonon frequency, Eq. (7), is transformed in the pseudopotential lattice[7] to

$$\omega_{ql}^2=\omega_M^2\left[1-\sum_\perp s_\perp^2(q)-\frac{\chi(q)F^2(q)}{1+\chi(q)}-\sum_\tau\left(\frac{\chi(q+\tau)[\vec{q}+\overleftrightarrow{\tau})/|\vec{q}+\vec{\tau}|\cdot\epsilon_{ql}]^2F^2(q+\tau)}{1+\chi(q+\tau)}-\frac{\chi(\tau)(\hat{\tau}\cdot\vec{\epsilon}_{ql})^2F^2(\tau)}{1+\chi(\tau)}\right)\right], \tag{9a}$$

$$\omega_{\vec{q}t}^2=\omega_M^2\left[s_\perp^2(\vec{q})-\sum_\tau\left(\frac{\chi(\vec{q}+\vec{\tau})[(\vec{q}+\overleftrightarrow{\tau})/|\vec{q}+\vec{\tau}|\cdot\vec{\epsilon}_{\vec{q}t}]^2}{1+\chi(\vec{q}+\vec{\tau})}\times F^2(\vec{q}+\vec{\tau})-\frac{\chi(\vec{\tau})(\hat{\vec{\tau}}\cdot\vec{\epsilon}_{\vec{q}t})^2}{1+\chi(\vec{\tau})}F^2(\vec{\tau})\right)\right]. \tag{9b}$$

It is assumed that phonon polarizations can be defined as longitudinal and transverse, which of course is strictly only for $\vec{q}$ along lines of symmetry. Also assumed is that lattice mixing of orthogonalized-plane-wave (OPW) is negligible. The effective electron-electron interaction of the jellium model, Eq. (5), now becomes

$$V_{\mathrm{el\text{-}el}}(\vec{q},\omega)=\frac{v(\vec{q})}{\Omega[1+\chi(\vec{q})]}\times\left(1-\frac{\omega_M^2F^2(\vec{q})}{1+\chi(\vec{q})}\,\frac{1}{\omega_{\vec{q}l}^2-\omega^2}\right) \tag{10}$$

for N processes, and

$$V_{\mathrm{el\text{-}el}}(\vec{Q},\omega)=\frac{v(\vec{Q})}{\Omega[1+\chi(\vec{Q})]}\times\left(1-\frac{\omega_M^2F^2(\vec{Q})}{1+\chi(\vec{Q})}\sum_\lambda\frac{(\hat{\vec{Q}}\cdot\vec{\epsilon}_{\vec{q}\lambda})^2}{\omega_{\vec{q}\lambda}^2-\omega^2}\right) \tag{11}$$

for U processes, $\vec{Q}=\vec{q}+\vec{\tau}$. Putting

$$\frac{(\hat{\vec{Q}}\cdot\vec{\epsilon}_{\vec{q}\lambda})^2F^2(\vec{Q})}{1+\chi(\vec{Q})}\equiv D_{\vec{Q}\lambda}\,,$$

and expressing $\omega_{\vec{q}\lambda}^2$ in units of ω_M^2 thus, $\omega_{q\lambda}^2=\omega_M^2s_{q\lambda}^2$, we write the above equations in the static limit, this being the relevant limit for the McMillan formula, Eqs. (2)–(4),

$$V_{\mathrm{el\text{-}el}}(q,0)=\frac{v(q)}{\Omega[1+\chi(q)]}\left(1-\frac{D_{ql}}{s_{ql}^2}\right), \tag{12a}$$

$$V_{\mathrm{el\text{-}el}}(Q,0)=\frac{v(Q)}{\Omega[1+\chi(Q)]}\left(1-\sum_\lambda\frac{D_{Q\lambda}}{s_{q\lambda}^2}\right), \tag{12b}$$

$$s_{ql}^2=1-\sum_\perp s_\perp^2(q)-D_{ql}\chi_q-\sum_\tau(D_{q+\tau,l}\chi_{q+\tau}-D_{\tau l}\chi_\tau), \tag{13a}$$

$$s_{qt}^2 = s_\perp^2(q) - \sum_\tau (D_{q+\tau,\,t}\chi_{q+\tau} - D_{\tau t}\chi_\tau) . \tag{13b}$$

The electron polarization $\chi(Q)$ at metallic densities includes correlation effects, neglected in random-phase approximation (RPA).

The renormalization of $\omega_{q\lambda}^2$ arises as follows. The distorted lattice, with its new periodicity, scatters electrons through $\vec{q}$ and $\vec{q}+\vec{\tau}$, mixing wave functions. The mixing is most pronounced among states which scatter elastically one into the other, i.e., states on the Fermi surface. Thus, the electron gas forms a screening cloud about the ions, with Fourier components $\vec{q}$ and $\vec{q}+\vec{\tau}$, provided that $|\vec{q}+\vec{\tau}| \leq 2k_F$ (for spherical Fermi surface). The latter condition is expressed by a sharp drop in $\chi(\vec{Q})$ when Q reaches $2k_F$. In other words, the electron cloud cannot respond with wavelengths too short with respect to interelectronic spacing, on account of Pauli repulsion.

$V_{\text{el-el}}$ is determined by $F(Q)$, as it affects the electron-phonon coupling both in the numerator $D_{\vec{Q}\lambda}$ and in the phonon frequencies $s_{\vec{q}\lambda}$. At small q, $q \ll q_D$, the Debye wave number, $V_{\text{el-el}}(\omega=0) \geq 0$ is required for stability, since over distances covering many ions, there can be no overscreening of a static disturbance in equilibrium under electrical forces. Within microscopic distances, say Q_0^{-1}, however, static overscreening can occur, depending on the strength of the pseudopotential, and $V_{\text{el-el}}(\omega=0)$ can be negative. We may therefore suspect that it is the behavior at large q, where $V_{\text{el-el}}$ is sensitive to the magnitude of Q_0 and $F(Q_0 \lesssim Q \lesssim 2k_F)$, and for which the phase space is large, that is determinant in superconductivity. The reader may be puzzled by our emphasis here on static properties. Of course the dominant negative region of $V_{\text{el-el}}(Q,\omega)$ is a dynamical phenomenon occurring at finite $\omega \sim \omega_D$. The point is that McMillan's dynamical calculation, which resulted in Eq. (2), delivers an answer which is expressed in terms of static electronic properties.

In this section, we have dealt with the effects of a single OPW on $V_{\text{el-el}}$. There are some cases, however, where there is considerable lattice mixing of several OPW, due to either Bragg reflection or strong pseudopotential scattering. These cases will be dealt with in turn in Sec. V.

