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Rigid-Atom Electron-Phonon Coupling in the Tight-Binding Approximation. I*

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The intraband electron-phonon coupling, calculated in the tight-binding approximation, is derived from an effective deformation potential. This coupling agrees with expressions obtained by previous authors. The potential reduces to the Bardeen-Shockley deformation potential and to the Longuet-Higgins–Salem result in the long-wavelength and short-wavelength limits, respectively. The phonon-induced *d-d* coupling alone is shown to account for the order of magnitude of the superconducting transition temperature in transition metals. The McMillan procedure for the computation of the superconductive coupling is analyzed in the case when the Fermi level falls close to a pronounced Van Hove singularity in the electron density of states. In this case the behavior of the density of states n may dominate the behavior of the product nV, where V is the electron-electron effective interaction.

I. INTRODUCTION

Extensive experimental work shows clearly that the cohesive properties of transition metals are determined mainly by d-band electrons. Cohesive energy, atomic volume, thermal expansion coefficient, elastic constants, melting point, and heat of fusion all depend in a simple way (with rare exceptions) on the number of electrons present in the d-band.

Many of these properties have been satisfactorily explained[1] within a tight-binding approximation applied to the band structure of d bands. The electronic density of states depends critically on the atomic arrangement, so that the energy of the d-band electrons varies appreciably with lattice configuration. The expansion of this variation in terms of small spatially homogeneous deformations of a given lattice yields the contribution of d electrons to be taken into account in the determination of equilibrium lattice parameters,[2,3] thermal expansion coefficients,[2] and elastic constants.[2–6] Similarly, the comparison of the energies of d electrons in different crystallographic structures gives reliable indications on the relative stability of different lattices.[7–9]

Phonons may be viewed as time- and space-dependent deformations of the lattice, locally changing the parameters—in the tight-binding approximation, the overlap integrals—which determine the unperturbed band structure. The way that such an effect gives rise to the scattering of electrons by phonons was shown long ago by Bardeen and Shockley for semiconductors in the limit of a slowly varying deformation.[10] This limit is not appropriate to transition metals, where phonons of shorter wavelength are generally important. But there is no conceptual difference: The local changes of band parameters are effective over the whole range of electron and phonon wavelengths.

To our knowledge, the first calculation of the properties of the electron-phonon system in the tight-binding approximation, which is also used here, is due to Ovchinnikov.[11] He calculated the phonon self-energy arising from the electron-phonon coupling in the linear chain. Labbé extended[12] this calculation to three dimensions, but in his formulation the coupling was not explicitly exhibited. This was done[13] by Mitra and applied to the superconductivity of transition metals in Ref. 14.

An alternative derivation of the electron-phonon coupling based on the deformation-potential approach is presented here. Some difficulties of this approach are analyzed in the simple case considered. The approximations and physics underlying the work of Refs. 11–14 are also examined and raise in an obvious way the question of self-consistency. The self-consistent electron-phonon coupling will be considered in Paper II; it will be shown that the non-self-consistent theory[11–14] may be expected to give reasonable results at least for transition metals with a (nearly) half-filled band. Finally, our derivation exhibits the basic equivalence of the approach of Ref. 11 with that of Refs. 12–14 and with some well-known work[15,16] concerning the lattice stability of one-dimensional systems. At present our calculations are restricted to a single nondegenerate band. In this sense we compute the electron-phonon *intraband* coupling.

The model is applied to transition metals. In this particular case the simplicity of the model precludes all but semiquantitative or qualitative conclusions. For transition metals the model shows unquestionably that the intraband coupling considered here cannot be neglected in superconductivity calculations. It is very likely that it would give the main contribution to the superconductive coupling.

However, in his recent work,[17] Hopfield attributed the electron-phonon coupling in transition metals to a d-band–p-band term, i.e., his formulation, which can, in principle, account for the intraband coupling, was interpreted as if this latter term could be neglected for transition metals. The procedure employed in his computation was perturbative; i.e., Hopfield computed the coupling among the band states of the unperturbed lattice. This will *not* be the case in our computation, where already suitably deformed, but still approximatively orthonormal states are coupled among themselves. This fact obscures somewhat the comparison of the two methods, since the term "intraband coupling" does not correspond to the same physical reality in the two cases. It is believed[13] that the present method of displaced local electronic states accounts also for an appreciable part of what appears as an intraband coupling in the straightforward perturbation calculation, if such a calculation is convergent.

II. TIGHTLY BOUND ELECTRONS IN STRAINED LATTICE

In Secs. II and III we shall essentially rederive Mitra's result[13] while pointing out that it is based on the rigid-atom approximation, which is generally non-self-consistent in the tight-binding situation. Our derivation perhaps also clarifies his[13] Eqs. (2.8b) and (2.12).

The one-electron tight-binding state in the undeformed lattice (with one atom per unit cell and six nearest neighbors) is of the type

$$|\psi_l^0\rangle = \sum_j a_j^l \,|d(\vec{r}-\vec{R}_j)\rangle \; . \tag{2.1}$$

$\vec{R}_j$ is the equilibrium position of the atom in the undeformed state, on which is centered the local function $|d\rangle$. j denotes a *set* of integers defined by equation $\vec{R}_j = \sum_\alpha j_\alpha \vec{a}_\alpha$, where the $\vec{a}_\alpha$ are the lattice unit vectors. Since $\langle d(\vec{r}-\vec{R}_j)|d(\vec{r}-\vec{R}_i)\rangle \simeq \delta_{ij}$ the coefficients a_j^l measure the amplitude of the probability of presence of the electron in the state $|d(\vec{r}-\vec{R}_j)\rangle$, i.e., roughly within the corresponding Wigner-Seitz (WS) cell. For an energy eigenstate this probability is, in the bulk of the material, independent of j.

