Effect of Localized and Resonant Impurity Modes on Energy Gap and Transition Temperature of Isotropic Superconductors

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The valence effect caused by a small concentration of light or heavy impurity atoms, giving rise to high-frequency localized modes or to low-frequency resonant modes, respectively, is studied in the framework of the Éliashberg electron-phonon model for an isotropic superconductor. The impurity atoms modify the phonon-induced electron-electron interaction and also the pseudo-Coulomb potential. The corresponding change $K_1(\omega,\omega')$ of the interaction kernel in the integral equation for the gap function of the impure metal $\Delta(\omega)$ is assumed to be small. With a perturbation calculation, a linear integral equation is derived at zero temperature for the impurity-gap function $\Delta_1(\omega)=\Delta(\omega)-\Delta_0(\omega)$. Assuming a single Lorentzian (or a superposition of two) for the phonon distribution of the host lattice, and an Einstein distribution for that of the impurity atoms, the integral equation is solved by Neumann's iteration procedure. The change of the gap parameter, $\Delta_{10}=\Delta_1(\omega=\Delta_{00})$, is calculated as a function of the impurity-mode frequency ω_{11}, the electron–impurity-mode coupling parameter $\alpha^2(\omega_{11})$, and the change U_1 of the pseudo-Coulomb potential. For a special case, dilute lead-indium alloys, $\Delta_1(\omega)$ is evaluated using the phonon spectra found from tunneling experiments. To determine the effect of impurity atoms on the transition temperature T_c, one starts from Éliashberg's gap equation for finite temperatures, which has solutions for $T\leq T_c$ and which becomes linear near T_c. The transition temperature is considered as an eigenvalue parameter. An exact formula for the change of this parameter δT_c, caused by $K_1(\omega,\omega)$, is derived by applying a theorem of Fredholm to the inhomogeneous integral equation for the impurity-gap function at the transition temperature. The final result for δT_c contains, besides the interaction kernels of host and impurity lattice, the solutions $\Delta_0(\omega,T_c)$ and $\tilde{\Delta}_0(\omega,T_c)$ of the gap equation and of the transposed gap equation of the pure metal, respectively. The theory is applied to dilute alloys of lead with In, Sn, Sb, Hg, Tl, and Bi. The results for δT_c are discussed using the available experimental data for these alloys.

I. INTRODUCTION

IN the contemporary theory of superconductivity two important parameters, namely, the energy Δ_0 necessary to break up a Cooper pair and the transition temperature T_c, depend on the electron-phonon (el-ph) interaction $\alpha^2(\omega)g(\omega)$.[1,2] The function $g(\omega)$ is the phonon density of states and $\alpha^2(\omega)$ is the interaction parameter depending on the energy ω of a phonon exchanged in an el-ph interaction. Furthermore, energy gap and transition temperature depend on the direct interaction between two electrons, that is, on the pseudo-Coulomb potential U.[3] It is the purpose of this paper to study simultaneously the effect of light or heavy impurity atoms, giving rise to localized or resonant modes, respectively, on the energy-gap function $\Delta(\omega)$, and in particular on the gap parameter $\Delta_0=\Delta(\omega=\Delta_0)$, and on the transition temperature T_c of an isotropic superconductor. Whereas impurities affect the shape of the gap function according to the change of $\alpha^2(\omega)g(\omega)$, the effect on T_c is a gross property of the impure metal depending on a well-defined average over the energy-gap function of the host lattice and the frequency-dependent electron–impurity-mode interaction.

The change of Δ_0 and T_c caused by this interaction and by the modification of the electronic structure [which, for a spherical energy band, is characterized by two parameters, the electron density of states $N(0)$ at the Fermi surface and the Fermi momentum k_F] is called the "valence" effect. It is linear in the impurity concentration and has its origin in a small but basic change of the electronic and dynamic properties of the lattice. This change is sometimes unimportant in the region of small impurity concentrations where the "mean-free-path" effect, i.e., scattering, strongly affects T_c. As pointed out by Anderson,[4] and studied in detail by other authors,[5–8] elastic impurity scattering leads to an admixture of Bloch functions of the conduction band and, therefore, the formation of Cooper pairs occurs between time-reversed scattered states, which are exact one-electron states of the impure metal. If the energy gap of the pure metal is anisotropic in $\mathbf{k}$ (wave vector) space because of an anisotropy in the effective electron-electron (el-el) interaction, the energy necessary to break up a Cooper pair in the impure metal is always smaller than the maximum binding energy of a pair in the pure metal. Therefore, Δ_0 and T_c decrease with increasing impurity concentration until impurity scattering becomes so strong that Bloch states from the entire Fermi surface become, with equal probability, admixed into a scattered-state wave func-