D. Core-Core Repulsion

So far we have considered metals where the lattice spacing is determined by the conduction-electron gas, roughly of the order of the screening length. The displacement of ions is resisted by the Pauli repulsion among the conduction electrons. Thus, in jellium, $\omega_q^2 = (\omega_M^2/\kappa^2)q^2$ for $q < \kappa$, where $\chi(q) = \kappa^2/q^2$, and in RPA

$$\frac{\omega_M^2}{\kappa^2} = \frac{mv_F^2}{3\Omega}\,\frac{\Omega}{M} = \frac{B_{\text{FE}}}{M/\Omega} ,$$

where B_{FE} is the free-electron bulk modulus. The situation is different when the ionic cores overlap between neighbors. These will likewise resist overlap by Pauli repulsion, now of the electrons in core states. Weak overlap splits a filled core shell into a narrow tight-binding band, which contributes little to the cohesive energy since the band is filled, bonding and antibonding states. Some cohesion arises from s-d mixing,[8] since while the total energy of the s and d bands remains unchanged, the compensatory higher s states are empty. However, a larger overlap (say due to displacement from equilibrium) between the *nonorthogonal* cores will raise the average d-band energy sharply.[9] For lattices where this effect comes into play, it can be incorporated into $\omega_{\vec{q}}^2$, Eqs. (9), by the addition of $\omega_{c\lambda}^2(\vec{q})$, given by nearest-neighbor forces. Brout[10,11] suggested that this extra stiffness will suppress D/s^2, and hence superconductivity in these metals. In jellium, the equations are modified as follows. The dielectric function of the medium $\epsilon(\vec{q},\omega)$ is given by

$$\epsilon(\vec{q},\omega) = 1 + \chi(\vec{q},\omega) - \omega_M^2/[\omega^2 - \omega_c^2(\vec{q})] , \tag{14}$$

leading to Eq. (5) for the effective electron-electron attraction, where $\omega_{\vec{q}}^2$ is now given by

$$\omega_{\vec{q}}^2 = \omega_M^2/[1 + \chi(\vec{q})] + \omega_c^2(\vec{q}) . \tag{15}$$

IV. TRENDS IN PSEUDOPOTENTIALS

We have shown in Sec. III C [Eqs. (10) and (11)] how the parameter λ of Eqs. (2) and (3) will be extremely sensitive to the form factor $F(Q)$ and hence $W(Q)$, in the region $Q \sim 2k_F$. We therefore present in this section a brief review of present understanding of pseudopotentials.[12,13] In our subsequent analysis of superconductivity trends, we will rely heavily on the qualitative behavior of the pseudopotential, as it varies through the Periodic Table.

A. Simple Metals

In this section, we consider metals with simple ionic cores, i.e., where the pseudopotential will be tiny within the core region on account of orthogonality. While macroscopic lattice disturbances will scatter electrons attractively via the screened Coulomb potential, electron-ion scattering within core dimensions will be only weakly repulsive.

To establish a notation, we write the OPW $|\chi(\vec{k})\rangle$ for simple metals

$$|\chi(\vec{k})\rangle = |\vec{k}\rangle - \sum_\alpha \langle\alpha|\vec{k}\rangle|\alpha\rangle , \tag{16}$$

where $|\alpha\rangle$ are the core states and $|\vec{k}\rangle$ is a plane wave. In simple metals no d bands overlap the conduction band. The true wave function $|\Psi\rangle$ is expanded in OPW, thus

$$|\psi\rangle = \sum_{\vec{\tau}} c_{\vec{k}+\vec{\tau}} |\chi(\vec{k}+\vec{\tau})\rangle \; .$$

This can then be written

$$|\psi\rangle = |\phi\rangle - \sum_{\alpha} \langle \alpha | \phi \rangle | \alpha \rangle \; , \tag{17}$$

where $|\phi\rangle$ is the expansion $\sum_{\vec{\tau}} c_{\vec{k}+\vec{\tau}} |\vec{k}+\vec{\tau}\rangle$. ($|\psi\rangle$ in an angular-momentum expansion about an ionic center has mainly s and p components near the ion.) $|\phi\rangle$, the pseudo-wave-function, is then the solution of the Schrödinger pseudopotential equation with pseudopotential W,

$$W = V + \sum_{\alpha} (E - E_{\alpha}) |\alpha\rangle\langle\alpha| \; , \tag{18}$$

where V is the real unscreened ionic potential and E_{α} is the energy of $|\alpha\rangle$. Within the core region, the deep attractive V is largely canceled by the repulsive term, the "cancellation theorem," so that in the metallic close-packed structures, W is an over-all smooth potential. Lattice scattering is therefore weak. Likewise, a lattice wave $\vec{q}$, scattering through $\vec{Q} = \vec{q}$ and $\vec{Q} = \vec{q} + \vec{\tau}$, will scatter only weakly when Q^{-1} lies within the core. Although W is a nonlocal operator, matrix elements connecting states on a Fermi sphere depend on momentum transfer only, for spherical atoms. Therefore, in a given problem, W is local to the extent that such matrix elements suffice and/or nonlocality is weak. The response of the interacting electron gas to the lattice (in equilibrium or disturbed) is to a good approximation[12–14] the response of a uniform charge density, i.e., the response as calculated with plane waves, viz., $[1+\chi(Q)]^{-1}$ in Sec. III. The true charge density, that engendered by $|\psi\rangle$, has a hole in the core region compensated by a uniform increase outside, but in view of the small size of the cores this correction is a small effect. Nonlocality is also a small effect. Furthermore, the linearity of the response is much better justified than for point ions. From now on [and in Sec. III C, Eq. (8)], we define $W(Q)$ with the screening included.

The general shape, then, of the local pseudopotential $W(Q)$ must be that of the screened Coulomb potential at small momentum transfer (relative to $\langle k|W|k\rangle$ plus surface energy), thus

$$W(Q \to 0) = -4\pi e^2 Z/\kappa^2 = -\tfrac{2}{3} E_F \tag{19}$$

rising to zero at $Q = Q_0$, where Q_0^{-1} is of the order of R_c, the core radius, and usually positive but small as Q^{-1} passes within R_c. $W(Q)$ may be written in the form of Eq. (8). A simple model for the pseudopotential, the empty-core model, takes the pseudopotential as zero within R_c and Coulombic outside. The screened pseudopotential is then given by $W(Q) = -4\pi e^2 Z \cos QR_c / Q^2[1+\chi(Q)]$, and Q equals $\pi/2R_c$. The parameter Q_0 is the one best determined so far by experimental information on $W(Q)$,[12] and systematic differences between the elements can be related simply to atomic properties.[13] On the other hand, details of the strength of $W(Q)$, at Q above Q_0, are not understood theoretically, nor in most cases well-established experimentally. In the following paragraph we briefly mention the fitting to experiment, and then go on to discuss the trends in Q_0.

