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Attractive Electron-Electron Interaction Induced by the Dynamical Jahn-Teller Effect Involving Degenerate Impurity Orbitals: A Theory of the Impurity Enhancement of the Superconductive Transition Temperature in Dilute Alloys

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The dynamical Jahn-Teller effect associated with a $3d$ transition-metal impurity atom substituted in a simple metal is examined theoretically. The impurity atom is assumed to carry an essentially twofold-degenerate partially filled E_g-type electronic level lying close to the Fermi surface of the host metal. These degenerate impurity orbitals are shown to couple dynamically to the lattice through the Jahn-Teller effect. This latter coupling is "seen" by the conduction electrons via the resonant "s-d" interaction. The resulting indirect conduction-electron phonon coupling gives rise to an additional pairing interaction in the second order and involves the impurity orbitals dynamically. Under certain conditions of the impurity-level broadening (Δ) and positioning (δ) relative to the Fermi level, the above mechanism leads to a BCS-type attractive interaction parameter $V_{e\text{-}e}$ given by

$$V_{e\text{-}e} \cong c_i \left[\Delta^2/(\Delta^2+\delta^2)^2\right] \left[E_{\text{J-T}}/2\pi^2\rho(\epsilon_F)^2\right],$$

where c_i is the fractional concentration of the impurity centers, $\rho(\epsilon_F)$ is the density of states at the Fermi level, and E_{JT} is the Jahn-Teller stabilization energy. The parameter $V_{e\text{-}e}$ has been estimated numerically for the Al : Fe system and is found to be in reasonable agreement with the experimental values reported in the literature. It appears that the anomalously large impurity enhancement of the superconductive transition temperature observed in certain dilute alloys, such as Fe dissolved in Ti, Zr, and Al up to 1 at.%, may find a semiquantitative explanation in terms of the present mechanism. In deriving the above expression, the approximate procedure of unitary transformation was made use of. All renormalization effects were neglected. Also, the quasimolecular approximation was used in treating the Jahn-Teller effect of the impurity center. The many-impurity effect was treated in the spatial random-phase approximation. Certain group-theoretical arguments were employed to arrive at the mixing matrix elements involved in the determination of the width parameter Δ, appropriate to the present mechanism. The actual calculations have been carried out for the case of a simple-cubic host lattice. However, the treatment holds for all centrosymmetric cubic lattices, the differences showing up only in the form of certain multiplicative form factors.

I. INTRODUCTION

Transition-metal impurities of the iron series such as Fe, Co, Ni, Cr, and Mn, when added in small proportions (< 10 at. %), have been reported to appreciably enhance the superconductive transition temperature (T_c) of hosts such as Ti, Zr, and Al.[1–3] These alloys are marked by the absence of the local magnetic moments.[3,4] At very low concentrations (< 1 at. %) the increase in the transition temperature is anomalous in that it far exceeds the effect expected from the valence-electron theory.[2] The latter represents just a static effect of the gradual filling up of the conduction band and the accompanying gross changes at the Fermi level of the host metal by the excess valence electrons contributed by the impurity atoms. This happens when the impurity is placed much to the right of the host element in the periodic table. This marked deviation from the empirical valence-electron concentration rule of Matthias[5] has been attributed by various authors to some purely electronic mechanisms of the superconductive pairing that involve the impurity atoms.[6–8] This implies ascribing certain polarizable structure to the impurity center giving it, thereby, certain energetically low-lying internal degrees of freedom. The latter could presumably be excited effectively by the conduction electrons lying close to the Fermi level. A typical one-body process of this kind involves an exchange or/and Coulomb excitation of the impurity center by an "incoming" conduction electron to a virtual state lying above and close to the Fermi level and its subsequent de-excitation by an "outgoing" electron. This is in complete analogy with the virtual exchange of phonons.[9] Apart from the above one-body processes, two-body processes have also been visualized. In a typical process of this kind two conduction electrons scatter simultaneously into virtual states lying above the Fermi level. These virtual states interact antiferromagnetically and are, therefore, conducive to the occurrence of superconductivity.[10,11] In point of fact the abnormally high transition temperature of lanthanum has been attributed to such antiferromagnetically interacting virtual $4f$ shells lying just above the Fermi level.

By virtue of their purely electronic character, however, the above mechanisms would lead to a marked deviation from the isotope effect as there appears to be no physical reason to employ the Debye cutoff in the resulting gap equations. Some recent detailed investigations of the isotope effect in pure transition metals do, on the other hand, strongly suggest that superconductivity is almost universally caused by the phonon-induced processes as in the standard BCS theory.[12] Motivated by these latter findings, we examine theoretically in the present paper a possible mechanism of the impurity enhancement of the superconductive transition temperatures of dilutely alloyed systems that is caused by phonons but involves the electronic structure of the impurity in an essential way. In this mechanism the electronic degeneracy of the partially filled impurity orbitals is shown to lead, under appropriate conditions, to an enhanced conduction-electron phonon coupling through the impurity Jahn-Teller (JT) effect[13-15] operating via the resonant s-d admixing.[16] This, of course, leads to an additional pairing interaction $V_{e\text{-}e}$ and, therefore, to an increase of T_c. The point essential to the present development is to treat the impurity atom as introducing a set of degenerate localized orbitals into the host metal. A simple but sufficiently general model for a $3d$ transition-metal impurity substituted in a host metal, sufficiently far removed from the former in the periodic table, can be based on the suggestion due originally to Mott and Stevens.[17,18] The transition-metal ion is expected to introduce a set of five degenerate $3d$-orbital states lying within the conduction-band continuum of the host metal. This is so, of course, provided the difference in the ionic potentials is sufficiently great and the screening effect due to the conduction electrons is not very large. The case when the impurity orbitals lie below the conduction band is devoid of any interest as far as the phenomena near the Fermi level are concerned. A possible exception can occur when the host is a degenerate semiconductor or a narrow band-gap insulator, where the orbitals of interest would be the localizable (heavy effective mass), excitonic states.[19] In fact, the conditions for the occurrence of such virtually bound orbital states can roughly be formulated[17] in terms of the screened impurity potential $|e|Z_{\text{imp}}e^{-k_c r}/r$. Here $|e|Z_{\text{imp}}$ is the relative impurity charge and is a measure of the effective valency difference. k_c is the electron-screening parameter, given by $k_c^2 = 6\pi ne^2/\epsilon_F$, from the many-body theory of the free-electron gas.[20] n is here the electron concentration, and ϵ_F is the Fermi energy. Now, it is well known from the general theory of scattering by the central potentials that the Yukawa potential $|e|Z_{\text{imp}}e^{-k_c r}/r$ has no bound states for[21]

$$k_c\hbar^2/Z_{\text{imp}}m^*e^2 \geq \sqrt{2} \quad . \tag{1}$$

Thus, an upper limit for the host conduction-electron concentration n, namely,

$$n \leq \tfrac{1}{24}\pi Z_{\text{imp}}^6 (me^2/\hbar^2)^3 \quad , \tag{2}$$

must be given for the appearance of an s-like bound state to be possible. Thus, for Al with 6×10^{22} atoms cm^{-3} and three valence electrons per atom, we have $n \simeq 1.8\times 10^{23}\ \text{cm}^{-3}$ and $Z_{\text{imp}} \geq 0.75$. Of course, the condition for the occurrence of the bound state with a higher angular-momentum quantum number will be much more restrictive, owing to the appearance of the repulsive centrifugal term, $[l(l+1)/r^2]\,2m/\hbar^2$. As only the operator $\hat{1}^2$ is involved here, the quenching effects do not alter the condition in any way.

Now, the fivefold degeneracy of the localized impurity level thus formed is of course lifted under the influence of the screened crystal field. The latter has the point-symmetry group appropriate to the host crystal.[18] Here we restrict ourselves to the quasimolecular approximation[15] and, therefore, the influence of the nearest neighbors only needs to be considered. Furthermore, we assume for simplicity a regular octahedral coordination. Thus, the point-symmetry group to be considered is O_h. Then the set of the fivefold-degenerate orbitals splits up into an upper subset of two degenerate orbitals carrying the irreducible representation E_g of the octahedral group O_h and another lower subset of three degenerate orbitals carrying the irreducible representation T_{2g} of O_h. The two subsets of orbitals are broadened appreciably by the resonant mixing effects, as these lie in the Bloch continuum.[22] As to the extent of broadening, however, the two subsets differ considerably. The three T_{2g}-type orbitals, transforming as xy, yz, and zx, are known to be highly bonding, and they almost merge into the conduction-band continuum (i.e., they have extended radial parts and thus contribute to the Fermi energy). On the other hand, the two E_g-type orbitals, transforming as (x^2-y^2) and $(2z^2-x^2-y^2)$, while strongly bonding, are very much localized, and are best described as nonconducting exciton-like bound states. The above characterization of the E_g- and the T_{2g}-type impurity substates in metals as being localized and extended, respectively, is known to be valid rigorously for metals with the body-centered cubic (bcc) crystal structure, and approximately so for those with the face-centered cubic (fcc) structure. However, as the point-symmetry group of the bcc, fcc, and the simple cubic (sc) systems is the same, namely O_h, the present treatment can readily be applied to the cases of the other lattices. As will be seen, the different coordinations have the effect of changing certain geometrical form factors only, as long as the symmetry remains the same.