In the presence of the (quasi) static deformation the more or less deformed d function will follow the moving ion because the circular motion of an electron about the nucleus is very fast. It is reasonable to assume that the quasiorthogonality relation based on the strong localization of the d states remains valid,

$$\langle d(\vec{r}-\vec{R}_j-\vec{u}_j)|d(\vec{r}-\vec{R}_i-\vec{u}_i)\rangle \simeq \delta_{ij} \; , \tag{2.2}$$

provided that the atom displacements $\vec{u}_j$ are small. Hence, an energy eigenstate (or an adiabatic one) in the deformed lattice should be of the form

$$|\psi_l\rangle = \sum_j a_j^l \,|d(\vec{r}-\vec{R}_j-\vec{u}_j)\rangle \; . \tag{2.3}$$

The orthonormalization of these states is based upon the orthonormalization of the a_j^l because by Eq. (2.2)

$$\langle \psi_l|\psi_{l'}\rangle \simeq \sum_j a_j^{l*} a_j^{l'} \; . \tag{2.4}$$

Since the translational symmetry of the lattice is broken, $|a_j^l|^2$ depends on j. The Bloch-like states studied by Mitra do not have this property and *are not* the adiabatic states. It is physically important to realize this point since the sum of the density of presence $|a_j^l|^2$ over all occupied states l yields the total charge present on the site j,

$$\rho_j = 2 \sum_{l\;\mathrm{occ.}} |a_j^l|^2 \; , \tag{2.5a}$$

and the charge-density wave appears in the strained state,

$$\delta\rho_j = \rho_j - Q \; , \tag{2.5b}$$

where Q is the average occupation of the site in the undeformed lattice. Here we shall develop a method for calculating the coefficients a_j^l in a non-self-consistent approximation which comes out to be physically equivalent to that of Ovchinnikov, Labbé, and Mitra. But if the forces between the d electrons are long ranged this is not strictly sufficient, except when $\delta\rho_j$ computed in the non-self-consistent theory vanishes. This problem will be considered in Paper II.

The tight-binding equations giving the one-electron energies and the corresponding a_j^l in the strained lattice are

$$\left\langle d(\vec{r}-\vec{R}_j-\vec{u}_j)\right|\left(\frac{p^2}{2m}+V(\vec{r}-\vec{R}_j-\vec{u}_j)-E_l\right)\left|d(\vec{r}-\vec{R}_j-\vec{u}_j)\right\rangle a_j^l$$
$$= -\sum_{\delta\neq 0}\langle d(\vec{r}-\vec{R}_j-\vec{u}_j)|V(\vec{r}-\vec{R}_{j+\delta}-\vec{u}_{j+\delta})|d(\vec{r}-\vec{R}_{j+\delta}-\vec{u}_{j+\delta})\rangle a_{j+\delta}^l \; . \tag{2.6}$$

Here, V is the potential of the neutral atom carried by the moving atom and *screened*, in particular, *by the moving d function* occupied by the charge Q.

Basically the most serious approximation in Eq. (2.6) is the omission of the interaction of the excess charge $\delta\rho_j$ with the excess charges on (the same and) the other sites. In Paper II this will be justified, within the model, for particular deformations and band occupations.

The two-center integrals

$$\langle d(\vec{r}-\vec{R}_j-\vec{u}_j)|V(\vec{r}-\vec{R}_{j+\delta}-\vec{u}_{j+\delta})|d(\vec{r}-\vec{R}_j-\vec{u}_j)\rangle ,$$

describing the interaction of the charge on the site j with the neighboring neutral atom, are for simplicity discarded here, but were retained by Mitra[13] and in our previous work.[18] In Paper II, we shall argue that the charge-density wave $\delta\rho_j$ compensates these terms more effectively than the terms retained here.

Related to terms of this type is also the problem of the choice of the zeroth-order phonon frequencies. Usually,[11-13] these are chosen so as to vanish in the long-wavelength limit, i.e., the interatomic forces in the zeroth-order phonon Hamiltonian are assumed to be short ranged. Therefore the energy of interaction of the charge Q with neighboring neutral atoms is *already accounted for* by the zeroth-order phonon frequencies and should not be counted once again in the Born-Oppenheimer phonon self-energy. This complication does not occur if the two-center integrals in question are small with respect to the bandwidth terms retained in Eq. (2.6), which is a condition sometimes accepted in the tight-binding approximation.[1]

Equation (2.6) can be rewritten in the shortened form:

$$(E_0 - E_l)a_j^l = -\sum_{\alpha,\delta_\alpha} J(\vec{a}_{\delta_\alpha} + \vec{v}_{j\delta_\alpha})a_{j+\delta_\alpha}^l . \qquad (2.7)$$

Here we have introduced the following notation:

$$\begin{aligned} \vec{a}_{\delta_\alpha} &= \vec{R}_{j+\delta_\alpha} - \vec{R}_j = \pm\vec{a}_\alpha , \\ \vec{v}_{j\delta_\alpha} &= \vec{u}_{j+\delta_\alpha} - \vec{u}_j , \qquad (2.8) \\ J(\vec{a}_{\delta_\alpha} + \vec{v}_{j\delta_\alpha}) &= \int d(\vec{r} + \vec{a}_{\delta_\alpha} + \vec{v}_{j\delta_\alpha})V(\vec{r})d(\vec{r})\,d^3 r , \end{aligned}$$

where δ_α denotes the two neighbors on the axis $\vec{a}_\alpha$.

Equation (2.7) stands for a system of N coupled linear equations each relating the amplitude of presence in the state d on the site j to the amplitudes of presence on the six nearby sites. This linear system can be readily transformed to a single differential equation (Appendix A) on introducing the translational operator in the j space,

$$\left\{E_0 - E_l + \sum_{\alpha,\delta_\alpha} J(\vec{a}_{\delta_\alpha} + \vec{v}_{j,\delta_\alpha}) \exp\left[i\delta_\alpha\left(-i\frac{\partial}{\partial j_\alpha}\right)\right]\right\}a_j^l = 0. \qquad (2.9)$$

Here j_α is the site index running along the axis α.

This differential representation of the relevant linear operator is valid under two not too restrictive assumptions:

(i) The deformation is of the type

$$\vec{u}_j = \vec{u}_j^H + \vec{u}_j' , \qquad (2.10)$$

where $\vec{u}_j^H$ is the homogeneous deformation changing the reciprocal-lattice vectors from $\vec{b}_\alpha$ to $\vec{b}_\alpha'$ (such that $\vec{a}_\alpha\vec{b}_\beta = \vec{a}_\alpha'\vec{b}_\beta' = \delta_{\alpha\beta}$) but not altering the number of first neighbors, while $\vec{u}_j'$ obeys the Born–von Kârmân boundary conditions on the homogeneously deformed lattice.

(ii) The electronic states of the homogeneously deformed lattice obey the Born–von Kârmân boundary conditions.

Then the differential version (2.9) is valid for all deformations (2.10) and not, as usually used,[19] only for long-wavelength ones. One can differentiate with respect to j as if it were a continuous variable.

With the help of Eq. (2.9), the general form of a_j^l in the presence of the (periodic) deformation is immediately obtained [Eq. (A3)] and it is shown that a charge-density wave actually appears [Eq. (A5)].