Empirically, the best source of information on pseudopotentials is Fermi-surface fitting.[12] The pseudopotential in Eq. (18) is not unique, the addition of a term $\sum_{\alpha} |\alpha\rangle F_{\alpha}$, with any function F_{α}, yields the same solutions for E and $|\psi\rangle$, when evaluated to all orders of perturbation theory, and so one makes the best choice for fast convergence of E. The freedom of choice lies at high Q; in practice, a suitable cutoff (or convergence) in W is made, and one fits the W at lower lying $\vec{\tau}$ to the Fermi surface. For application to electron-phonon scattering, however, W must be extrapolated between points $\vec{\tau}$, and made to pass to the correct limit for macroscopic ionic displacements, viz., Eq. (19). Clearly, uncertainties exist at various levels. First, the choice of cutoff is dictated by the information available from Fermi-surface data, and usually lies too low to produce reliable W in the region $Q \sim 2k_F$, crucial for electron-phonon scattering. Second, extrapolation between even well-established $W(\vec{\tau})$ can be ambiguous. Finally, although the validity of W, as in Eq. (18) and other forms, in the electron-phonon matrix, was established by Sham[15] and Austin *et al.*,[16] it is not certain that a truncated W, chosen for the energy calculation, is applicable to electron-phonon matrix elements. Otherwise, the equivalence of the screening and Coulomb vertex corrections of the electron-ion interaction in both the static and vibrating lattice was proven in Ref. 17.

The strongest trend in Q_0 can be understood as follows.[13] Along a row of the Periodic Table, R_c will decrease as the valency Z_{val} increases, since the higher ionic charge will pull in the core. The average lattice spacing, however, remains roughly constant relative to the changes in R_c. It turns out that the increase of Q_0 with Z_{val} goes roughly as does k_F, i.e., $Z_{\text{val}}^{1/3}$. Along a column of the Periodic Table, however, R_c stays roughly unchanged, because although the ionic charge increases so does the charge and principal quantum numbers of the core. It has been found that $Q_0 \sim 0.8(2k_F)$. Thus, scattering on the Fermi surface through Q in the range $Q_0 \lesssim Q \lesssim 2k_F$ is wide-angle scattering in the extended zone, with constant relative phase space. These processes are mostly umklapp even in monovalent metals.

A weaker trend[13] is a slight increase in $Q_0/2k_F$ on moving down a column of the Periodic Table. The series of heavy elements, Hg to Bi, have larger Q_0 on account of a relativistic effect which lowers the energy of the s state. The effective core radius Q_0^{-1}, must be small enough with respect to lattice spacing, for electrons to be (weakly) attracted towards ionic centers; in particular, Q_0 must be a little larger than the lowest τ for $W(\tau)$ to be negative. In group IIB, Q_0 comes out too close to the first shell of τ in Hg, for simple structures,[13] so that $|W(\tau)|$ would be tiny and lattice scattering suppressed. The distorted crystal structures are probably due to the energetic advantage of keeping $\vec{\tau}$ off Q_0 so as to increase $|W(\tau)|$. In the heavier group IIIB, this occurs in Ga and In; in Tl, Q_0 is sufficiently large with respect to the lowest $\vec{\tau}$ in the simple hcp structure, but a slight increase in lattice spacing is favorable to lattice scattering. Similarly, lattice spacing increases in passing from Sn to Pb.

The trend to smaller R_c, on moving to the right in the Periodic Table, leads to strong negative $W(\tau)$ for the first shell of $\vec{\tau}$, and the breakdown of perturbation theory for pseudo-wave-functions. Open-structured covalent bonding then becomes energetically preferable, with filled Brillouin zones in k space.[13]

The strength of $W(Q > Q_0)$ is in most cases less well established experimentally.[12] For this discussion we shall simply assume $W(Q > Q_0)$ to be small by the cancellation theorem, unless there is theoretical reason otherwise. In the remainder of this section, we review the physical mechanisms which can lead to the enhancement or further suppression of $W(Q)$, for Q greater than Q_0. These, together with the trends in Q_0, will subsequently be incorporated into a conceptual scheme for λ. However, alternatively proposed forms of $W(Q)$, with less theoretical basis, can be substituted as the case may be. The effects to be considered, now, are those of insufficient cores in the light metals, and of d states in the heavy metals. These lead to differences in the l components of W, and hence nonlocality.

B. Li and Be (First Short Period)

In these metals of the first short period there are no p states in the core, and so the p component of the pseudopotential about each ion remains totally uncanceled.[12] The lattice pseudopotential is therefore less smooth and strongly attractive midway between lattice sites, so that conduction electrons are attracted away from ions, thus enhancing p-like (with respect to ions) components in the wave functions. (Higher-l components are too small near ionic centers to be relevant.) Similarly, ionic displacements strongly repel conduction electrons. $W(Q)$ therefore has a large and positive hump above Q_0, and the lowest $\vec{\tau}$ lie in this region. Further elements along the row take up open covalent structures, presumably because of the large $W(Q > Q_0)$.[13]

C. Effect of d Band

Here we review the effect on the pseudopotential of d bands overlapping the conduction band.[12–14, 18] There are three cases to consider: the transition metals, where E_F lies within the overlap region; post-transition metals, where the d bands lie below E_F; and the pretransition metals, where a d band exists above E_F. In these metals, the $l = 2$ crystal potential near ionic centers, with centrifugal potential included, is deep enough, due to high atomic number and absence of core, to overcome the centrifugal potential and form troughs which localize d states. The potential for $l = 2$ is totally uncanceled by a core in the $3d$ series, and uncanceled in the n-core shell of the nd series for $n > 3$. The localized d states lie in the conduction band continuum. Resonance with degenerate states in the continuum, and neighboring localized d states, broadens these states into a band or subbands. In passing from left to right along a series, the d bands become increasingly narrow as the potential troughs deepen.