Now, for an orbitally degenerate electronic level to be JT active, the former must be strongly bonding or antibonding.[23] The strength of the interaction, or the "reduced matrix element," depends on this. Furthermore, the wave function must be of the localized character. In the case of a narrow band, or a resonantly broadened virtual level, this latter condition implies that the width must be relatively small, i.e., $\Delta < E_{JT}$, the JT stabilization energy.[19] Thus, the two partially filled degenerate E_g-type orbitals assumed to lie close to the Fermi level are expected effectively to couple the electrons to the lattice through the dynamical JT effect.

There is still another condition that must be satisfied in order to make the above mechanism effective. It follows from the following considerations. As noted earlier, the two localized degenerate orbitals are appreciably broadened in energy through the resonant admixing with the symmetry-adapted linear combinations of the degenerate Bloch states belonging to the host metal. The energy width Δ of this broadened level is known explicitly from Anderson's theory[16] of localized states in dilute alloys. It is given by the relation

$$\Delta = \pi \langle |M_{k_F}|^2 \rangle \rho(\epsilon_F) , \tag{3}$$

where $\langle |M_{k_F}|^2 \rangle$ denotes the mixing matrix element squared and averaged over the Fermi sphere in the momentum space. $\rho(\epsilon_F)$ is the density of the conduction-electron states, of proper symmetry, at the Fermi sphere. The width Δ is directly related to the lifetime τ of the level through the uncertainty principle, as used in the theory of adiabatic line broadening, namely,

$$\tau \sim 2\pi\hbar/\Delta \quad . \tag{4}$$

Now, the JT effect associated with the orbital degeneracy of the impurity level is operative only if the lifetime of the level in question is greater than the characteristic response time of the lattice. The latter can be taken to be the reciprocal of the frequency of a typical lattice vibrational mode, i.e., $\tau \sim 2\pi/\omega_D$, where ω_D is the Debye frequency. Thus, one gets the condition

$$\hbar\omega_D > \Delta \ . \tag{5a}$$

Also, for the JT effect to be fully dynamical, we must have[15]

$$\hbar\omega_D > E_{JT} \ . \tag{5b}$$

Further, from the elementary considerations of the energy denominator involved in the perturbation theory it follows that the level in question must lie with respect to energy, within $\hbar\omega_D$ of the Fermi level. The exact position $\delta (= \epsilon_d - \epsilon_F)$ of the impurity level must, however, be correlated with the observed fact that these dilute alloys exhibit no localized magnetic moment. The latter is known to depend in a complicated way on the extent of screening of the inner-shell correlation energy, and on the width and the position of the impurity level relative to the host Fermi level. In the present treatment, however, we shall assume δ to be known, and also $\delta \sim \Delta$. Finally, therefore, we have

$$\hbar\omega_D > E_{JT} > \Delta \sim \delta \equiv \epsilon_d - \epsilon_F \ . \tag{6}$$

Thus, we assume a narrow, doubly degenerate localized impurity level lying close to the Fermi level. The narrowness of the level implies small mixing matrix elements. It will be seen later that the matrix elements should not be very small either, as it is via this mixing effect that the conduction electrons "see" the lattice dynamics induced by the JT effect. There is indeed an optimal value.

We envisage, therefore, an electron-phonon interaction induced by the dynamical JT distortion of the lattice associated with the *transient* occupation (due to the resonant mixing) of the twofold orbitally degenerate impurity level lying close to the Fermi level. A revealing semiclassical coordinate description of the above process is the following. An incoming conduction electron moving in a general direction encounters an impurity ion and is transiently trapped in one of the many possible almost periodic (quasibound) orbits and subsequently escapes in another direction, in general, different from the original, after the lapse of a certain time interval τ (the resonant mixing effect). While trapped temporarily in an orbit around the impurity center, the electron experiences the perturbing field of the ligands which can, in turn, react to the electron motion. Now, for a certain type (symmetry) of the ligand equilibrium configuration (corresponding to the essential orbital degeneracy), the electron-ligand motion is dynamically unstable (JT instability); this leads to the scattering of the conduction electron. The ligands, however, respond very slowly to the electronic motion owing to their large inertia and, therefore, the above process will take place only if the itinerant electron would normally stay in orbit around the impurity longer than it takes the ligands to respond. Otherwise, it will simply be a case of adiabatic fast passage (semiclassical Franck-Condon principle).[24]

Another point to be noted here is regarding the relative significance of the two types of normal modes, namely the energy-splitting mode E_g and the breathing mode A_{1g}, that are allowed by the selection rules. In the case of the spectral studies of the electronically degenerate complexes involving the JT effect, the breathing mode is rendered inconsequential since it only position-modulates the degenerate levels without causing any splitting. As such, it does not contribute any extra structure to the spectrum. In the present case, however, the physical effect of interest is the dynamical electron-lattice coupling, and there is no group-theoretical reason for the A_{1g} mode to be ineffective in this respect. Indeed, the A_{1g} mode corresponds to a purely scalar local strain. It should be an effective isotropic scatterer. It may be remarked in passing that for the centrosymmetric systems in question only the even-parity modes are JT active. For such modes, of course, the impurity center remains at rest. Thus, inertia being a convective property, the isotropic mass of the impurity is not involved.

In the present paper we have dealt with the one-impurity problem. The many-impurity effect has been treated in the spatial random-phase approximation in the second Born order.[25] It may well be remarked here that the extension of the present treatment to the concentrated systems, in which cooperative JT effects and coherent scattering must must be considered, is completely nontrivial.[19,26,27]

In the foregoing pages we described in physical terms the principles that contribute to the proposed mechanism, to be formulated more precisely in the following sections. In Sec. II of the paper the interaction Hamiltonian is formulated in terms of the resonant mixing and the quasimolecular JT effects associated with an isolated impurity through a diagonalization procedure suggested by the group-theoretical considerations. In Sec. III a reduced Hamiltonian is obtained through a suitable canonical transformation, and the many-impurity effect is treated in a spatial random-phase approximation. An expression is derived for the effective electron-electron interaction parameter which is found to correspond to attraction. In Sec. IV certain physical features of the expression derived in Sec. III are noted and the various approximations made are examined. Based on these, some estimates of the enhancement of T_c for the case of iron as an impurity in aluminum are presented.

II. FORMULATION OF THE INTERACTION HAMILTONIAN

We first consider the case of an isolated $3d$ transition-metal impurity substituted in a simple host metal.

The basic model used can best be summarized by writing the Hamiltonian

$$H_{\text{total}} = H_c + H_d + H_{\text{mix}} + H_p + H_{JT} \ . \tag{7}$$

Here H_c is the unperturbed Hamiltonian of the conduction-electron system. In second-quantized notation, we have

$$H_c = \sum_{\vec{k}\vec{\sigma}} \epsilon_k c^{\dagger}_{\vec{k}\vec{\sigma}} c_{\vec{k}\vec{\sigma}} \ , \tag{8}$$

where $c_{\vec{k}\vec{\sigma}}{}^{\dagger}$, $c_{\vec{k}\vec{\sigma}}$ are the fermion creation-annihilation operators for states characterized by wave vector $\vec{k}$ and spin $\vec{\sigma}$. We assume a nearly free-electron model for the host metal and take care of the periodic lattice potential in the effective mass (m^*) approximation. Thus,

$$|\vec{k}\rangle = \Omega^{-1/2} e^{-i\vec{k}\cdot\vec{r}}, \quad \epsilon_k = \hbar^2 k^2 / 2m^* \ , \tag{9a}$$

where Ω is the box-normalization volume. Also, for certain formal mathematical (enumerational) simplicity, we consider a large but finite crystal (of volume Ω) having simple cubic (sc) lattice structure containing $N(=N_1 \times N_2 \times N_3)$ unit cells and having one atom per unit cell. Cyclic boundary conditions are assumed following Born and von Karman. Then, the reduced wave vector $\vec{k}$ is a denumerable quantum label with the permissible ith value given by

$$\vec{k}_i = 2\pi\left(\vec{b}_1 \frac{l_i}{N_1} + \vec{b}_2 \frac{m_i}{N_2} + \vec{b}_3 \frac{n_i}{N_3}\right) , \tag{9b}$$

where $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ are the reciprocal-lattice basis vectors, and l_i, m_i, and n_i are integers given by

$$\begin{aligned} -\tfrac{1}{2}(N_1 - 1) &\le l_i \le \tfrac{1}{2}(N_1 - 1) \ , \\ -\tfrac{1}{2}(N_2 - 1) &\le m_i \le \tfrac{1}{2}(N_2 - 1) \ , \\ -\tfrac{1}{2}(N_3 - 1) &\le n_i \le \tfrac{1}{2}(N_3 - 1) \ . \end{aligned} \tag{9c}$$