III. EFFECTIVE DEFORMATION POTENTIAL

In this section we shall consider in some detail that part of the effective potential appearing in Eq. (2.9), which is linear in displacements. In fact, this term only is important for the conventional theory of superconductive pairing of electrons. The higher-order off-diagonal matrix elements lead to effects of a higher order than that usually considered in pairing, while the diagonal matrix elements do not contribute to pairing at all, but must, for example, be considered[11,12] in the computation of the phonon self-energy.

Following Ovchinnikov, Labbé, and Mitra we expand Eq. (2.9) with respect to displacements and retain only the linear term,

$$J(\vec{a}_{\delta_\alpha} + \vec{v}_{j\delta_\alpha}) = J(\vec{a}_\alpha) + \left.\frac{\partial J(\vec{R})}{\partial\vec{R}}\right|_{\vec{R}=\vec{a}_{\delta_\alpha}} \vec{v}_{j\delta} . \qquad (3.1)$$

It is here that the rigid-atom assumption is introduced, since the deformation of d functions and consequently of the short-range potential V in Eq. (2.8) would depend on displacements of all atoms, especially if the charge-density wave $\delta\rho_j$ does not vanish. But in Eq. (3.1) only the relative distance between the neighbors considered comes into play. This is certainly a rather rough approximation because the atom is quite polarizable.

As far as the charge displacement is concerned the rigid-atom assumption is more drastic in the tight-binding limit than in the free-electron limit. In the former case the entire charge density, related to the *well-localized* d function, follows the moving ion. In the latter case only a small, but *long-range* part, of the charge density, related to the departure from the uniform distribution, moves with the ion on which it is centered.[20] The strong divergence of the bare d pseudopotential at the ionic site justifies roughly the rigid-atom assumption in the tight-binding limit.

If the band is of the s type, the overlap integral depends only on the distance between sites; hence we have

$$\left.\frac{\partial J(\vec{R})}{\partial \vec{R}}\right|_{\vec{R}=\vec{a}_{\delta_\alpha}} = -q_0 J(\vec{a}_\alpha)\frac{\vec{a}_{\delta_\alpha}}{|\vec{a}_\alpha|} . \qquad (3.2)$$

Here q_0^{-1}, related to the range of the d function, is of the order of the interatomic distance.

This same relation should often be valid even for more complicated d functions, but then the interband coupling of several tight-binding bands must also be taken into account. Combining Eqs. (3.1), (3.2), and (2.9), we get

$$(E_l - E_0)a_j^l = (K + V_{\text{BS}})a_j^l . \qquad (3.3)$$

Equation (3.3) can be interpreted as an eigenvalue problem for the effective Hamiltonian $K + V_{\text{BS}}$, where K is the kinetic energy of electron hopping among the sites in the undeformed state,

$$K = \sum_{\alpha\delta_\alpha} J(\vec{a}_\alpha)\exp\left[i\delta_\alpha\left(-i\frac{\partial}{\partial j_\alpha}\right)\right] , \qquad (3.4)$$

and V_{BS} is the (linearized) effective potential introduced by the deformation of the lattice

$$V_{\text{BS}} = -q_0 \sum_{\alpha\delta_\alpha} J(\vec{a}_\alpha)\frac{\vec{a}_{\delta_\alpha}}{a_\alpha}\cdot\vec{v}_{j\delta_\alpha}\exp\left[i\delta_\alpha\left(-i\frac{\partial}{\partial j_\alpha}\right)\right]. \qquad (3.5)$$

It describes the variation of the hopping frequency of the electron towards the nearby sites when the distance between atoms is altered by the deformation. This is a short-range phenomenon and hence, as is easily seen from Eq. (A6), V_{BS} depends on j through the derivatives of $\vec{u}_j$ with respect to j rather than through $\vec{u}_j$ itself, in agreement with general theorems concerning broken symmetry. For slowly varying deformations and a simple cubic lattice with an s band, V_{BS} reduces to

$$V_{\text{BS}} \simeq 2q_0 J\left[\frac{\partial u_j^x}{\partial j_x}\cos\left(-i\frac{\partial}{\partial j_x}\right) + \frac{\partial u_j^y}{\partial j_y}\cos\left(-i\frac{\partial}{\partial j_y}\right) + \frac{\partial u_j^z}{\partial j_z}\cos\left(-i\frac{\partial}{\partial j_z}\right)\right] , \qquad (3.6)$$

where x, y, and z are the axes of the cube. For electrons (or holes) close to the extremities of the band, V_{BS} has the same form as the well-known Bardeen-Shockley deformation potential,[10] proportional to the divergence of the displacement.

Intuitively, one expects[12] that the static periodic deformation will open gaps in the original band structure, splitting the original Brillouin zone into smaller ones, corresponding to the new periodicity introduced by the deformation. This is established in Appendix A for the simple case considered here.

For example, Eqs. (3.3), (3.5), and (A3) can be combined in order to yield E_l in the presence of the *short-wavelength* static deformation $u_j = u_\pi e^{i\pi j}$ of the linear chain of the initially equidistant atoms. The result, shown in Fig. 1, is *essentially equivalent* to the Longuet-Higgins–Salem "exact" electronic spectrum[15] of an alternating chain. It is interesting to note that $\delta\rho_j$ [Eq. (A5)] vanishes[16] (whatever the occupation of the band), hence this result is self-consistent.

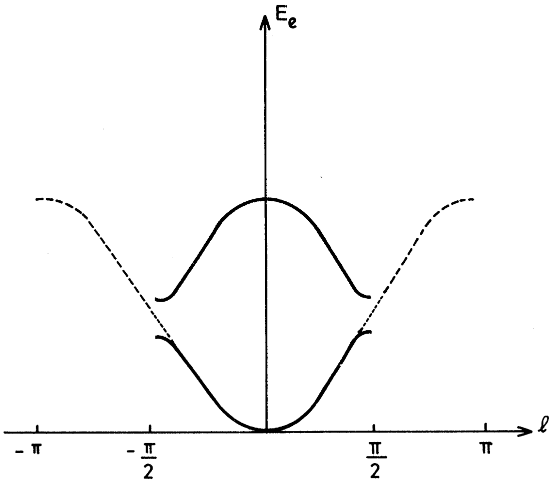

FIG. 1. Longuet-Higgins–Salem electronic spectrum of an alternating linear chain, $F_l = \pm 2J(\cos^2 l + 4q_0^2 u_\pi^2 \sin^2 l)^{1/2}$, derived from the linearized potential V_{BS} for a real deformation $u_j = u_\pi e^{i\pi j}$.