In the post- and pre-transition metals, the d bands are too far removed from E_F to participate in the virtual phonon exchange mechanism. On the other hand, the conduction electron-ion interaction must include the effect of hybridization with the ionic d states. First, in the undisturbed lattice in post-transition metals, the energy of single OPW on the Fermi surface is raised, anisotropically (i.e., nonlocal), in accordance with the coupling, and in pre-transition metals, is lowered, since hybridization separates states. Second, the periodic array of localized unhybridized d states will scatter the unhybridized OPW through $\vec{\tau}$, repulsively in post- and attractively in pre-transition metals, and similarly will a lattice wave $\vec{q}$. The strength of the effect depends on the proximity of the d states to E_F. The hybridized state on the Fermi surface has the wave function

$$|\tilde{\psi}\rangle = |\psi\rangle + \sum_d \frac{\langle d|\delta V|\psi\rangle}{E_F - E_d} |d\rangle .$$

δV is the difference between the free-ion potential V_{ion} and the potential V in the crystal in the neighborhood of an ion, and $|d\rangle$ is the free-ion d orbital. Unlike for the deeper-lying core states $|\alpha\rangle$, δV varies appreciably over $|d\rangle$, thus giving an appreciable hybridization matrix element. The single OPW components of $|\psi\rangle$ [which now include $|d\rangle$ with the core states in Eq. (16)] are coupled in second order by virtual d-level exchange with matrix elements,

$$\sum_d \frac{\langle \chi(\vec{k}+\vec{\tau})|\delta V|d\rangle \langle d|\delta V|\chi(\vec{k})\rangle}{E_F - E_d} . \tag{20}$$

E_d is the energy expectation value of the free ion $|d\rangle$ in the crystal. It is convenient in the pseudopotential formulation to proceed in this way whatever the distortion of real d orbitals in the crystal in the outer regions of a cell. This may entail truncating the free ion $|d\rangle$ to eliminate overlap between neighbors, with consequent redefinition of V_{ion} and δV; the correct d-band Bloch functions in the overlap region between ions is then build out of hybridization with OPW. In this way, Harrison[14,18] has generalized pseudopotential theory for d-band metals. The dominant additional contribution to W acting on the pseudo-wave-function ϕ at the Fermi surface, when E_d lies close, has matrix elements between pseudo-plane-waves $|\vec{k}\rangle$ and $|\vec{k}+\vec{\tau}\rangle$ obtained from expression (20) by substituting for the OPW and recalling that $\langle d|\delta V|\alpha\rangle = 0$. With $\vec{\tau}$ replaced by $\vec{Q}$ for lattice wave scattering, the matrix element takes the form

$$\sum_d \frac{\langle \vec{k}+\vec{Q}|\Delta|d\rangle \langle d|\Delta|\vec{k}\rangle}{E_F - E_d} ,$$

where

$$\Delta\,|d\rangle = \delta V\,|d\rangle - |d\rangle\langle d|\delta V|d\rangle .$$

In the noble metals, this term gives to the pseudopotential matrix element, $W(\vec{k}, \vec{k}+\vec{Q})$, a large positive hump for Q above Q_0. We refer to this as the hybridization repulsion. The consequent strong OPW mixing by the lattice ($\vec{Q}=\vec{\tau}$), as well as the nonlocality of $\langle \vec{k}|W|\vec{k}\rangle$, seems to be responsible for the strong Fermi-surface distortion, and at the same time strong wide-angle electron-phonon coupling ($Q > Q_0$). However, the noble metals are not superconductors, and their electrical resistivity is very low. We believe the explanation to lie in the low compressibility,[10,11] see Secs. III D and V A 2. The present form of W, with its characteristic hump, is derived in most band-structure fits.[12,13,19,20] However, a quite different form emerges from the fitting procedure of Fong and Cohen.[21] The pseudopotential we have chosen for the present discussion is the more easily understood physically,[22] though that of Ref. 21, employed in a recent calculation by Allen,[23] is easily accommodated into our scheme.

In the group-IIB metals, the d states are more strongly bound due to higher atomic number, and E_d lies further below E_F. Therefore, there is less hybridization than in the noble metals. There remains, however, some repulsion due to hybridization, in addition to the now more effective orthogonality repulsion. Hence in group IIB also (the positive), $W(Q \sim 2k_F)$ is enhanced.

The pre-transition metals, among alkalis and alkaline earths, have wide d bands near to and above E_F. Hybridization now lowers W in the region $Q \sim 2k_F$, so that it becomes small and even negative in the event that hybridization dominates the orthogonality repulsion. Metals higher up in groups IA and IIA (Na and Mg) have atomic numbers too small for the $l = 2$ ionic potentials to overcome the centrifugal potential. There are, then, no d troughs and hence no hybridization effects.

The validity of the present pseudopotential formalism for electron-phonon matrix elements has been investigated recently by Allen,[23] who finds that it is almost as good as Sham's theorem[15] for simple metals.

In the transition series, the d band overlaps the sp band at E_F. The $l = 2$ component of W, totally uncanceled in the $3d$ series, and uncanceled in the n-core shell of the higher nd series, is now of prime importance at Fermi energy. The use of perturbation theory is no longer valid for estimating the effect on $|\psi\rangle$ in the overlapping regions of the Fermi surface, since W is now large. $|\tilde{\psi}\rangle$ is a thoroughly mixed function of the $|\psi\rangle$ and $|d\rangle$. Augmented-plane-wave-type methods are specially suited to this case, since the hybridization is automatically included. The d resonance and its coupling to the d component of $|\psi\rangle$ is expressed by the $l = 2$ phase shift δ_2 of the suitably chosen muffin-tin potential; δ_0 and δ_1 are usual weak pseudopotential phase shifts, and higher δ_l are usually negligible. The method is useful for estimating electron-phonon matrix elements, from parameters fixed by band-structure calculations, both in transition[24] and nontransition metals.[23,25,26] In these calculations, muffin displacements are assumed for lattice waves, and a suitable choice of muffin plateau relative to E_F ensures the condition in Eq. (19).[20]

V. TRENDS IN T_c

A. Monovalent Metals

1. Group IA. Alkali Metals

The free-electron Fermi sphere for $Z = 1$ lies well within the first Brillouin zone. With the exception of Li, $W(Q)$ is small in $Q_0 \lesssim Q \lesssim 2k_F$, and the Fermi surface is nearly spherical. We may therefore assume single OPW and small electron-phonon coupling at high Q. (Distortion of the Fermi surface increases in the heavier pre-transition alkalis, due to anisotropy of the single OPW energy $\langle k|W|k\rangle$, i.e. nonlocality and some OPW mixing towards zone boundaries.) Q_0 is of the order of q_D, the Debye wave number, so that wide-angle scattering processes $Q > Q_0$ are mostly U processes. The small electron-phonon coupling means small $\sum_\lambda D_{Q\lambda}/s^2_{q\lambda}$ on two accounts; directly through the above discussion, and because $s^2_{q\lambda}$ is raised by the reduction in electronic screening of the ions. U processes on the Fermi surface ($Q < 2k_F$) can only take place with sufficiently large q, $q > \tau - 2k_F$. Then, although $s^2_{q\lambda}$ itself is renormalized [Eqs. (13)], the effect is small because of small $D_{Q\lambda}$. Roughly, for U processes

$$\sum_\lambda \frac{D_{Q\lambda}}{s^2_{q\lambda}} \sim \frac{D_{Ql}}{1 - \sum_\perp s^2_\perp(q)} + \sum_\perp \frac{D_{Q\perp}}{s^2_\perp(q)} \;.$$