Thus, there are $N_1 \times N_2 \times N_3 = N$ allowed values of the wave vector in the reduced zone scheme, and the $\vec{k}_i$ lie in the first Brillouin zone. In any actual calculation, however, the following limiting procedure is implicitly understood:

$$\lim (1/\Omega) \sum_{\vec{k}_i} \to (1/2\pi)^3 \int_{I\,\text{BZ}} d^3k \quad \text{as } \Omega \to \infty \ . \tag{10}$$

The second term H_d is the unperturbed Hamiltonian for the twofold-degenerate E_g-type impurity level (localized at site R_l) and is explicitly given by

$$H_d = \sum_{\vec{\sigma}} \epsilon_d (d^{\dagger}_{\theta\vec{\sigma}} d_{\theta\vec{\sigma}} + d^{\dagger}_{\epsilon\vec{\sigma}} d_{\epsilon\vec{\sigma}}) \ , \tag{11}$$

where $|\theta\rangle$ and $|\epsilon\rangle$ are the two orthonormal basis states carrying the irreducible representation E_g and transforming under O_h as $(2z^2 - x^2 - y^2)$ and $(x^2 - y^2)$, respectively, and ϵ_d is the common unperturbed energy. $d^{\dagger}_{\theta\vec{\sigma}}$, $d_{\theta\vec{\sigma}}$ and $d^{\dagger}_{\epsilon\vec{\sigma}}$, $d_{\epsilon\vec{\sigma}}$ are the corresponding fermion creation-annihilation operators. Since the interaction mechanism has no explicit spin dependence, we shall, in the following, omit writing spin indices explicitly.

H_{mix} and H_{JT} are the Hamiltonians describing, respectively, the mixing effects between the band states and the localized impurity states, and the interactions between electrons and phonons. Their explicit forms will be given at appropriate stages.

H_p is the unperturbed lattice Hamiltonian and has the explicit form

$$H_p=\sum_{\vec{q}} \hbar\omega_q(\beta_{\vec{q}}^\dagger\beta_{\vec{q}}+\tfrac{1}{2}) , \tag{12}$$

where $\beta_{\vec{q}}^\dagger$, $\beta_{\vec{q}}$ are the Boson creation-annihilation operators for the phonon of wave vector $\vec{q}$, and $\hbar\omega_q$ is the corresponding quasiparticle energy. The mode-branch indices are included in $\vec{q}$ in the present notation.

In writing H_c and H_d, it has implicitly been assumed that the states $|\vec{k}\rangle$ and $|\theta\rangle$, $|\epsilon\rangle$ are orthogonal, or, what is the same, that the impurity states are orthogonal to the Wannier functions belonging to the conduction band. They are approximately so, and, in any case, can be made so through the well-known Schmidt orthogonalization procedure. The precise definition of these impurity states is the same as that used in the theory of localized states in metals by Anderson,[16] where the effect of the solute atom is treated as that of a separate localized level, and not as an impurity potential only acting on the conduction electrons in the sense of Friedel.

To introduce the electron-phonon interaction through the anticipated JT effect in a systematic manner, the electronic Hamiltonian $H_c+H_d+H_{\text{mix}}$ must be diagonalized, and the essential (symmetry-induced) degeneracy recognized. The diagonalization is carried out in two steps, as follows.

We note that the Hilbert space spanned by the electronic Hamiltonian is composed of the direct sum of the subsets $\{|\vec{k}\rangle\}$ and $\{|\theta\rangle, |\epsilon\rangle\}$, which together form, for the purpose of the present treatment, a dynamically complete set of basis functions. Now, guided by group-theoretical reasons, we perform a change of basis such that the set of states $\{|\vec{k}\rangle\}$ goes into an equivalent set {"star" of $|\vec{k}\rangle$} of symmetry-adapted linear combinations of $|\vec{k}\rangle$, carrying the irreducible representation E_g of the point group O_h, while the set $\{|\theta\rangle, |\epsilon\rangle\}$ remains unaltered. Here " 'star' of k" denotes the "star" of the space group and is generated by successively applying all the symmetry operations of the parent point-symmetry group (O_h) to a distinct test basis $|\vec{k}\rangle$.[28] It is to be noted here that each star of the reduced wave vectors forms a basis for the regular representation of the parent point-symmetry group, and each irreducible representation of the point group occurs in the regular representation as many times as its dimension. Thus, we must have two sets of two-dimensional symmetry-adapted basis functions transforming as components of E_g; these can be constructed by the standard method of projection operator.[29] In general the ith component $|\vec{k}_\Gamma^{ij}\rangle$ of the basis of the g_Γ-dimensional irreducible representation Γ of the point-symmetry group G of order g_G in its jth occurrence is projected out from the star of $|\vec{k}\rangle$ as

$$|\vec{k}_\Gamma^{ij}\rangle=\left(\frac{g_\Gamma}{g_G}\right)^{1/2}\sum_{\hat{R}} \breve{D}_\Gamma(\hat{R}_{ij})\hat{R}|\vec{k}\rangle e^{-i\vec{R}_l\cdot(\hat{R}\vec{k})} , \tag{13a}$$

where $\breve{D}_\Gamma(\hat{R}_{ij})$ is the contragredient matrix representation of the symmetry element $\hat{R}$ in the irreducible representation Γ. In the following, we only have the transformation matrices which are orthogonal and, hence, $\breve{D}_\Gamma(\hat{R}_{ij})=D_\Gamma(\hat{R}_{ij})$. The phase factor $e^{-i\vec{R}_l\cdot(\hat{R}\vec{k})}$ has been shown explicitly to take into account the fact that the impurity center is located at the lattice site $\vec{R}_l$. We note the orthogonality relations

$$\sum_{\hat{R}} D_{\Gamma'}(\hat{R}_{i'j'})D_\Gamma(\hat{R}_{ij})=\delta_{i'i}\delta_{j'j}\delta_{\Gamma'\Gamma} . \tag{13b}$$

In the present case, we have $G\equiv O_h$, $g_G=48$, and $\Gamma\equiv E_g$, $g_\Gamma=2$, and the transformation matrices $D_{Eg}(\hat{R}_{ij})$ $(i,j=1,2)$ are readily available in standard tables.[29] We have, thus, after some algebra, the orthonormalized symmetry-adapted basis functions for E_g as

$$\begin{aligned}
|\vec{k}_{Eg}^{11}\rangle&=[1/\sqrt{(6\Omega)}](4\lambda-2\gamma-2\mu-2\xi-2\eta-4\zeta)\equiv|\theta_{\vec{k}}^1\rangle,\\
|\vec{k}_{Eg}^{12}\rangle&=[1/\sqrt{(6\Omega)}](2\mu-2\xi-2\nu+2\eta)\equiv|\theta_{\vec{k}}^2\rangle ,\\
|\vec{k}_{Eg}^{21}\rangle&=[1/\sqrt{(6\Omega)}](-2\mu+2\nu-2\xi+2\eta)\equiv|\epsilon_{\vec{k}}^1\rangle ,\\
|\vec{k}_{Eg}^{22}\rangle&=[1/\sqrt{(6\Omega)}](4\lambda-2\mu+2\xi-2\nu+2\eta-4\zeta)\equiv|\epsilon_{\vec{k}}^2\rangle ,
\end{aligned} \tag{14a}$$

where

$$\begin{aligned}
\lambda&=\cos k_x x\cos k_y y\cos k_z z ,\\
\nu&=\cos k_x y\cos k_y z\cos k_z x ,\\
\mu&=\cos k_x z\cos k_y x\cos k_z y ,\\
\zeta&=\cos k_x y\cos k_y x\cos k_z z ,\\
\xi&=\cos k_z x\cos k_y z\cos k_z y ,\\
\eta&=\cos k_x z\cos k_y y\cos k_z x .
\end{aligned} \tag{14b}$$