In three dimensions, the perturbative theory can be applied to the above set of equations. To the first order in V_{BS}^s the eigenstate (A3) of the Hamiltonian (3.3) is of the form

$$\exp(i\textstyle\sum_\alpha l_\alpha j_\alpha) + A_{ls}\exp[i\textstyle\sum_\alpha (l_\alpha + s_\alpha)j_\alpha] .$$

This agrees with Labbé's variational choice.[12] Then, not surprisingly, Labbé's phonon self-energy is the same as that computed, in Paper II, from the electron-phonon coupling, to be derived now.

First, we define a fermion operator $c_l^\dagger$ creating an electron in the state $|l\rangle$, Eq. (A1), and form the operator $\sum\langle l'|V_{\text{BS}}|l\rangle c_{l'}^\dagger c_l$ using Eq. (A2). In the absence of the homogeneous deformation only the off-diagonal terms appear in the sum. Next, we consider $\vec{u}_j$ as time dependent, i.e., expand it in terms of the usual phonon-creation–annihilation operators. This yields the electron-phonon coupling

$$g_{ls}^\lambda = (\hbar^2/2NM\omega_{s\lambda}^0)^{1/2} I_{ls}^\lambda ,$$
$$I_{ls}^\lambda = 2iq_0\textstyle\sum_\alpha J(\vec{a}_\alpha)(\vec{a}_\alpha/|\vec{a}_\alpha|a_\alpha)\cdot\vec{\epsilon}_{s\lambda}[\sin l_\alpha - \sin(l_\alpha + s_\alpha)] . \qquad (3.7)$$

Here, g_{ls}^λ describes the annihilation of one phonon with the polarization $\vec{\epsilon}_{s\lambda}$ and reduced wave vector $\vec{q}_s = \sum s_\alpha \vec{b}_\alpha$ with the scattering of an electron from the state with reduced momentum $\vec{k}_l = \sum l_\alpha \vec{b}_\alpha$ to the state with reduced momentum $\vec{k}_{l'} = \vec{k}_l + \vec{q}_s + \vec{K}_n$, where $\vec{K}_n = 2\pi\sum n_\alpha \vec{b}_\alpha$ is the reciprocal-lattice vector required for reducing $\vec{k}_l + \vec{q}_s$ to the first Brillouin zone. We note that a final state $\vec{k}_{l'}$ is coupled to the given initial state $\vec{k}_l$ by a coupling which depends only on the *reduced* phonon wave vector $\vec{q}_s$, irrespective of whether the process is a normal or an umklapp one. This property of the model is, in particular, in agreement with Sham and Ziman's statement that the umklapp matrix elements vanish in the phonon long-wavelength limit.

Equation (3.7) is essentially equivalent to Mitra's expression except that the arbitrary polarization replaces the longitudinal displacement, the variation of the overlap is assumed of the form (3.2) and the zeroth-order vibrational energy $\omega^0_{s\lambda}$ is specified to be related only to that part of d-electron energy which is not involved in the band formation. In one dimension it becomes the expression used by Ovchinnikov.

In the simple cubic lattice and for an s-band state l close to the extremity of the band I^λ_{ls} reduces for small s to

$$I^\lambda_{ls} \simeq -2iq_0 aJ(\vec{q}_s \cdot \vec{\epsilon}_{s\lambda}) , \qquad (3.8)$$

irrespective of whether we go to the final state by a normal or an umklapp process. The umklapp processes do not favor in any way the coupling of electrons to transverse phonons. However, Eq. (3.8) rapidly fails when the wavelength of the initial electron is neither too long nor too short and these electrons are coupled even to long-wavelength transverse phonons. Note that such behavior is particular to s electrons; the electrons with more complicated local functions would be coupled to the transverse phonons even in the long-wavelength limit.

It is perhaps worthwhile noting that in the work of Migdal and of Eliashberg, a model[21] was used in which $\omega^0_{s\lambda} \sim |s|$, and the electron-phonon coupling is of the type (3.8), as far as the s dependence is concerned.

In this section we have derived the electron-phonon Hamiltonian using a one-electron effective deformation potential, which was shown to be consistent with a Bardeen-Shockley or equivalent to a Longuet-Higgins–Salem Hamiltonian in the long- and short-wavelength limits, respectively. This effective potential gives *both* Labbé's renormalization of phonon frequencies and Mitra's electron-phonon coupling, which, as expected, is formally the same as that obtained in Ref. 14 from the Hubbard Hamiltonian.

IV. APPLICATION TO SUPERCONDUCTIVITY

The single-band six-nearest-neighbors rigid-atom model considered here is far too simple to account for the details of the situation in real solids. However, it allows more complete computations and contains explicitly two properties usually not found in the nearly free-electron models, namely, (i) the well-separated van Hove singularities in the electron spectrum, i.e., the points on the energy surface where the electron velocity vanishes; (ii) an exact treatment of umklapp processes. We shall discuss these points in some detail in relation to the superconductivity problem. For present purposes we need only the *weak-coupling limit* of the strong-coupling equations[21] determining T_c; i.e., we neglect the normal-state electron self-energy arising from the coupling with phonons. In this limit we have (see Appendix B)

$$1 \simeq \frac{1}{2}\int n(\omega')V_F(\omega', T_c)\,\frac{\tanh(\omega'/2k_B T_c)}{\omega'}\,d\omega' , \qquad (4.1)$$

where $n(\omega')$ is the electron density of states per spin and $V_F(\omega', T_c)$ the retarded[21] superconducting interaction. Usually only the unretarded part of $V(\omega', T_c)$ is considered (see Appendix B),

$$V_F(0) = \int_{E_F}\frac{d\sigma}{v_l}\int_{E_F}\frac{d\sigma'}{v_{l'}}\sum_\lambda \frac{\hbar^2|I^\lambda_{l,l-l'}|^2}{M\omega^{\lambda 2}_{l-l'}}\,\delta_{l'}\Big/ \int_{E_F}\frac{d\sigma}{v_l}\int_{E_F}\frac{d\sigma'}{v_{l'}} . \qquad (4.2)$$

The electron velocity v_l figures also in the definition of $\delta_{l'}$:

$$\delta_{l'} = \lim \mathrm{Re}\Delta_{l'}/\overline{\Delta}_{\mathrm{ph}} \quad \text{as } T \to T_c ,$$
$$\overline{\Delta}_{\mathrm{ph}} = \int_{E_F}(\Delta^{\mathrm{ph}}_l/v_l)\,d\sigma\Big/\int_{E_F}(d\sigma/v_l) . \qquad (4.3)$$

Here, $I^\lambda_{l,l-l'}$ is the coupling (3.7), $\Delta_{l'}$ is the total gap, and $\Delta^{\mathrm{ph}}_{l'}$ the phonon contribution to it. $d\sigma$ and $d\sigma'$ are the elements of the Fermi surface E_F at T_c, corresponding to the integrations over l and l', respectively. It is convenient, although not necessary, to define $\overline{\Delta}_{\mathrm{ph}}$ as in Eq. (4.3), and *consequently* $V_F(0)$ by Eq. (4.2).