Similarly, for N processes with $Q = q \sim q_D \sim Q_0$, one has $D_{ql}/s^2_{ql} \sim D_{ql}/1 - \sum_\perp s^2_\perp(q)$. The reduction in the electronic screening of large-q lattice waves can be understood as follows. On account of the orthogonal-core effect, the screening charge will reside outside the core, in the region where the pseudopotential is most attractive. Within short wavelengths, therefore, there is no screening between the displaced ions, and they interact with their "bare" potential. These ideas are consistent with neutron spectroscopy data,[28] which indicate $\omega_{ql} \sim \frac{1}{2}\omega_M$ at large q in Na, K, and Rb. Vosko *et al.*[7] have made numerical calculations of the "bare" ionic transverse frequencies $\omega_M s_\perp(q)$ in Na, see Eqs. (6) and (9), and found that the experimental ω_{qt} are very nearly equal to $\omega_M s_\perp(q)$, and that $\omega^2_{ql} \gtrsim 0.75\omega^2_M[1 - \sum_\perp s^2_\perp(q)]$. Therefore, at high q, there appears to be very little screening indeed. The absence of superconductivity, then, has been traced to large ionic cores and weak pseudopotentials,[27] see Secs. IV A and IV C.

We remark parenthetically how the reduction in $W(q)$ is reflected in the stability of the metal, by studying the small-q limit (not relevant to superconductivity, see Sec. III C). At small q, $q \ll q_D$, $F^2(q) = 1 - \frac{1}{4}\pi^2 q^2/Q_0^2$ in the empty-core model (Sec. IV A), and $\chi(q) = \kappa^2/q^2 \gg 1$ and $s^2_\perp(q) = s^2_\perp q^2$ in Eqs. (13). Then s^2_{ql}, Eq. (13a), becomes

$$s^2_{ql} = q^2\left(\frac{1}{\kappa^2} + \frac{\pi^2}{4}\frac{1}{Q_0^2}\right) - \sum_\perp s^2_\perp q^2 \;. \tag{20}$$

The screening length κ^{-1} has been increased to $(1/\kappa^2 + \pi^2/4Q_0^2)^{1/2}$, which expresses the fact that the screening cloud is situated outside the core. We have, for small-angle scattering,

$$\frac{D_{ql}}{s^2_{ql}} = \frac{q^2/\kappa^2}{q^2/\kappa^2 + \pi^2 q^2/4Q_0^2 - \sum s^2_\perp q^2} \;.$$

The condition $D_{ql}/s^2_{ql} \leqslant 1$, for stability, is satisfied when $\pi^2/4Q_0^2 \geqslant \sum s^2_\perp$. (In the absence of core as in metallic H, the condition is satisfied by the increase in lattice scattering. This is the case treated by Pines[5] and will be further discussed below.)

Li presents a special case with a strongly repulsive pseudopotential for $Q_0 < Q \lesssim 2k_F$, and so $\sum D_{Q\lambda}/s^2_{q\lambda}$ is not suppressed. In contrast to the other alkalis, the strong repulsion of conduction electrons within the ionic core reduces the frequencies of short-wavelength phonons. The very-high-momentum components of the electron wave functions are therefore repelled. In consequence they follow the vibrating ions out of phase. It is these components which are the efficient screeners of phonons of wave numbers $q \sim q_D$, due to U processes. Similarly, in electron-electron scattering through $Q > Q_0$, the ions repelled by electrons in turn repel electrons, leading to a net attraction.

The strongly repulsive pseudopotential gives rise to strong lattice scattering of OPW. However, only in a small region about Q_0, where D/s^2 is suppressed for single OPW, will D/s^2 be effectively enhanced; otherwise D/s^2 is not sensitive to multi-OPW. Likewise, the direct Coulomb interaction, anyway unsuppressed, will be insensitive in order of magnitude. For small q, $q \ll q_D$, one has $D/s^2 \leqslant 1$, but for intermediate q large enough, D/s^2 should be larger than in other alkalis on account of U renormalization of s^2. From these considerations, it would seem that Li should be superconducting at low temperature; the continued absence of superconductivity in the range 10^{-3} °K remains unexplained, see Ref. 25.

A high-pressure metallic phase of H (hydrogen) would be expected to superconduct in this scheme, as there is no suppression of the Coulomb potential of the protons. Strong lattice scattering will mix off-Fermi-sphere states, which will have little effect on orders of magnitude at large Q, but play an important role at small q. This is to reduce the matrix elements at small q[5] so as to prevent an unstable solution, $V_{\mathrm{el\text{-}el}}(q, 0) < 0$, arising from the reduction of ionic plasma frequency by $\sum_\perp s^2_\perp(q)$. Thus, the lattice structure reduces the electronic screening, simultaneously with the ionic plasma frequency. The predicted metallic H should superconduct and may have a very high T_c on account of its light M (high Θ_D).

2. *Group IB. Noble Metals*

We believe, following Refs. 10 and 11, that the absence of superconductivity in the noble metals is due to core-core repulsion, impeding lattice vibrations, as discussed in Sec. III D. The stiffness of the lattice by d-core-core repulsion is indicated both by the compressibility, and the high-frequency end of the phonon spectrum. Taking as a rough reference the free-electron compressibility $\chi_{\mathrm{FE}} \equiv B^{-1}_{\mathrm{FE}} \propto r_s^5$, comparison of the measured compressibility[28] χ of noble metals, with those of alkalis, shows a drop in the χ of noble metals, far exceeding what might be expected from the high dependence on r_s in χ_{FE}. Comparison of the noble metals with Mg, group II*B*, and the metals of the nontransition groups III*B* and IV*B*, all with r_s of comparable order, indicate the χ values for noble metals grouped at a factor roughly $\frac{1}{2}$ smaller. Apart from Mg which has no d core, the higher-valence metals have smaller d cores (Sec. IV). Further evidence is supplied at the opposite end of the spectrum from neutron scattering data[29] for Cu and Ag, which indicate values of ω_{ql} greater than ω_M. Moreover, Born-Von Karman fits to the data need assume only nearest-neighbor forces, since the dispersion curves are smooth. The longer-range forces via conduction electrons, out to fifth-nearest neighbors in Na and K, are reduced to a secondary role in noble metals.

Counter to the core-core repulsion, stiffening the lattice, is a strong pseudopotential scattering electrons. As discussed in Sec. IV C, the proximity of d-band energies to E_F raises the electron-phonon coupling for wide-angle scattering by hybridization, so that the noble metals are expected to have strongly repulsive pseudopotentials for $Q_0 < Q \lesssim 2k_F$ (see, however, Refs. 21 and 23). Nevertheless, d-core-core repulsion seems to dominate, and suppress D/s^2 at all Q as discussed in Sec. III D. This is in contrast to the metals of group II*B*, see Sec. V C 1.