Here k_x, k_y, k_z are the Cartesian components of the test-reduced wave vector $\vec{k}$. As indicated in (14a), $|\vec{k}_{Eg}^{11}\rangle$, $|\vec{k}_{Eg}^{12}\rangle$ transform as the basis components $|\theta\rangle\sim(2z^2-x^2-y^2)$, and $|\vec{k}_{Eg}^{21}\rangle$, $|\vec{k}_{Eg}^{22}\rangle$ as $|\epsilon\rangle\sim(x^2-y^2)$. The limiting forms of these functions for small values of arguments are noted below for later reference:

$$\begin{aligned}
|\theta_{\vec{k}}^1\rangle&\cong-[1/\sqrt{(6\Omega)}]\,(2k_z^2-k_x^2-k_y^2)(2z^2-x^2-y^2) ,\\
|\theta_{\vec{k}}^2\rangle&\cong-[\sqrt{3}/\sqrt{(6\Omega)}]\,(k_x^2-k_y^2)(2z^2-x^2-y^2) ,\\
|\epsilon_{\vec{k}}^1\rangle&\cong[\sqrt{3}/\sqrt{(6\Omega)}](2k_z^2-k_x^2-k_y^2)(x^2-y^2) ,\\
|\epsilon_{\vec{k}}^2\rangle&\cong-[3/\sqrt{(6\Omega)}]\,(k_x^2-k_y^2)(x^2-y^2) ,
\end{aligned} \tag{15}$$

for $|\vec{k}||\vec{r}|\ll 1$.

Using (13b), it can be easily verified that $|\vec{k}^{ij}_{E_g}\rangle$ form an orthonormal set

$$\langle \vec{k}'^{i'j'}_{E_g} | \vec{k}^{ij}_{E_g} \rangle = \delta_{ii'} \delta_{jj'} \delta_{\vec{k}\vec{k}'} \ . \tag{16a}$$

Also, as noted earlier,

$$\langle \vec{k}^{ij}_{E_g} | \theta \rangle \sim \langle \vec{k}^{ij}_{E_g} | \epsilon \rangle \cong 0 \ . \tag{16b}$$

We now recall from group theory that only those functions that transform alike under the operations of the symmetry group are connected by an operator invariant under the group operations. Thus, the only nonvanishing off-diagonal mixing terms appearing in H_{mix} will be those connecting $|\theta\rangle$ with $|\theta^1_{\vec{k}}\rangle$, $|\theta^2_{\vec{k}}\rangle$ and $|\epsilon\rangle$ with $|\epsilon^1_{\vec{k}}\rangle$, $|\epsilon^2_{\vec{k}}\rangle$. This results in the decomposition of the electronic Hamiltonian in θ-like and ϵ-like disjoint (commuting) parts which can in turn be diagonalized relatively easily. Thus, in terms of the new basis we have

$$H_{\text{electronic}} = H_\theta + H_\epsilon$$

with

$$\begin{aligned} H_\theta &= \sum_{j,\vec{k}} \epsilon_k c^\dagger_{\theta^j_{\vec{k}}} c_{\theta^j_{\vec{k}}} + \epsilon_d d^\dagger_\theta d_\theta + \sum_{j,\vec{k}} (M^\theta_{\theta^j_{\vec{k}}} c^\dagger_{\theta^j_{\vec{k}}} d_\theta + \text{H.c.}) \ , \\ H_\epsilon &= \sum_{j,\vec{k}} \epsilon_k c^\dagger_{\epsilon^j_{\vec{k}}} c_{\epsilon^j_{\vec{k}}} + \epsilon_d d^\dagger_\epsilon d_\epsilon + \sum_{j,\vec{k}} (M^\epsilon_{\epsilon^j_{\vec{k}}} c^\dagger_{\epsilon^j_{\vec{k}}} d_\epsilon + \text{H.c.}) \ , \end{aligned} \tag{17}$$

where H.c. denotes the Hermitian conjugate.

Here we have neglected the energy-renormalization effects. For the moment, we do not need the admixing matrix elements explicitly. We may, however, note from symmetry that, say,

$$\begin{aligned} M^\theta_{\theta^j_{\vec{k}}} &= M^\epsilon \quad = M_{jk} \ , \\ \langle |M^\theta_{\theta^i_k}|^2 \rangle &= \langle |M^\theta_{\theta^j_{\vec{k}}}|^2 \rangle = \langle |M_{\vec{k}}|^2 \rangle \ . \end{aligned} \tag{18}$$

The advantage gained by the change of basis can now at once be seen. The only off-diagonal matrix elements occurring in the commuting Hamiltonians H_θ and H_ϵ are those connecting the impurity states $|\theta\rangle$ and $|\epsilon\rangle$ to the rest of the states $|\theta^j_{\vec{k}}\rangle$ and $|\epsilon^j_{\vec{k}}\rangle$, respectively. This circumstance enables us explicitly to diagonalize the two disjoint Hamiltonians separately through the standard Schmidt orthogonalization procedure in a particularly simple fashion. Carrying this out, we get after some reduction

$$H_{\text{electronic}} = H_\theta + H_\epsilon \ ,$$

where

$$\begin{aligned} H_\theta &= \sum{}'_\lambda \ E_\lambda c^\dagger_{\theta\lambda} c_{\theta\lambda} + E_{\lambda d} c^\dagger_{\theta\lambda d} c_{\theta\lambda d} \ , \\ H_\epsilon &= \sum{}'_\lambda \ E_\lambda c^\dagger_{\epsilon\lambda} c_{\epsilon\lambda} + E_{\lambda d} c^\dagger_{\epsilon\lambda d} c_{\epsilon\lambda d} \ . \end{aligned} \tag{19}$$

Here,

$$|\theta_\lambda\rangle = \left[\sum_{j,\vec{k}} \left(\frac{M_{j\vec{k}}}{E_\lambda - \epsilon_k} \right) |\theta^j_{\vec{k}}\rangle + |\theta\rangle \right] \left[\sum_{j\vec{k}} \frac{|M_{j\vec{k}}|^2}{(E_\lambda - \epsilon_k)^2} + 1 \right]^{-1/2} ,$$

and $c^\dagger_{\theta\lambda}$, $c_{\theta\lambda}$, etc., are the new Fermion operators.

The eigenvalues E_λ are to be obtained from the eigenvalue integral equation

$$\sum_{j\vec{k}} \frac{|M_{j\vec{k}}|^2}{(E_\lambda - \epsilon_k)} + \epsilon_d - \epsilon_\lambda = 0 \ . \tag{20}$$

The corresponding quantities of the ϵ type can be obtained from (19) and (20) simply by letting $\theta \to \epsilon$. Here summation over $\vec{k}$ spans only a fraction $1/g_{O_h} (= \frac{1}{48})$ of the reciprocal-space lattice points in the first Brillouin zone.

The qualitative features of the integral eigenvalue equation (20) can be seen relatively easily by regarding $\vec{k}$ as a discrete variable given by (9b) and (9c). In particular, aside from an overall shift, the conduction-electron states as well as the impurity states are shifted differentially in energy, causing bunching of states near the impurity level. (As a consequence of Ledermann's theorem, however, the number of eigenvalues lying in any energy interval cannot change by more than 2 since only one row and the corresponding column of the Hermitian matrix are being modified by mixing.) For a macroscopic crystal, of course, $\vec{k}$ is a quasicontinuous variable and the above effect shows up as a resonant broadening of the impurity level when the latter lies within the continuum, as is assumed here. The resonance is mathematically treated by letting the energy variable have an infinitesimal positive imaginary part and making use of the Dirac identity

$$\lim_{\eta\to 0^+} [1/(x \pm i\eta)] \equiv P(1/x) \mp i\pi\delta(x) \ ,$$

(P = principal part), in (20) while changing summation to integration following (10). Thus, we have

$$P \int \left(\frac{g_{E_g}}{g_{O_h}} \right) \frac{\langle |M_{k_F}|^2 \rangle}{E_\lambda - \epsilon_k} \rho(\epsilon_F) \, d\epsilon_k + i\Delta + \epsilon_d - E_\lambda = 0 , \tag{21a}$$

where

$$\Delta = (g_{E_g}/g_{O_h}) \pi \langle |M_{k_F}|^2 \rangle \rho(\epsilon_F) ,$$

and the slowly varying quantities have been replaced by their average values at the Fermi level. The reduction factor (g_{E_g}/g_{O_h}) has appeared, since only this fraction of the Brillouin zone is effectively spanned by the summation in (20). As is well known, the real part of Eq. (21a) gives the renormalized position of the impurity level (ϵ'_d), while Δ gives the resonance width. The above effect can be taken into account in the subsequent perturbation treatment by using the complex eigenvalue

$$E_{\lambda d} = \epsilon'_d + i\Delta \cong \epsilon_d + i\Delta \tag{21b}$$

in place of ϵ_d whenever the latter occurs as a pole.