Equation (4.1) differs from the usual expression by the fact that $n(\omega')$ and $V_F(\omega', T_c)$ are retained under the sign of integration. In fact the characteristic variable in Eq. (4.1) is $\omega'/k_B T_c$; therefore it is only when $n(\omega')V_F(\omega', T_c)$ varies slowly on this scale that it may be reasonably replaced by the Fermi-level value $n_F V_F \equiv \lambda - \mu$ of McMillan[22]; but this is even better justified if the variation is slow on the scale fixed by ω_D. Here λ is the phonon contribution,

$$\lambda \equiv n_F V^{\mathrm{ph}}_F(0), \qquad (4.4)$$

and μ the Coulomb pseudopotential correction. V^{ph}_F is defined on replacing in Eq. (4.2) $\delta_{l'}$ by $\delta'_{l'}$, where $\delta'_{l'}$ is defined by an expression such as (4.3) except that the total average gap $\overline{\Delta}$ replaces $\overline{\Delta}_{\mathrm{ph}}$. McMillan puts also $\delta'_{l'} = 1$.

In Refs. 22 and 17 it was proposed that $n_F V^{\mathrm{ph}}_F$ is a smooth function of the position of the Fermi level [and *a fortiori* $n(\omega')V^{\mathrm{ph}}_F(\omega', T_c)$ of ω']. We shall examine this proposal within our tight-binding model and distinguish between two opposite situations: (i) when the magnitude of the electron velocity is (roughly) constant over the relevant energy surfaces; (ii) when it vanishes at certain points of the relevant energy surfaces, giving rise to the pronounced Van Hove singularities in the density of states.

V. TRANSITION METALS

McMillan proposed[22] that the computation of $V_F^{\text{ph}}(0)$, given by Eq. (4.2), may be separated in the computation of an electronic quantity given by

$$\langle I^2\rangle = \int \frac{d\sigma}{v_l}\int \frac{d\sigma'}{v_{l'}} \sum_\lambda \left| I^\lambda_{l,l-l'}\right|^2 \bigg/ \int \frac{d\sigma}{v_l}\int \frac{d\sigma'}{v_{l'}}, \tag{5.1}$$

and a phonon quantity, which strictly speaking is mixed, given by

$$M\langle\omega^2\rangle = \hbar^2\langle I^2\rangle / V_F^{\text{ph}}(0), \tag{5.2}$$

V_F^{ph} being itself defined below Eq. (4.4). As is easily seen from Eqs. (5.1), (5.2), and (4.2), the necessary condition for $\langle\omega^2\rangle$ to be determined by the phonon spectrum only is that the electron-velocity weighting factor should not play an important role. This occurs if the electron velocity is nearly constant over the Fermi surface. Usually, this amounts *at least* to the requirement that the Fermi energy falls far from the Van Hove singularities in the density of states, since in the Van Hove points the inverse of the electron velocity diverges and $\langle\omega^2\rangle$ becomes a complicated mixed electron-phonon quantity. An analysis of the tunneling experiments[23] on Ta actually suggests that $\langle\omega^2\rangle$ is, at least in this metal, mostly determined by the phonon characteristics. Hence we adopt the McMillan separation for transition metals.

The computation of $\langle I^2\rangle$ within the model was described in detail in our previous work[14]; the result for an orthorhombic lattice was

$$n_F\langle I^2\rangle \approx q_0^2 E_c^d, \tag{5.3}$$

where E_c^d is the cohesive energy of d electrons

$$E_c^d = -2\int^{E_F} E\, n(E)\, dE. \tag{5.4}$$

Therefore, *far from* the Van Hove singularities the density of states is eliminated from the coupling constant λ. E_c^d goes through a broad maximum[8] for a half-filled band even if the density of states goes there through a marked minimum. Such a minimum occurs in our model when one overlap in Eq. (3.4) dominates strongly over the two others. The maximum in $n_F\langle I^2\rangle$ remains, however, since the phonons which are important when the band is half-filled are strongly coupled to the electrons.

One should be careful when applying result (5.3) to transition metals. In transition metals the d band is fivefold degenerate. The densities of states in bcc metals arising from e_g and t_{2g} d functions, however, have nearly the same form as the total density of states.[1] As is easily seen the d-interband electron-phonon coupling is of the same order of magnitude as the intraband one. According to Ref. 24 this can be roughly accounted for on counting E_c^d in Eq. (5.3) not per atom per d function but only per atom. If the whole procedure is meaningful the *effective* q_0 should then be of the order of 1 Å^{-1}. Moreover it should be almost constant within a period, even when the crystallographic structure changes, and eventually weakly varying from one period to another. The numerical results are shown in Table I. The agreement of the empirical values of $n_F\langle I^2\rangle$ with our semiquantitative prediction is astonishing. Thus, we believe that the superconductivity in transition metals may be attributed to d electrons coupled by phonons alone. Moreover the relative smallness[25–27] of $n_F\langle I^2\rangle$ in the fourth ($3d$) period is understood from Eq. (5.3) without the introducing the q_0^2 values. In our model, the relative smallness of overlap integrals in this period is due to the better localization of the $3d$ functions.

The elimination of n_F from the product $n_F\langle I^2\rangle$ in Eq. (5.3) should not be taken as a serious proof that this occurs exactly also in λ of real metals. This result is based on the assumption that $\langle\omega^2\rangle$ is an electron-independent quantity and, furthermore, on the oversimplified model used in the calculation of $n_F\langle I^2\rangle$.