B. Polyvalent Metals $Z \geqslant 3$

There is no theoretical understanding of the relative strength of $F(Q \sim 2k_F)$ in these metals. However, we shall see that on the mere assumption of weak pseudopotentials, $F(Q \sim 2k_F)$ small by the cancellation theorem (Sec. IV A), the polyvalent metals would have stronger attractive electron-electron interaction than monovalent metals, due to stronger $s^2_{q\lambda}$ renormalization. Furthermore, more attractive U-scattering processes can take place. Finally, OPW mixing by the lattice might enhance electron-phonon coupling when this is weak[30] rendering $V_{\text{el-el}}$ less sensitive to the strength of single OPW coupling.

Our explanation will be based on the dependence of Q_0 on Z. We recall that Q_0 increases with Z as does k_F, while the average lattice spacing stays relatively constant. Therefore, Q_0 is greater than q_D. The actual positions of the $\vec{\tau}$ relative to Q_0, however, is a subtle matter,[13] see Sec. IV.

Phonon frequencies for large q are more strongly renormalized in polyvalent than in monovalent metals, as follows. Since q_D is well below Q_0, the N contribution is not suppressed in Eqs. (13), in contrast to the alkali metals, nor is the U contribution with $|\vec{q}+\vec{\tau}| < Q_0$. The expressions for $s^2_{q\lambda}$, Eqs. (13), become

$$s^2_{ql} \sim \frac{1}{1+\kappa^2/q^2} + \frac{\pi^2 q^2}{2Q_0^2} - \sum_{\perp} s^2_{\perp}(q) - \sum_{\substack{\tau \\ |\vec{q}+\vec{\tau}|<Q_0}} D_{q+\tau,\, l}\,\chi_{q+\tau}\,, \tag{21a}$$

$$s^2_{qt} \sim s^2_{\perp}(q) - \sum_{\substack{\tau \\ |\vec{q}+\vec{\tau}|<Q_0}} D_{q+\tau,\, t}\,\chi_{q+\tau}\,. \tag{21b}$$

The ions are more effectively screened in polyvalent metals because the ion core, which keeps the polarized electron cloud *out*, is pulled *in* by the higher ionic charge, without there being any corresponding change in lattice spacing. Hence, even short-wavelength ionic displacements are well screened. Finally, taking account of multi-OPW states, there would be an additional contribution from components $|q+\tau| \gtrsim Q_0$, otherwise suppressed when the single OPW form factor is weak above Q_0 (discussion below). Neutron spectroscopy[29] or superconductor tunneling data[31] confirm the high degree of cancellation in $\omega^2_{q\lambda}$; at large frequencies one obtains for the ratio ω^2_{ql}/ω^2_M (or s^2_{ql}), values $s^2_{ql} \lesssim 0.07$ for Pb, 0.06 for Sn, 0.07 for In, and 0.09 for Al and Tl, all to be contrasted with the results for alkalis, quoted previously. Furthermore, in contrast to alkalis and noble metals, there is a high degree of structure in $\omega^2_{q\lambda}$, confirming the influence of the electron gas; see also Kohn anomalies, Sec. V D. The high screening of phonons in these metals is indeed reflected in strong-coupling superconductivity.

On account of the strong renormalization of large-q phonons, one expects that wide-angle scattering, whether between single OPW states on the spherical parts of the Fermi surface or multi-OPW states, would be far more attractive than in alkali metals. Furthermore, the larger Q_0 relative to q_D implies more U processes for intermediate-angle scattering.

In this paragraph, we discuss in more detail the effect of multi-OPW. In the polyvalent metals, where the Fermi sphere crosses Brillouin edges, even small $W(\tau)$ strongly mix OPW by diffraction near intersections. When the single OPW form factor is weak, the electron-phonon matrix element can be effectively enhanced.[30] This would occur for states separated by $|\vec{Q}| > Q_0$ on the Fermi surface in the extended zone, if at least one of the states is multi-OPW. Only rarely would any destructive interference conspire to cancel the overall enhancement. Although in many polyvalent metals only a small fraction of Fermi surface is distorted [$W(\tau)$ being small], the density of states is very high there, a small Fermi velocity accompanying strong OPW mixing. Similar considerations apply when both states are multi-OPW. In that case, however, q can also go to zero, and the screened matrix element than passes to zero as $\vec{q}(4\pi e^2 Z/\kappa^2)$. There is no lattice distortion when q goes to zero, the two states are separated by $\vec{\tau}$ in the extended zone, and are equivalent on account of Bragg scattering. In that case, $V_{\text{el-el}} \geqslant 0$ is required for stability. However, for q large enough (larger than the separation between two sections of Fermi surface at the zone edge), the attraction is enhanced. We remark that quite generally the direct Coulomb repulsion will not be so sensitive in order of magnitude to OPW mixing.

In summary, it is conjectured that polyvalent metals favor the electron-electron attraction for the following reasons: phonon frequencies are more effectively screened due to smaller ion cores relative to lattice spacing, there are more U processes for intermediate angle scattering, and when pseudopotentials are weak for Q above Q_0, multi-OPW states enhance a significant amount of wide-angle scattering in the extended zone, both directly and in the phonon renormalization. Pseudopotentials need not be particularly strong for Q above Q_0 (but can be), and this seems qualitatively consistent with the nearly-free-electron nature of most of the Fermi-surface area. These ideas corroborate well in a qualitative way with the apparent rise in electron-phonon coupling strength with electron concentration, observed in the data on $\omega_{q\lambda}^2$ and T_c,[28,31,32] see above and Secs. V D and V E.

Finally, the present considerations offer an understanding of Matthias's empirical rules, that λ increases in going from $Z=3$ to $Z=4$, and that for fixed $Z=3$ or $Z=4$, λ increases with lattice spacing. The latter rule could be understood from the tendency towards larger Q_0, accompanying the increase in lattice spacing, as one moves down the Periodic Table to heavier metals (Sec. IV A). The shortening of the effective core radius Q_0^{-1} will then enhance the electron screening of $\omega_{q\lambda}^2$.

C. Divalent Metals

1. Group IIB

These metals have strong pseudopotential above Q_0 on account of hybridization with the d core (Sec. IV C). Unlike in the noble metals, we do not expect the core effect on ionic frequencies to impede superconductivity. Indeed, d cores are more strongly bound than in noble metals, and less likely to impede ionic vibrations. This relative unimportance of the core has been confirmed experimentally by neutron scattering on Zn,[29] and by superconductor tunneling in Hg.[31] At the high-frequency end of the spectra, ω_{ql}^2 is of the order $0.2\ \omega_M^2$, in marked contrast to noble metals. Thus, the difference between noble metals and group II*B*, with regard to superconductivity, most probably lies in the extent of d binding.