In writing (19), terms corresponding to the resonantly broadened impurity orbital states have been written out separately. The prime over the summation sign indicates their exclusion.

As pointed out earlier, it is the degeneracy of these localized impurity states that is effective in producing the JT distortion; accordingly, we now include the latter explicitly into our Hamiltonian:

$$H_{\text{total}}=H_\theta+H_\epsilon+\sum_{\vec{q}}\hbar\omega_q(\beta_q^\dagger\beta_q+\tfrac{1}{2})+H_{JT}$$

with

$$H_{JT}=\sum_{\Gamma,\gamma}J_{\Gamma\gamma}^{\theta\theta}Q_{\Gamma\gamma}c_{\theta\lambda_d}^\dagger c_{\theta\lambda_d}+\sum_{\Gamma,\gamma}J_{\Gamma\gamma}^{\epsilon\epsilon}Q_{\Gamma\gamma}c_{\epsilon\lambda_d}^\dagger c_{\epsilon\lambda_d}+\sum_{\Gamma,\gamma}J_{\Gamma\gamma}^{\theta\epsilon}Q_{\Gamma\gamma}c_{\theta\lambda_d}^\dagger c_{\epsilon\lambda_d}+\sum_{\Gamma,\gamma}J_{\Gamma\gamma}^{\epsilon\theta}Q_{\Gamma\gamma}c_{\epsilon\lambda_d}^\dagger c_{\theta\lambda_d}\,, \tag{22}$$

where $Q_{\Gamma\gamma}$ is the quasimolecular normal mode transforming as the γth component of the basis of the irreducible representation Γ which is contained in the symmetric square $[E_g{}^2]=E_g+A_{1g}$. Thus, Γ is either A_{1g} or E_g, and accordingly, $Q_{\Gamma\gamma}$ is the breathing mode $Q_1\sim a_{1g}$ or the splitting modes $Q_2\sim(x^2-y^2)$ and $Q_3\sim(2z^2-x^2-y^2)$. $J_{\Gamma\gamma}^{\epsilon\epsilon}$, $J_{\Gamma\gamma}^{\theta\theta}$, $J_{\Gamma\gamma}^{\theta\epsilon}$, and $J_{\Gamma\gamma}^{\epsilon\theta}$ are the matrix elements of the "JT force" connecting the respective states, and, from the Wigner-Eckart theorem, each of these factors into a reduced matrix element (the radial factor) and an angular matrix element (the former is the same for all matrix elements subtended within a given irreducible representation and is to be treated as a parameter), while the angular factor is readily known from group theory in the form of what is essentially a Clebsch-Gordan coefficient. Thus,[29] we have

$$J_{\Gamma\gamma}^{\alpha\beta}=J_\Gamma\begin{pmatrix}E_g & E_g & \Gamma\\ \alpha & \beta & \gamma\end{pmatrix}$$

and, in particular, we have

$$\begin{aligned}&J_{A_{1g}a_{1g}}^{\theta\theta}=J_{A_{1g}a_{1g}}^{\epsilon\epsilon}=J_{A_{1g}a_{1g}}^{\theta\epsilon}=(1/\sqrt{2})J_{A_{1g}}\,,\\ &J_{E_g\theta}^{\theta\theta}=-J_{E_g\theta}^{\epsilon\epsilon}=J_{E_g\epsilon}^{\theta\epsilon}=J_{E_g\epsilon}^{\epsilon\theta}=(1/\sqrt{2})J_{E_g}\,,\\ &J_{E_g\epsilon}^{\theta\theta}=J_{E_g\epsilon}^{\epsilon\epsilon}=J_{E_g\theta}^{\theta\epsilon}=J_{E_g\theta}^{\epsilon\theta}=0\,.\end{aligned} \tag{23}$$

It may be remarked here that the reducible representation of O_h spanned by the $(3Z-3)$ displacement coordinates of the Z ligands (nearest neighbors) of the quasimolecular complex is not necessarily regular, and a given irreducible representation need not occur as many times as its dimension.

Further, in the quasimolecular approximation, only the nearest-neighbor displacements are effectively involved, and the latter can be completely expressed in terms of the unperturbed lattice-displacement field. Thus, in general, we have for the quasimolecular normal mode $Q_{\Gamma\gamma}$,

$$Q_{\Gamma\gamma}=\sum_{\vec{q}}S_{\Gamma\gamma}(\vec{q})(\beta_{\vec{q}}{}^\dagger-\beta_{-\vec{q}})e^{-i\vec{q}\cdot\vec{R}_l}\,, \tag{24}$$

where $\beta_q^\dagger$, $\beta_{\vec{q}}$ are the phonon creation-annihilation operators associated with the wave vector $\vec{q}$, and $S_{\Gamma\gamma}(\vec{q})$ is the projection of the phonon mode of wave vector $\vec{q}$ onto the normal mode $Q_{\Gamma\gamma}$. The mode-branch index is incorporated in the label $\vec{q}$. Thus, for the breathing mode Q_1 transforming as a_{1g} of the irreducible representation A_{1g} under the octahedral group O_h associated with a sc lattice with one atom per unit cell, we have

$$\begin{aligned}S_{Q_1}(\vec{q})\equiv S_{A_{1g}a_{1g}}(\vec{q})&=2(\hbar/2MN\omega_q)^{1/2}\\ &\times(\sin\alpha qa+\sin\beta qa+\sin\gamma qa)\,,\end{aligned} \tag{25}$$

where a is the lattice constant, MN is the total mass of the crystal, and ω_q is the mode-branch frequency. α, β, and γ are the direction cosines of the wave vector $\vec{q}$. $\hbar$ is Planck's constant divided by 2π. Only longitudinal acoustical modes have been considered. Thus, a given quasimolecular mode has associated with it a whole range of phonon modes, weighted by $|S_{\Gamma\gamma}(\vec{q})|^2$ and, of course, the phonon density of states.

Since all the normal modes act independently of each other and, as noted earlier, the mode a_{1g} of A_{1g} is likely to be as effective as the modes Q_2 and Q_3 of E_g, we present in the following a set of calculations taking into account the mode Q_1 only for simplicity. Thus the electron-phonon interaction term (22) in conjunction with (23) and (24) simplifies to

$$\begin{aligned}H_{JT}=&\sum_{\vec{q}}(1/\sqrt{2})S_{Q_1}(\vec{q})J_{Q_1}e^{-i\vec{q}\cdot\vec{R}_l}\\ &\times(\beta_{\vec{q}}{}^\dagger-\beta_{-\vec{q}})(c_{\theta\lambda_d}^\dagger c_{\theta\lambda_d}+c_{\epsilon\lambda_d}^\dagger c_{\epsilon\lambda_d})\,.\end{aligned} \tag{26}$$

Now, reexpressing $c_{\theta\lambda_d}^\dagger$, $c_{\theta\lambda_d}$, etc. in terms of the original conduction-electron operators $c_{\vec{k}}^\dagger$, $c_{\vec{k}}$, etc. with the help of (13a), (19), and (21) and retaining such terms as give (to the lowest order in the coupling parameter) interactions between conduction electrons and phonons only, we get

$$H_{JT}=\sum_{\vec{k}',\vec{k},\vec{q}}D_{\vec{k}',\vec{k}}(\vec{q})e^{-i\vec{R}_l\cdot(\vec{k}'-\vec{k}+\vec{q})}\cdot(\beta_{\vec{q}}^\dagger-\beta_{-\vec{q}})c_{\vec{k}'}{}^\dagger c_{\vec{k}}$$

with (27)

$$D_{\vec{k}',\vec{k}}(\vec{q})=\frac{1}{2\sqrt{2}}\left(\frac{g_{E_g}}{g_{O_h}}\right)J_{Q_1}S_{Q_1}(\vec{q})\frac{\langle|M_{kF}|^2\rangle}{(\Delta^2+\delta^2)}\times\sum_{j'ji}D(\hat{R}_{ij'})D(\hat{R}_{ij})\,.$$

Here $\vec{k}$ and $\vec{k}'$ now span the entire first Brillouin zone and the symmetry operators $\hat{R}$ and $\hat{R}'$ are determined by the inverse conditions that $\hat{R}^{-1}\vec{k}$ and $\hat{R}'^{-1}\vec{k}'$ should belong to the original set of the test wave vectors constituting the stars we started with. In deriving (27), the conduction-electron wave-vector–dependent scalar quantities have been replaced by their angular averages over the Fermi sphere.