VI. VAN HOVE SINGULARITIES

The separation given by Eqs. (5.1) and (5.2) is not useful when the Van Hove singularity is close to the Fermi level, since, as has already been pointed out, $M\langle\omega^2\rangle$ becomes a mixed electron-phonon quantity, which must be calculated. Thus, we must actually calculate V_F^{ph}. The calculation of $n\langle I^2\rangle$ becomes superfluous.

For simplicity we shall consider only Van Hove singularities such that most of the density of states at relevant energies for superconductivity comes from the energy surface elements close to the Van Hove points. Then we have

$$n(\omega') \approx \textstyle\sum_p n_p(\omega'), \tag{6.1}$$

where $n_p(\omega')$ is the contribution of the pth point.

The reciprocal of the vanishing electron velocity appears not only in Eq. (6.1), but also in Eq. (4.2) [and (4.3)]. If

$$\sum_\lambda \frac{\hbar^2 |I^2_{l,l-l'}|^2}{M\,\omega^{\lambda 2}_{l-l'}}\,\delta'_{l'}$$

is a slowly varying function, characterized by some average value V_{pq}, with l and l' each close to the pth and qth Van Hove points, respectively, then from Eq. (4.2)

TABLE I. Starred elements are superconducting. E_c are the measured values of cohesive energy. $q_0^2 E_c$ is obtained on multiplying the first line by q_0^2 except for Cr, Mn, and Fe. $n_F \langle I^2 \rangle$ are the Hopfield (H) and McMillan (M) estimations of this parameter. q_0 is fitted to V and Ta.

$q_0 = 0.93$ Å^{-1}	Ti*	V*	Cr	Mn	Fe	Co
E_c (eV/at.)	4.85	5.3	4.1	2.9	4.3	4.4
$q_0^2 E_c$ (eV/Å^2 at.)	4.2	(4.6)	≈ 4.8	≈ 4.6	≈ 4.2	3.8
$n_F \langle I^2 \rangle$ (eV/Å^2 at.)	2.7^{H}	4.6^{M}				
$q_0 = 0.91$ Å^{-1}	Zr*	Nb*	Mo*	Tc*	Ru*	Rh
E_c (eV/at.)	6.3	7.6	6.8	6.6	6.7	5.8
$q_0^2 E_c$ (eV/Å^2 at.)	5.2	6.3	5.7	5.5	5.6	4.8
$n_F \langle I^2 \rangle$ (eV/Å^2 at.)	3.0^{H}	7.2^{M}	6.8^{M}			
$q_0 = 0.87$ Å^{-1}	Hf*	Ta*	W*	Re*	Os*	Ir*
E_c (eV/at.)	6.3	8.1	8.6	8.1	8.1	6.9
$q_0^2 E_c$ (eV/Å^2 at.)	4.8	(6.1)	6.5	6.1	6.1	5.2
$n_F \langle I^2 \rangle$ (eV/Å^2 at.)	2.7^{H}	6.1^{M}	6.3^{M}	8.1^{H}		

$$V_F^{\mathrm{ph}}(0) \approx \sum_{pq} n_p(0)\, n_q(0)\, V_{pq} \Big/ \sum_{pq} n_p(0)\, n_q(0). \qquad (6.2)$$

Usually only one kind of Van Hove singularity will appear in the relevant energy interval, i.e., n_p is independent of p. Therefore, according to Eq. (6.2), $V_F^{\mathrm{ph}}(0)$ is approximately independent of the density of states. Note that, owing to the definition (4.3), $\delta'_{l'}$ is roughly equal to one in the interesting region. The argument (6.2) can be readily extended to small ω'.

In the model considered in the preceding sections, such Van Hove singularities can occur at the high-symmetry points X of the Brillouin zone. As is easily seen from Eq. (3.7), if the vector joining two points p, q is a reciprocal-lattice vector, then by umklapp $V_{pq}^{(U)} = V_{pp}$ [and also $(V_{pp} = V_{qq})$]. In the computation of such V_{pq}, the long-wavelength modes lying approximately within the Van Hove energy surface E_H are selected out from the phonon spectrum. But when the low-frequency phonons become important, retardation effects are favored and the validity of the replacement of $V(\omega', T_c)$ by the unretarded interaction (4.2) should be reexamined for each particular case (see also Appendix B).

In conclusion, if the magnitude of the electron velocity is small over some localized parts of the Fermi surface, then the behavior of the density of states may determine the behavior of the product nV. However, according to Eq. (4.1) the density of states at the Fermi level will not be the parameter determining $k_B T_c$ if it varies rapidly on this scale.

This can be easily seen in an oversimplified model where the "Van Hove peak" is represented by a δ function, i.e., $n(\omega') = B\delta(\omega' - \omega_H^C)$. Here $2B$ is a total number of states per atom in the peak and $\omega_H^C = E_H - E_F$, where E_F is the Fermi-level position at T_c. Inserting this density of states in Eq. (4.1) it follows immediately (V is the superconducting interaction) that

$$4 k_B T_c = \frac{2\omega_H^C}{\tanh^{-1}(2\omega_H^C / BV)} \; . \qquad (6.3)$$

This is exactly the Thouless "strong-coupling" result[28] for T_c [his Eq. (8)]. Thus, the BCS equation for T_c contains, as pointed out by Thouless, his result for $\omega_H^C = 0$, but it also contains his same result for arbitrary ω_H^C. Note that T_c is weakly dependent on the occupation of the peak for $\omega_H^C \approx 0$, where it goes through a broad maximum. A similar calculation[29] at 0 °K yields also the well-known relation $2\Delta_0 = 4k_B T_c$ for $\omega_H^C = 0$. Note that for $\omega_H^C = 0$ the superconducting interaction V coincides strictly with $V_F(0, T_c) \simeq V_F(0)$.

This "strong-coupling" result is obtained here from the weak-coupling equation (4.1); the term "strong coupling" is taken here with a different meaning from that given by Eliashberg, Schrieffer, Scalapino, and Wilkins. Note however that Eq. (6.3) remains valid, with a redefined V, if the phonon-induced renormalization of electrons in the normal state is taken into account.

The high values of T_c in V_3Si, Nb_3Sn, ..., were previously attributed by us[30] to peak effect similar to that first considered by Thouless, i.e., to the broad maximum of T_c on the occupation scale. A more detailed discussion of $V(\omega', T_c)$ for this case than that of Appendix B will be presented elsewhere.