The relatively low values of T_c in Zn and Cd emerges from the numerical calculations of Allen and Cohen,[2] as follows. Since $W(\tau)$ is strong and the metals are divalent, it is energetically preferable to fill out the first Brillouin zone rather than the free-electron Fermi sphere. [Since $W(\tau)$ is repulsive, the electron concentrations are between rather than at ionic centers as in tight binding, but the energetic advantage is the same, independent of the sign of $W(\tau)$.] Thus, although multi-OPW will have little effect on the coupling, already strong for single OPW, it considerably reduces the area of Fermi surface by zone boundaries. As a consequence of the smaller phase space, λ is reduced both directly[2] and by the smaller renormalization of $s_{q\lambda}^2$. (The latter applies for U processes, especially where $q<Q$, since the screening in the numerator of D/s^2 is also diminished.) Thus, Zn and Cd are weak-coupling superconductors, in spite of strong pseudopotentials.[2]

In Hg, however, $|W(\tau)|$ is not so large (Sec. IV A), on account of the proximity of Q_0 to the lowest $\vec{\tau}$, and lattice scattering does not suppress the Fermi surface. At the same time, wide-angle scattering feels the strongly repulsive pseudopotential due to d hybridization, and so Hg is a strong-coupling superconductor.

2. Group IIA. Alkaline Earths

Be, with its strong pseudopotential, is a superconductor of low T_c, like Zn and Cd.[2] The main difference is the origin of the strong pseudopotential, viz., the absence of p core in Be (Sec. IV B).

Mg has a weak pseudopotential, as expected in view of the absence of any enhancing characteristics. The Fermi surface, therefore, is free-electron-like except at the intersection with the zone boundary. There is too little OPW mixing in the divalent metal to affect the electron-phonon coupling in λ.[2] However, the effect mentioned previously in the polyvalent metals, whereby phonons of large q are more effectively screened, due to the smaller core, than in alkalis, thereby increasing the attraction in wide-angle scattering, would begin to take effect here; see Eqs. (21). This may be responsible for the result of Allen and Cohen,[2] predicting superconductivity at low temperature.

Ca, Sr, and Ba are pre-transition metals, where d hybridization would suppress the repulsion of W, leaving a very weak (repulsive or attractive) pseudopotential for $Q_0 \lesssim Q \lesssim 2k_F$ (Sec. IV C) with complex Fermi surfaces due to the anisotropy of the hybridization, i.e., nonlocal effect. The weakening of pseudopotential, when a d band lies close above the Fermi surface (though not too near), is reflected in larger values of ω_D^2/ω_M^2 due to weaker screening; up to 0.4 in Sr, from specific-heat data,[28] compared to 0.2 in Be and Mg, from neutron spectroscopy.[29] The present considerations, therefore, predict no superconductivity at zero pressure in Ca, Sr, and Ba.

D. Kohn Anomalies

The U contribution to the screening of $\omega_{q\lambda}^2$ undergoes abrupt changes at $\vec{q}$ satisfying $|\vec{q}+\vec{\tau}|=2k_F$. This leads to kinks in the dispersion curve $\omega_{q\lambda}$, which suffers a little sharp drop as each new U process appears. Strictly speaking, the anomalies occur where $\vec{q}+\vec{\tau}=\vec{K}$, $\vec{K}$ being the extremum of the distorted Fermi surface in that direction. The strength of this effect is a measure of the strength of wide-angle electron-phonon coupling and electron density of states, both directly, in the pertinent scattering amplitude, and indirectly, in the size of the smooth background. In practice, the kinks are often difficult to observe, but all nontransition materials with relatively large Kohn anomalies are superconductors, viz., Zn, Al, Sn, Pb, and Pb-Tl alloys, and several transition metals.[29] Strong anomalies are accompanied by high T_c; thus Pb has stronger Kohn anomalies then Zn, Al, and Sn, and these move and grow weaker in Pb-Tl alloys as Tl is added and T_c drops. The prominence of the effect depends on the size of the smooth background, which emphasizes the link with T_c. Thus, in Cu, Kohn anomalies are tiny against a background dominated by core-core repulsion, whereas in Pb, the discontinuities are superimposed on a very small smooth background. These results corroborate well with the ideas above.

E. Alloys

The previous model can be employed for substitutional disordered alloys, of approximately equal atomic mass, with the common ("rigid") band of NZ electrons (Z is the mean electron-to-atom ratio) immersed in a lattice of fictitious "average" ions, each with average pseudopotential W, such that $W \to Ze^2 e^{-\kappa r}/r$ outside each ion core. The difference from true ions acts as a perturbation. $\omega_{q\lambda}$, in first approximation, is given by the ionic plasmon, charge Ze, screened by the electron gas[29, 32] (with shifts and finite lifetime due to the random differences). The electrons in first approximation are in OPW or lattice scattered multi-OPW states. However, the perturbation breaks the periodicity and mixes the states. As long as the single Bloch states have lifetime $\tau \gg E_F^{-1}$, the wave functions are not much affected; if $\tau < \Delta^{-1}$, the energy gap is isotropic (Sec. II). When the impurity concentration is high enough, then τ approaches E_F^{-1} (unless there is too little difference between pseudopotentials), and the OPW are thoroughly mixed (e.g., higher electron attraction towards more strongly charged ions).

Factors determining the variation of T_c with Z are difficult to disentangle. Only when pseudopotential differences are negligible are the determining factors simply the density of states and, where λ is sensitive to OPW mixing, the changes with Z in Fermi surface-Brillouin edge intersections. Otherwise, there are also changes in mean W and in "impurity" scattering of OPW. For want of detailed knowledge, however, it is difficult to discern trends, but we make some comments in the following paragraph.

Neutron scattering data on $\omega_{q\lambda}$, for binary alloys of Tl-Pb-Bi,[29] show that screening increases with electron concentration, thus indicating an increase of electron-phonon coupling (see Sec. V B). Dynes *et al.*[32] have made numerical computations of the gap equation, using pseudopotentials extracted from the $\omega_{q\lambda}$, but assuming absence of appreciable band effects. Havinga[30] on the other hand, arguing that an increase in electron-phonon coupling with Z is a consequence of greater lattice mixing of OPW, explains observed T_c variations in Tl-Pb alloys and several alloys of In, purely in those terms, by rough semiquantitative estimates. The inherent uncertainties of these estimates is apparent in the further observations on In-Sn alloys by Lambert *et al.*[33]; Allen and Cohen,[2] on the basis of their calculations, predict that dilute alloys of either group IB or group IIIB metals in Zn and Cd should have higher T_c, due to the "freeing" of the Fermi surface from the zone boundaries, see Sec. V C 1.