We note from (27) that the information regarding the impurity position is contained in the form of a phase factor. Thus, for noninteracting many-impurity centers (for sufficiently low impurity concentration), we can generalize (27) to

$$H_{\mathrm{JT}}=\sum_{\vec{k}',\vec{k},\vec{q},l} D_{\vec{k}'\vec{k}}(\vec{q})\,e^{-i\vec{R}_l\cdot(\vec{k}'-\vec{k}+\vec{q})}\,(\beta_{\vec{q}}^{\dagger}-\beta_{-\vec{q}})\,c_{\vec{k}'}^{\dagger}c_{\vec{k}}\,. \tag{28}$$

Incorporating this electron-phonon interaction term in the Hamiltonian for the noninteracting system of conduction electrons and phonons, we finally arrive at the effective electron-phonon Hamiltonian H_{eff} given by

$$\begin{aligned} H_{\mathrm{eff}}&=\sum_{\vec{k}}\epsilon_k c_{\vec{k}}^{\dagger}c_{\vec{k}}+\sum_{\vec{q}}\hbar\omega_q(\beta_{\vec{q}}^{\dagger}\beta_{\vec{q}}+\tfrac{1}{2})\\ &+\sum_{\vec{k}',\vec{k},\vec{q},l} D_{\vec{k}'k}(\vec{q})\,e^{-i\vec{R}_l(\vec{k}'-\vec{k}+\vec{q})}(\beta_{\vec{q}}^{\dagger}-\beta_{-\vec{q}})\,c_{\vec{k}'}^{\dagger}c_{\vec{k}}\,,\end{aligned} \tag{29}$$

which is essentially of the same form as that obtained by Fröhlich[30] and used in the standard BCS theory.[31]

III. REDUCED HAMILTONIAN AND SUPERCONDUCTING ENERGY GAP

To arrive at the effective electron-electron interaction induced by the virtual exchange of phonons via the impurity mechanism derived in the preceding sections, we perform the well-known canonical transformation[30] in order to eliminate terms containing the electron-phonon coupling coefficient in the first order in (29). Thus, we obtain the reduced Hamiltonian H_{red} (on neglecting the energy renormalization effects) as

$$\begin{aligned} H_{\mathrm{red}}&=\sum_{\vec{k}}\epsilon_k c_{\vec{k}}^{\dagger}c_{\vec{k}}+\sum_{\vec{q}}\hbar\omega_q(\beta_{\vec{q}}^{\dagger}\beta_{\vec{q}}+\tfrac{1}{2})\\ &+\sum_{\vec{k}'\vec{k}\vec{q};\,\vec{k}'''\vec{k}'';\,ml} V_{\vec{k}'\vec{k};\,\vec{k}'''\,\vec{k}''\,ml}(\vec{q})\,c_{\vec{k}'''}^{\dagger}c_{\vec{k}''}\,c_{\vec{k}'}^{\dagger}c_{\vec{k}}\,,\end{aligned} \tag{30}$$

where

$$\begin{aligned} V_{\vec{k}'\vec{k};\,\vec{k}''',\vec{k}'';\,ml}(\vec{q})&=D_{\vec{k}'''\vec{k}''}(\vec{q})\\ &\times D_{\vec{k}'\vec{k}}(q)\,\hbar\omega_q\left(\frac{1}{(\epsilon_{k'}-\epsilon_k)^2-(\hbar\omega_q)^2}\right)\\ &\times e^{-i(\vec{R}_m-\vec{R}_l)\cdot\vec{q}}\,e^{iR_m(\vec{k}'''-\vec{k}'')}\,e^{i\vec{k}_l(\vec{k}'-\vec{k})}\,.\end{aligned}$$

At this state we make use of the spatial random-phase approximation in that we set

$$\begin{aligned}\sum_{m,l;\,\vec{q}} e^{-i(\vec{R}_m-\vec{R}_l)\cdot\vec{q}}\,e^{i\vec{R}_m(\vec{k}'''-\vec{k}'')}\,e^{i\vec{R}_l(\vec{k}'-\vec{k})}\\ \cong N_i\sum_{\vec{q}}\delta_{\vec{k}'''-\vec{k}'',\,\vec{k}-\vec{k}'}\,,\end{aligned} \tag{31}$$

where N_i is the total number of impurity centers dispersed randomly over the macroscopic crystal. The condition expressed by (31) is significant. It implies that only such terms in (30) contribute coherently to the sum as satisfy the over-all electron momentum conservation. (The intermediate virtual processes need not conserve the momentum.) The over-all momentum conservation is, of course, characteristic of any local two-body interaction.

Making use of the coherence condition (31) in (30) and replacing the coefficients containing phonon variables by their respective values in the Debye limit (as is usually done for reasons of density of states) and noting that only those electron states which lie in the thin energy shell to within ± $\hbar\omega_q$ (the Debye cutoff) of the Fermi level are significant here,[20] we obtain for the induced electron-electron interaction $H_{e\text{-}e}$:

$$\begin{aligned} H_{e\text{-}e}\cong-\frac{1}{N}&\sum_{\vec{k}'\vec{k};\,\vec{k}'''\vec{k}''} V_{\vec{k}'\vec{k};\,\vec{k}'''\vec{k}''}\\ &\times(q_D)\,c_{\vec{k}'''}^{\dagger}c_{\vec{k}''}c_{\vec{k}'}^{\dagger}c_{\vec{k}}\,\delta_{\vec{k}'''-\vec{k}'',\,\vec{k}-\vec{k}'}\,,\end{aligned} \tag{32}$$

where

$$\begin{aligned} V_{\vec{k}'\vec{k};\,\vec{k}'''\vec{k}''}(q_D)&=c_i\left(\frac{E_{\mathrm{JT}}}{2\pi^2}\right)\left(\frac{\Delta^2}{\Delta^2+\delta^2}\right)\frac{1}{\rho^2(\epsilon_F)}\langle|S_{Q_1}|^2\rangle\\ &\times\left[\left(\sum_{j''',j'',i}D(\hat{R}_{ij'''})\,D(\hat{R}_{ij''})\right)\right.\\ &\times\left.\left(\sum_{j',j,i}D(\hat{R}_{ij'})\,D(\hat{R}_{ij})\right)\right].\end{aligned}$$

Here $\langle|S_{Q_1}|^2\rangle$ is the angular average of the geometrical form factor for the Q_1 mode in the Debye limit and, as shown in Appendix A, is approximately 0.89 for a sc lattice with one atom per unit cell, considering the longitudinal acoustical phonons only. c_i is the fractional impurity concentration ($=N_i/N$). E_{JT} is the JT stabilization energy given by $E_{\mathrm{JT}}=|J_{Q_1}|^2/2M\omega_{q_D}^2$.

Now, from very general considerations of the Cooper phenomenon in the ground state, pairing needs to be considered only between time-reversed states $+\vec{k},-\vec{k}$.[31,32] (The antiferromagnetic spin alignment, denoting a spin singlet ground state for the pair, follows from exchange stabilization.) Accordingly we set

$$\begin{aligned}\vec{k}&=-\vec{k}''\ \text{ or }\ \hat{R}=\hat{I}\hat{R}''\,;\\ \vec{k}'&=-\vec{k}'''\text{ or }\ \hat{R}'=\hat{I}\hat{R}'''\end{aligned} \tag{33}$$

($I\equiv$inversion operation). Since the irreducible representations permitted by the selection rules for JT effect in centrosymmetric crystals are necessarily of even parity (e.g., A_{1g}, E_g), we have

$$D_{E_g}(\hat{R}_{ij}) = D_{E_g}(\hat{I}\hat{R}_{ij}). \tag{34}$$

Thus, the two factors in the angular bracket in (32) form a perfect square (and the latter is found to be of the order of unity from the transformation matrix table of O_h[29]). Thus, $V_{\vec{k}',\vec{k};\vec{k}''',\vec{k}''}(q_D) \equiv V_{\text{imp}}$ stays always positive, signifying attractive interaction.