VII. CONCLUSION

The approach presented here makes explicit the close interrelationship of properties such as cohesive energy, equilibrium lattice parameters, elastic constants, and electron-phonon interaction. This is achieved through the introduction of an effective Hamiltonian describing the tightly bound electrons in the homogeneously or periodically strained lattice. In particular, it is shown how the variation of the electronic band energy due to the opening of new gaps in the presence of periodic deformations is just a static counterpart of the electron-phonon interaction.

The part of this paper dealing with superconductivity is based on the single-band model and is therefore only qualitative or semiquantitative. The importance of the band-structure effects is exhibited through the study of Van Hove singularities. The answer to the question how important is n_F in the product $n_F \langle I^2 \rangle$ thus depends on the detailed knowledge of the band structure of transition metals.

A hint was given by Ovchinnikov and Mitra on how to obtain the electron-phonon coupling from a knowledge of the band structure; here we show how important it is for superconductivity. This should give rise to new developments in the vast and still so superficially understood area of metals and metallic compounds containing electrons which are far from free.

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APPENDIX A

First we prove that Eq. (2.9) is valid under assumptions quoted in the text. For simplicity's sake we limit the proof to the linearized potential (3.5) only; the proof can be extended to some more complicated situations.

Owing to its additivity V_{BS} can be splitted into $V^H_{\mathrm{BS}} + V'_{\mathrm{BS}}$, corresponding to the two deformations (2.10). $\vec{\mathrm{v}}^H_{j\delta_\alpha}$ and hence V^H_{BS} are independent of j; i.e., V^H_{BS} is of the same type as K, Eq. (3.4). Hence the functions $e^{i\Sigma_\alpha l_\alpha j_\alpha}$ are the (derivable) eigenfunctions of $K + V^H_{\mathrm{BS}}$, whatever the magnitude of V^H_{BS}. Here, l_α are the components of the reciprocal wave vector $\vec{\mathrm{k}}'_l = \sum_\alpha l_\alpha \vec{\mathrm{b}}'_\alpha$; since the Born–von Kármán conditions are kept valid all along the growth of $\vec{\mathrm{u}}^H_j$, l_α, and thus the product $l_\alpha j_\alpha$, *is an invariant* of the deformation $\vec{\mathrm{u}}^H_j$. The energy variation (3.3) of such states arises only from the variation of overlap integrals, as required by Eq. (2.7).

When V'_{BS} is present the state $e^{i\Sigma_\alpha l_\alpha j_\alpha}$ is no longer an invariant state of the effective Hamiltonian; however the space spanned by these states is an invariant space. This is a sufficient condition for a^l_j to be derivable with respect to j. Again we split $V'_{\mathrm{BS}} = \sum_s V^s_{\mathrm{BS}}$, each corresponding to a particular deformation component $e^{i\Sigma s_\alpha j_\alpha}$ of the wave vector $\vec{\mathrm{q}}_s = \Sigma_\alpha s_\alpha \vec{\mathrm{b}}'_\alpha$. Applying (successively) each V^s_{BS} on the given electron state $e^{i\Sigma_\alpha l_\alpha j_\alpha}$ we obtain, as required, the states $e^{i\Sigma_\alpha (l_\alpha + s_\alpha) j_\alpha}$ belonging to the original space.

The only remaining complication arises from the fact that when j is considered as a set of continuous variables the states such as $e^{i\Sigma_\alpha l_\alpha j_\alpha}$ and $e^{i\Sigma_\alpha (l_\alpha + 2\pi n_\alpha) j_\alpha}$, n_α integer, are distinguishable, while with j_α discrete they represent the same electron state $|l\rangle$. This is taken account of if, *after* operating with $V_{\mathrm{BS}}(j, \partial/\partial j)$, the quantity j is taken as discrete, i.e, the above two states are taken as equivalent. This is explicitly exhibited through the relations

$$\langle l' | l \rangle = \frac{1}{N} \sum_j e^{i\Sigma_\alpha (l_\alpha - l'_\alpha) j_\alpha} = \prod_\alpha \delta_{l_\alpha, l'_\alpha + 2n_\alpha \pi} , \tag{A1}$$

$$\begin{aligned} \langle l' | V | l \rangle &= \frac{1}{N} \sum_j e^{-i\Sigma_\alpha l'_\alpha j_\alpha} V\left(j, \frac{\partial}{\partial j}\right) e^{i\Sigma_\alpha l_\alpha j_\alpha} \\ &= \frac{1}{N} \sum_j e^{-i\Sigma_\alpha l'_\alpha j_\alpha} \; V e^{i\Sigma_\alpha (l_\alpha + 2\pi n_\alpha) j_\alpha} . \end{aligned} \tag{A2}$$

The above prescription conserves the property that the space of functions $e^{i\Sigma_\alpha l_\alpha j_\alpha}$ is an invariant space of V_{BS}, only l now can be considered as belonging to the first Brillouin zone. The only thing which remains to show is that V_{BS} is Hermitian with the prescription (A2). Using this equation it is easily shown by explicit calculation that with $\vec{\mathrm{u}}_j$ real,

$$\langle l' | V_{\mathrm{BS}} | l \rangle = \langle l | V_{\mathrm{BS}} | l' \rangle^* ,$$

as required.

Several difficulties[31] of the deformation-potential approach related to the choice of the Brillouin zone both for deformations and electrons in the deformed state are avoided here by the use of the deformation invariant variables j, s, l. Our formulation obeys *the analog* of the "empty-lattice" test,[31] i.e., there is no scattering if the bandwidth vanishes; the spurious[31] potential related to the Brillouin-zone redefinition by a (quasi) homogeneous part of deformation does not appear.

Next we show that the static periodic deformation opens the new gaps in the original band structure. In the presence of periodic deformation, with the period $p_\alpha = 2\pi / s_\alpha$, the Bloch theorem can be applied to V^s_{BS} since the part containing $\partial/\partial j$ commutes manifestly with the operator representing *any* translation in the space of sites j. Therefore the eigenfunctions of $K + V^s_{\mathrm{BS}}$ are of the form

$$a_j^l = e^{i\Sigma l_\alpha j_\alpha}\, w_j^l ,$$

where

$$w(j_\alpha + p_\alpha) = w(j_\alpha). \tag{A3}$$

Moreover, the functions a_j^l are orthonormal in the sense of Eq. (3.6),

$$\langle a^{l'} | a^l \rangle = \textstyle\sum_j a_j^{l*} a_j^{l'} = \prod_\alpha \delta_{l_\alpha, l'_\alpha + 2n_\alpha\pi} . \tag{A4}$$

This establishes, according to Eq. (2.4), the approximate orthonormality of the eigenstates of the one-electron Hamiltonian in the deformed lattice.