A different effect of alloying is the elimination of the core-core effect in noble metals. In concentrated alloys, where noble metal ions are no longer nearest neighbors, the lattice spacing is determined by the s-p electron gas resisting compression, rather than the repulsion between the closed d cores,[13] and likewise the phonon frequencies. Therefore, one would expect this change to be accompanied by the advent of superconductivity. Experiments by Luo and Andres[34] have indeed demonstrated that a phase transition in several alloys of a noble metal and base metal (including nonsuperconductors), semimetal or semiconductor, occurring at a high enough concentration of base metal, induces superconductivity. The mean valency Z has a range 1.3–1.8. In Robert's tables[35] are listed many such alloys and compounds; in particular, we may note CuS_2, CuSSe, $CuSe_2$, and CuSeTe all with lattice spacing of order 6 Å, to be compared with 2.6 Å in pure Cu.

F. Amorphous Metals

Bulk metallic glass with density close to the crystalline state should have a higher tendency to superconductivity. The looser structure reduces resistance to shear, so that s_{qt}^2 are smaller. Jellium has no resistance to shear, neither in the positive jellium nor the electron gas, but a random distribution of discrete ions will resist shear, together with its electron gas, especially at short wavelengths. OPW will be thoroughly mixed on the Fermi surface, where wavelengths are short. In practice, however, it is difficult to prepare bulk specimens of amorphous metals.[36] Amorphous superconductors are thin films, where effects due to low density, microcrystallinity, strong defects, and surface modes, may all play an intricate role, outside the domain of the present discussion.

G. Pressure Effects

A large number of metals are known to become superconducting at high pressures.[37] Furthermore, nonmetallic elements (insulators and semiconductors) in groups IV*B*, V*B*, and VI*B*, upon being squeezed into metals at high pressure (W becoming smooth), are good superconductors. At the opposite end of the periodic system, high pressure induces superconductivity in Cs, Ba, Y, and Ce, and raises the T_c of La quite spectacularly. On the other hand, in many other superconductors, T_c falls under pressure. We consider the consistency of these facts with the previous discussion.

The high-pressure metallic phases in groups IV*B*, V*B*, and VI*B* fall into the category of polyvalent metals, and so their superconductivity is consistent. Where single-phase T_c-P relationships are known, they show negative dT_c/dP (with the exception of Ge). Likewise, the zero-pressure metals in groups III*B* and IV*B* lower their T_c continuously with pressure, for each single crystalline phase. Discontinuities in T_c in either direction occur with crystalline phase transitions; the Tl I-Tl II phase transition is accompanied by a drop in T_c, whereas Sn II-Sn III has an increase in T_c, and likewise high-pressure modifications of Bi. However, for each single phase, T_c continues to drop under further application of pressure. These results can be understood within the previous scheme as follows. Under pressure, q_D and k_F are raised on account of smaller lattice spacing, leaving Q_0 unchanged; i.e., the lattice spacing is reduced with respect to the ionic-core radius, rendering the latter more effective in impeding electronic screening of short-wavelength lattice vibrations. Phonon frequencies are thereby raised. At the same time, the core reduces electron-phonon scattering through a wider range of scattering angle $Q_0 \lesssim Q \lesssim 2k_F$, between points on spherical parts of the Fermi surface, where states are single OPW. OPW mixing will also be affected by changes in $W(\tau)/\Omega$. Simple compressions of a lattice will not affect the Brillouin-zone–Fermi-surface intersections, but these are affected by lattice distortions, and at crystalline-phase transitions. It is too hard at present to discern trends in T_c accompanying crystal structure changes; there will be effects of OPW mixing on $g(E_F)$ and electron-phonon coupling, and some dependence on $s_1^2(q)$.

The negative dT_c/dP in Zn and Cd could be attributed to the increasing role of the core-core repulsion under pressure. The previous factors will be less important here, as the pseudopotentials are strong due to d hybridization. Likewise, in the noble metals, pressure would presumably not induce superconductivity, on account of the core-core effect. Very high pressure, however, will broaden the core band up to the Fermi energy, and the core will evaporate into the conduction band in the ground state. Thus, the noble metals will become superconducting transition metals; similarly, in group II*B*, T_c will rise, and ultimately in all polyvalent elements. In this connection, it is interesting to note a recent estimate[38] of the pressure of metallization of rare-gas solids to be about 5 Mbar, of order ten times presently attainable pressures.

The pre-transition metals Cs, Ba, and Y become relatively good superconductors under pressure.[39] (Y is included as pre-transition here, because the d band seems to be too little occupied in the ground state at zero pressure for the metal to superconduct.) Under pressure, the bands will be broadened and the occupation of the d band in the ground state increased, thus converting these metals into superconducting transition metals. The pre-transition metals higher up the Periodic column have increasingly wider s-d energy separation, and would require higher pressures. La, with a sufficient concentration of d electrons to be a good superconductor at zero pressure, exhibits a steep rise in T_c under pressure. In Cs, the induced T_c is accompanied by a crystalline phase transition, but, in the other metals, the rise of T_c with P can be seen in single-phase pressure ranges. In view of the phenomenon in Y, any influence of $4f$ states in La, Ba, and Cs seems secondary.

The present description is consistent with high-pressure resistivity data at normal-state temperatures.[40]

VI. SUMMARY

The trend favoring superconductivity in the right-hand side of the Periodic Table, both in zero-pressure metals and high-pressure metallic phases, was related to the reduction in ionic-core size for high valency ions, accentuated in heavy elements by a relativistic effect. The reduced core allows the screening cloud to sit closer to the ion, thus making for better screening of short wavelength lattice distortions, and at the same time, more electron-phonon U processes take place for intermediate-angle scattering. If pseudopotentials within the core are weak, as expected by orthogonality cancellation, then Bragg diffraction will enhance part of the wide-angle scattering in extended zone, and thereby also electronic screening of phonons; this will reduce sensitivity to the strength of single OPW coupling. Under pressure, T_c falls in a single phase, as lattice spacing is diminished with respect to the core. In alkalis, other than Li, the large core and orthogonality cancellation, further accentuated by empty d-band hybridization in the pre-transition alkalis, is unfavorable to superconductivity, and likewise in pre-transition group II*A* metals. Under pressure, d-transition character is induced as the d band reaches the Fermi level, and T_c appears. In post-transition metals, filled d bands will strengthen the repulsion of pseudopotential within the core region by hybridization, but, at the same time, resist lattice vibration by core-core repulsion. In noble metals, the latter dominates the phonon frequency and suppresses T_c, except in some alloys with base elements; in group IIB, the deeper-lying d core will not be felt except under pressure, when T_c drops.

The scheme proposed offers an over-all coherent picture in terms of simple physical principles, but is open to alternative descriptions at various stages.

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