The above mechanism (V_{imp}) operates in addition to the usual phonon-induced mechanism of BCS (V_{ph}). As the cutoff employed is the same in both the cases, the over-all $[V\rho(\epsilon_F)]_{\text{total}}$ parameter occurring in the BCS gap equation, or equivalently in the expression for the transition temperature,[20] namely,

$$T_c = 1.14\,\hbar\omega_D\, e^{-1/V\rho(\epsilon_F)}, \tag{35}$$

is simply the sum of the two terms, i.e.,

$$\begin{aligned}[V\rho(\epsilon_F)]_{\text{total}} &= (V_{\text{ph}} + V_{\text{imp}})\,\rho(\epsilon_F), \\ &\cong V_{\text{ph}}\,\rho(\epsilon_F) + c_i\,\frac{E_{\text{JT}}}{2\pi^2}\,\frac{\Delta^2}{(\Delta^2+\delta^2)^2}\,\frac{1}{\rho(\epsilon_F)}\,.\end{aligned} \tag{36}$$

IV. DISCUSSION AND CONCLUSION

Some simple features of the expression (36) can at once be noted. The parameter $[V\rho(\epsilon_F)]_{\text{total}}$, and therefore T_c, is a monotonically increasing function of the impurity concentration c_i. T_c regarded as a function of the density of states at the Fermi level alone shows a maximum at

$$\rho(\epsilon_F) = \left[c_i\,\frac{E_{\text{JT}}}{2\pi^2}\,\frac{\Delta^2}{(\Delta^2+\delta^2)^2}\right]^{1/2}.$$

These variables are, however, interrelated and the net behavior may be much more complicated. The above assertions hold only within the range of validity of the physical approximations made, namely, the low impurity concentration and its random distribution. By the low impurity concentration we mean the following: The concentration should be low enough to justify the neglect of (i) the direct impurity-impurity interaction, and (ii) the mean free path effect due to the real impurity scattering, but still be sufficiently large to justify the spatial averaging over the dimensions of the order of the coherence length of the superconducting pairs formed. The mean free path effect may eventually cause a depression of T_c for large impurity concentrations as is actually observed. The former could be taken into account by adopting the more sophisticated formalism of Green's function.[33]

Apart from the above physical approximations, certain mathematical approximations have also been made in the foregoing treatment, primarily for reasons of simplicity. These are not essential to the physical model chosen and are not expected to have affected the results obtained in quality at least. Thus, in order to derive the effective electron-electron interaction, we have used the approximate procedure of unitary transformation as given by Fröhlich and subsequently used by Bardeen and Pines. As is well known, for any quantitative treatment of the problem of superconductivity it is necessary to employ a much more exact formalism, such as the one developed by Eliashberg.[34] Our numerical estimates are, therefore, not to be overemphasized. Moreover, the JT effect was treated within the quasimolecular approximation. However, the quasimolecular displacement was expanded in terms of the displacement field of the unperturbed lattice. Thus, the local modes due to changes in the lattice force constants were neglected altogether. Further, the calculation was done only for the Q_1 normal mode constituted from the longitudinal acoustical phonon modes of the lattice. As all the normal modes, which are active (i.e., satisfy the selection rule for JT effect), act independently and differ only to the extent of some "reduced matrix elements" and geometrical "form factors," their inclusion will simply enhance the numerical value of the parameter V_{imp}. Thus, the present estimate is going to be pessimistic.

The optimizable behavior of V_{imp}, or of T_c, with respect to the width parameter Δ [and indirectly $\rho(\epsilon_F)$] completely conforms to the physical picture outlined heuristically earlier in Sec. I. The apparent anomaly with respect to Δ when $\delta = 0$ in (36) (the level lies just at the Fermi level) is due purely to the mathematical approximation of replacing ϵ_k, $\epsilon_{k'}$, etc. by ϵ_F in the integrands of (19), which is justified only if δ is at least of the order of the cutoff $\hbar\omega_D$ employed.

To estimate the enhancement expected, we have first to estimate $\langle |M_{k_F}|^2\rangle$ and E_{JT} [Δ is related to the $\langle |M_{k_F}|^2\rangle$ and $\rho(\epsilon_F)$ through Eq. (3)]. As the nearly free-electron model is known to hold quite well for aluminum,[35] we consider the case of iron added as impurity to aluminum. Aluminum (fcc) has four atoms per unit cell with three valence electrons per atom (outer electron configuration being $3s^2 3p$), and the lattice constant is 4.04 Å. This gives the free-electron Fermi energy ~ 11.6 eV and the Fermi wave vector magnitude $k_F \sim 1.75 \times 10^8\ \text{cm}^{-1}$. To estimate $\langle |M_{k_F}|^2\rangle$ we need the radial part of the impurity wave functions $|\theta\rangle$, $|\epsilon\rangle$, which can be approximated as the one-electron atomic $3d$ radial function, but with the actual nuclear charge replaced by an effective charge $|e|Z_{\text{eff}}$.

The latter is obtained by equating the (accurately) known mean-squared radius[36] $\langle r^2\rangle_{3d} \sim 14$ a.u.^{2} of the $3d$ orbital for iron in the ground state to that obtained from the relation[37]

$$\langle r^2\rangle_{nl} = \tfrac{1}{2} n^2 [5n^2 + 1 - 3(l)(l+1)] / Z_{\text{eff}}^2 , \tag{37}$$

where n is the principal quantum number, in this case equal to 3, and l is the angular-momentum quantum number, in this case equal to 2. This gives $Z_{\text{eff}} \sim 13$. Further, approximating the Hartree-Fock field in the neighborhood of the impurity center by the screened Coulomb potential $|e| Z_{\text{imp}} \bar{e}^{k_c r}/r$ of the excess-valency charge $|e| Z_{\text{imp}}$ on the impurity (relative to the parent ion substituted), we finally get, after a straightforward integration and substitution in (21b) (see Appendix B),

$$\Delta \cong 0.625 \times 10^6 \left(\frac{\Omega_B}{\Omega_L}\right) \left(\frac{Z_{\text{eff}} Z_{\text{imp}} m^* e^4}{\hbar^2 (1 + 3k_c a_0)}\right)^2 \times \left(\frac{a_0 k_F}{1 + 3k_c a_0}\right)^4 \rho(\epsilon_F) \left(\frac{g_{E_g}}{g_{O_h}}\right) , \tag{38}$$

where Ω_L = unit cell volume,

$$\Omega_B = \tfrac{4}{3} \pi a_0^3 , \quad a_0 = \hbar^2 / Z_{\text{eff}} m^* e^2 .$$

The above physical approximation is essentially the Fermi-Thomas approximation. Also, with the above data for aluminum, we have $k_c = 2.05 \times 10^8$ cm^{-1}.

Assuming $Z_{\text{imp}} \sim 1$, we get $\Delta \sim 0.0186$ eV. Thus, under the optimal conditions $\Delta \sim \delta$, we have $V_{\text{imp}} \rho(\epsilon_F) \sim 0.006$ for $c_i = 0.001$ (= 0.1 at. %), while that due to the usual BCS mechanism calculated from (35), and using the experimental value T_c (aluminum) = 1.175 °K and the Debye temperature Θ_D of aluminum at 375 °K, is 0.172. Thus, the expected increase in T_c for aluminum with 0.1 at. % of iron as impurity is by about 25%. While an appreciable enhancement of this order has been suspected as reported recently for the Al : Fe system[3] we have no definite quantitative experimental results to compare with the calculated values. The only systems that have been investigated in detail, experimentally, are alloys of titanium and zirconium with transition-metal impurities of the iron series. Unfortunately, the available results on these systems cannot be interpreted unambiguously in terms of such mechanisms as the present one due to the appearance of additional Hume-Rothery phases (due to the change in the valence-electron concentration with the change in the impurity concentration) which differ considerably with respect to their superconducting properties.[38] More experimental data on simpler systems such as Al : Fe would be of considerable help in resolving this problem.

In conclusion, we can say that we have considered an impurity-assisted phonon-induced electron-electron (attractive) interaction mechanism which rightly retains all the aspects of the usual phonon mechanism of BCS (e.g., isotope effect), quite unlike the other purely electronic mechanisms (where there is no natural reason for using the Debye cutoff in the equation), and still the impurity structure (e.g., degeneracy) is included in an essential way. Apart from possibly accounting for the observed impurity enhancement effects on the superconductive transition temperature, it could also be intrinsically responsible for the abnormally high transition temperatures of some pure metals like lanthanum. In the latter case the localized virtual $4f$ shells lying just above the Fermi surface presumably serve as the degenerate impurity orbitals (or, more precisely, as narrow impurity band). In this connection it may be remarked here that the systematics of the high-transition-temperature superconducting alloys indicate a definite preference for certain crystal structures and stoichiometries, such as the β-W structure with V_3X-type (or in general A_3B_1-type where A is a transition metal) stoichiometry, where X could be Si or Ga. Here again we have three degenerate narrow bands corresponding to the three equivalent vanadium atoms,[39] and a cooperative JT effect may be invoked. Also, the possibility of such a mechanism in superconducting semiconductors and narrow band-gap insulators with localizable (heavy effective mass) excitonic states cannot be ruled out.