Equation (A3) gives for a charge-density wave $\delta\rho_j$ the expression

$$\delta\rho_j = 2 \sum_{l\,\mathrm{occ}} |w_j^l|^2 - Q. \tag{A5}$$

The cell with the dimensions p_α is now a new unit cell.

Finally, note that by the definition of $\vec{u}_j$, Eq. (2.10), $\vec{v}_{j\delta}$ can also be expressed in the differential form

$$\vec{v}_{j\delta_\alpha} = (T_{\delta_\alpha} - I)\vec{u}_j , \tag{A6}$$

where T_{δ_α} is the tensorial product of the translation operator in the j space with the unity of the three-dimensional space.

The introduction of the effective Hamiltonian playing only with the coefficients a_j^l allowed us to isolate the zeroth-order Hamiltonian for electrons (K) and for phonons ($\omega_{s\lambda}^0$). Mitra's state (2.8b) is an exact excited state of this Hamiltonian, and his Eq. (2.12) [our Eqs. (3.5) and (3.7)] gives the exact coupling of these states within a model.

APPENDIX B

The gap $\bar{\Delta}_{\mathrm{ph}}$ *at the Fermi level*, averaged over all directions, as in Eq. (4.3), is given in the linearized weak-coupling limit by[21]

$$\bar{\Delta}_{\mathrm{ph}} = \frac{1}{2}\int n(\omega')\,d\omega' \int_{E_F} \frac{d\sigma}{v_l} \int_{E_F+\omega'} \frac{d\sigma'}{v'_l} \sum_\lambda \frac{\hbar^2 |I^\lambda_{l,l-l'}|^2 \Delta_{l'}}{M\,\omega^\lambda_{l-l'}\,\omega'}\; \frac{\omega^\lambda_{l-l'} \tanh(\omega'/2k_BT_c) - \omega'}{\omega^{\lambda 2}_{l-l'} - \omega'^2} \Big/ \int_{E_F} \frac{d\sigma}{v_l} \int_{E_F+\omega'} \frac{d\sigma'}{v_{l'}} . \tag{B1}$$

The behavior of the expression

$$E(\omega', \omega^\lambda_{l-l}) = \frac{\omega^\lambda_{l-l'} \tanh(\omega'/2k_BT_c) - \omega'}{\omega'(\omega^{\lambda 2}_{l-l'} - \omega'^2)} = E(-\omega', \omega^\lambda_{l-l'}) \tag{B2}$$

is plotted in Fig. 2. We note that $E(\omega', \omega^\lambda_{l-l'})$ may be roughly approximated by

$$E(\omega', \omega^\lambda_{l-l'}) \approx \frac{1}{\omega' \omega^\lambda_{l-l'}} \tanh\frac{\omega'}{2k_BT_c} , \tag{B3}$$

i.e., $V(\omega', T_c)$ by $V_F(0)$ (with a cutoff at ω_D), if the phonons with $\omega^\lambda_{l-l'} \gg 2k_BT_c$ contribute appreciably to the gap. In fact, for $\omega' \approx 0$, say, the phonons with $\omega^\lambda_{l-l'} < 2k_BT_c$ contribute negatively to Δ_{ph}. If there is a Van Hove singularity near to the Fermi level, this may become important for the gap at the Fermi level because of the large weight of the processes involving long-wavelength acoustical phonons in Eq. (B1).

The negative contribution of the low-frequency phonons must be first compensated by somewhat higher frequencies and by the region $|\omega'| > \omega^\lambda_{l-l'}$. Even if Eq. (B3) can be used, $V_F(0)$ in Eq. (4.2) should rather be computed with a low-frequency cutoff in $\omega^\lambda_{l-l'}$. This "cutoff frequency" is a complicated function of T_c, ω', and the "localization" of the Van Hove singularity; however, it is expected to be at least of the order of $2k_BT_c$.

Such an effect may be *partially* responsible for a relative insensitivity of T_c in Nb$_3$Sn to the cubic-to-tetragonal transition, in which the frequencies of long-wavelength acoustical phonons, which are strongly coupled to d electrons, undergo large variations.

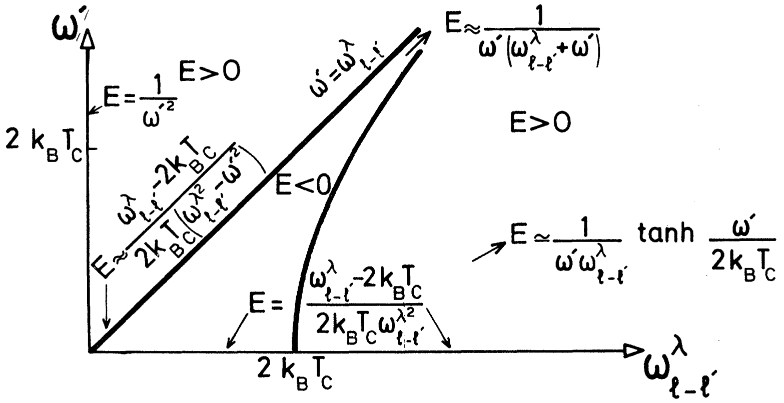

FIG. 2. Various limiting forms of the expression $E(\omega', \omega^\lambda_{l-l'})$, given by Eq. (B2). Arrows indicate the region of validity of each form. The curves on which $E(\omega', \omega^\lambda_{l-l'})$ changes sign are also shown.

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Self-Consistent Electron-Phonon Coupling in the Tight-Binding Approximation. II[*]

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The validity of the rigid-atom model for electron-phonon coupling in the tight-binding approximation is examined within the linearized self-consistent theory. It is shown that the deformation-induced charge-density wave will generally reduce the strength of the coupling, thus reducing the Kohn anomaly in the phonon spectrum and the superconducting transition temperature computed from the rigid-atom model. The charge-density wave does not appear for certain modes; the optimal situation is that of the (nearly) half-filled band, when the rigid-atom model gives approximately correct results.

I. INTRODUCTION

In Paper I of this work, referred to as I, an electron-phonon coupling model was examined. In I the long-range repulsive force acting between tightly bound electrons displaced by deformation was neglected. The elimination of the long-range part of the interaction can be attributed, by usual but more or less hand-waving arguments, to light conduction electrons, which, owing to their high mobility, are the only electrons effectively contributing to the screening. In particular, the model Hamiltonian describing the deformed lattice was shown, in this approximation, to be just a simple