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APPENDIX A: EVALUATION OF THE FORM FACTOR FOR THE Q_1 MODE IN OCTAHEDRAL COORDINATION

From (25) we have

$$\langle |Q_1(g_D)|^2 \rangle = (1/4\pi) \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} [\cos\theta \sin(\pi \cos\theta) + \sin\theta \cos\phi \sin(\pi \sin\theta \cos\phi) + \sin\theta \sin\phi \sin(\pi \sin\theta \sin\phi)]^2 \sin\theta \, d\theta \, d\phi \equiv 3I_1 + 6I_2 , \tag{A1}$$

with

$$I_1=(1/4\pi)\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\cos^2\theta\,\sin^2(\pi\cos\theta)\sin\theta\,d\theta\,d\phi=\tfrac{1}{2}\int_{-1}^{+1}x^2\sin^2(\pi x)\,dx=\tfrac{1}{6}-(1/4\pi^2)\cong 0.141\,, \qquad \text{(A2)}$$

$$I_2=(1/4\pi)\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}(\sin\theta\sin\phi)(\sin\theta\cos\phi)\sin(\pi\sin\theta\sin\phi)\sin(\pi\sin\theta\cos\theta)\sin\theta\,d\theta\,d\phi\,. \qquad \text{(A3)}$$

Now, making use of the expansions

$$\sin((\pi\sin\phi)\sin\theta)=2\sum_{m=\text{odd}}^{\infty}J_m(\pi\sin\phi)\sin m\phi\,, \qquad \sin((\pi\cos\phi)\sin\theta)=2\sum_{n=\text{odd}}^{\infty}J_n(\pi\cos\phi)\sin n\theta\,,$$

(A3) reduces to

$$I_2=\sum_{m,n=\text{odd}}^{\infty}(4/4\pi)\int_{\theta=0}^{\pi}\sin^3\theta\sin m\phi\sin n\theta\,d\theta\int_{\phi=0}^{2\pi}J_m(\pi\sin\phi)\,J_n(\pi\cos\phi)\sin\phi\cos\phi\,d\phi$$

$$=(32/4\pi)\sum_{m,n=0}^{\infty}\int_0^{\pi/2}\sin m\theta\sin n\theta\sin^3\theta\,d\theta\int_0^{\pi/2}\sin n\theta\cos\phi\,J_m(\pi\sin\phi)J_n(\pi\cos\phi)\,d\phi$$

$$\equiv(32/4\pi)\sum_{m,n=\text{odd}}^{\infty}C_{mn}\int_0^{\pi/2}\sin\phi\cos\phi\,J_m(\pi\sin\phi)J_n(\pi\cos\phi)\,d\phi\,. \qquad \text{(A4)}$$

The integral appearing in (A 4) is a particular case of the general form investigated by Bailey.[40] Substituting directly from the latter, we get

$$I_2=\frac{4\sqrt{2}}{\pi^2}\sum_{\substack{m,n=\text{odd}\\ r,s}}^{\infty}C_{mn}\,(\tfrac{1}{4}\pi)^{(1/2)(m+n)+(r+5)}\frac{(\tfrac{1}{2}m)_r(\tfrac{1}{2}n)_s}{r!\,s!}$$

$$\times\frac{\Gamma(\tfrac{1}{2}m+1)\,\Gamma(\tfrac{1}{2}n+1)}{\Gamma(m+r+1)\,\Gamma(n+s+1)}J_{1+(1/2)(m+n)+(r+s)}(\sqrt{2}\pi). \qquad \text{(A5)}$$

Noting that $J_n(x)$ for real x and integral n falls off rapidly for $n>x$, the above series is seen to converge rapidly. The first three significant terms give

$$I_2=0.078\,. \qquad \text{(A 6)}$$

Finally, from (A 1), (A 2), and (A 6) we have

$$\langle|Q_1(q_D)|^2\rangle\cong 0.89\,. \qquad \text{(A 7)}$$

APPENDIX B: EVALUATION OF MIXING MATRIX ELEMENTS M_{jk} AND $\langle|M_{k_F}|^2\rangle$ AND OF THE WIDTH PARAMETER Δ

The nature of the approximations involved in evaluating the admixing matrix element $M_{j\vec{k}}$, and hence $\langle|M_{k_F}|^2\rangle$ and Δ, can best be seen by writing down the effective one-electron Hamiltonian H, in first quantization, for the system of an isolated impurity substituting a parent atom in an otherwise perfect metallic host crystal:

$$H=-(\hbar^2/2m)\nabla^2+V_l+(V_{\text{imp}}+V_{\text{nn}})-(V_{\text{pa}}+V_{\text{nn}})\,. \qquad \text{(B1)}$$

The first term on the right-hand side of (B 1) is the kinetic-energy operator; the second term is the unperturbed periodic lattice potential; the third and the fifth terms are, respectively, the impurity potential and the potential of the parent atom substituted; and the fourth, as well as the compensatory sixth term, is the potential of the nearest neighbors of the impurity center. The above effective potential fields are assumed to incorporate the many-electron effects in a self-consistent manner. Furthermore, we have

$$\left(-\frac{\hbar^2}{2m^*}\nabla^2+V_l\right)|\vec{k}\,^{ij}_{E_g}\rangle\cong-\frac{\hbar^2}{2m^*}\nabla^2|\vec{k}\,^{ij}_{E_g}\rangle=\epsilon_k|\vec{k}\,^{ij}_{E_g}\rangle\,,$$

$$\left(-\frac{\hbar^2}{2m^*}\nabla^2+V_{\text{imp}}+V_{\text{nn}}\right)|\theta\rangle=\epsilon_d|\theta\rangle\,, \qquad \text{(B2)}$$

$$\left(-\frac{\hbar^2}{2m^*}\nabla^2+V_{\text{imp}}+V_{\text{nn}}\right)|\epsilon\rangle=\epsilon_d|\epsilon\rangle\,.$$

In addition, we have the approximate orthogonality (16b). Thus, the only term in (B1) connecting the impurity states and the corresponding symmetry-adapted band states is $(V_{\text{imp}}-V_{\text{pa}})=V_{\text{excess}}$. The latter is to be regarded as due to the excess valency charge $(|e|Z_{\text{imp}})$ of the (ionized) impurity atom relative to the (ionized) parent atom substituted, and depends upon the relative degree of ionization.[40] An estimate of Z_{imp} can be made from the data on the normal-state resistivity changes due to the addition of the impurity.[41,42] The self-consistent potential due to the excess impurity charge imbedded in the electron sea of the metallic host is given, in the Thomas-Fermi approximation, by[41] the screened Coulomb potential $|e|Z_{\mathrm{imp}}e^{-k_c r}/r$, as noted earlier, where k_c is the Thomas-Fermi screening parameter given by $k_c^2 = 6\pi h e^2/\epsilon_F$.

Using the above potential and the approximate wave functions (15) and making use of the effective charge $|e|Z_{\mathrm{eff}}$ approximation (37) for the radial part of the impurity orbitals, we get at once, after straightforward integration and angular averaging,

$$\langle |M_{kF}|^2\rangle \cong \left(\frac{2^{14}3^4\pi}{5\Omega}\right) a_0 \left(\frac{k_F a_0}{1+3k_c a_0}\right)^4 \left(\frac{Z_{\mathrm{imp}}e^2}{1+3k_c a_0}\right)^2 . \tag{B3}$$

In arriving at (B3) we have made use of the relation

$$\langle |2k_z^2 - k_x^2 - k_y^2|^2\rangle = 3\langle |k_x^2 - k_y^2|^2\rangle . \tag{B4}$$

Substituting (B3) in the expression for Δ, we get finally

$$\Delta \cong 0.625\times 10^6 \left(\frac{\Omega_B}{\Omega_L}\right)\left(\frac{a_0 k_F}{1+3k_c a_0}\right)^4 \left(\frac{Z_{\mathrm{eff}}Z_{\mathrm{imp}}m^* e4}{\hbar^2(1+3k_c a_0)}\right)^2 . \tag{B5}$$

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