[1] G. M. Éliashberg, Zh. Eksperim. i Teor. Fiz. **38**, 966 (1960) [English transl.: Soviet Phys.—JETP **11**, 696 (1960)].
[2] J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters **10**, 336 (1963); Phys. Rev. **148**, 263 (1966).
[3] P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).
[4] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).
[5] T. Tsuneto, Progr. Theoret. Phys. (Kyoto) **28**, 857 (1962).
[6] C. Caroli, P. G. de Gennes, and T. Matricon, J. Phys. Radium **23**, 707 (1962).
[7] D. Markowitz and L. Kadanoff, Phys. Rev. **121**, 563 (1963).
[8] P. Hohenberg, Zh. Eksperim. i Teor. Fiz. **45**, 1208 (1963) [English transl.: Soviet Phys.—JETP **18**, 834 (1964)].

tion having energy $E\sim E_F$ (= Fermi energy). Under this condition of "strong scattering," the mean-free-path effect saturates. Hohenberg[8] finds saturation if $2\pi T_c\tau_r\ll 1$ (or if $l_r/\xi_0\ll 1$; l_r=mean free path due to impurity scattering; $\tau_r=l_r v_F$, where v_F is the Fermi velocity); whereas Markowitz and Kadanoff,[7] because they use the correct cutoff frequency in the gap equation for the impure superconductor, find saturation if $\omega_D\tau_r\ll 1$, where ω_D is the Debye frequency (the magnitude of the gap anisotropy does not enter the saturation criteria). For a weak-coupling superconductor, the Markowitz and Kadanoff criterion requires the impurity concentration to be one order of magnitude larger than that given by $l_r/\xi_0\ll 1$.[9] It is an experimental fact that the mean-free-path effect saturates when l_r becomes comparable with the coherence distance ξ_0,[10,11] corresponding to an impurity concentration of the order of one percent. For larger impurity concentrations, the valence effect determines the change of T_c.

To study the valence effect, a straightforward perturbation procedure is applied to the Éliashberg[12] gap equation and to the equation for the renormalization parameter. The perturbation consists of a small change of the interaction kernel. The change of the phonon-induced el-el interaction and of the pseudo-Coulomb potential completely accounts for the effect of impurities on the energy-gap function and the transition temperature of an isotropic superconductor.[13] It has been shown by Tsuneto[5] that elastic impurity scattering in itself does not affect the energy-gap function found from the Éliashberg equation (isotropic superconductor). At zero temperature (Sec. II), the result of our perturbation procedure is a linear inhomogeneous integral equation for the impurity-gap function $\Delta_1(\omega)$. The solution of this equation, and in particular Δ_{10}, will be discussed in Sec. III assuming that the interaction kernel of the host lattice is characterized by Lorentzian phonon distribution and that the impurity modes have an Einstein distribution. This simple phonon model is sufficient to study, e.g., the dependence of Δ_{10} on the impurity-mode frequency ω_{11}. For the application to a concrete case, dilute lead-indium alloys (Sec. IV), the phonon spectrum is approximated by a superposition of two Lorentzians, using the results of Rowell, McMillan, and Anderson[14] for $\alpha^2(\omega)g(\omega)$. In Sec. V, a perturbation technique is applied to the finite temperature-gap equation to derive an exact formula for the transition temperature change. The theory is applied to dilute alloys of lead with In, Sn, Sb, Hg, Tl, and Bi using proper values for the three impurity parameters ω_{11}, $\alpha^2(\omega_{11})$, and U_1.

Before the valence effect is discussed in the framework of the Éliashberg electron-phonon model, let us mention the Bardeen-Cooper-Schrieffer (BCS) result for the interaction (BCS notation)

$$\begin{aligned} V_{kk'}&=+V_0 \quad \text{if } |\epsilon_k|,|\epsilon_{k'}|<\omega_1,\\ &=+V_1 \quad \text{if } |\epsilon_k|,|\epsilon_{k'}|<\omega_{11},\\ &=0 \quad \text{otherwise.}\end{aligned} \tag{1}$$

One finds

$$\frac{\Delta_{10}}{\Delta_{00}}=\frac{1}{N(0)V_0}\frac{V_1/V_0}{1-N(0)V_1\log(\omega_{11}/\omega_1)}, \tag{2}$$

where $\Delta_{00}=2\omega_1\exp[-1/N(0)V_0]$. The impurity-gap parameter Δ_{10} is approximately linear in V_1 and is almost independent of ω_{11}.

II. PERTURBATION CALCULATION OF THE IMPURITY-GAP FUNCTION ($T=0$)

In the Éliashberg theory of the electron-lattice interaction in superconductors, the effective el-el interaction is not a constant, as in the BCS theory, but it is a frequency- and wave-vector-dependent function that can be written in terms of the dynamic dielectric constant of the electron-phonon system.[15] If one assumes the validity of the random phase approximation to describe the effective el-el interaction, the set of coupled integral equations for the gap function $\Delta(\omega)$ and for the renormalization parameter $Z(\omega)$ are given by

$$\Delta(\omega)=\frac{1}{Z(\omega)}\int_{\Delta_0}^{\omega_c}d\omega'\,\mathrm{Re}\left\{\frac{\Delta'}{(\omega'^2-\Delta'^2)^{1/2}}\right\}\times[K_+^{\mathrm{ph}}(\omega,\omega')-U], \tag{3}$$

and

$$[1-Z(\omega)]\omega=\int_{\Delta_0}^{\omega_c}d\omega'\,\mathrm{Re}\left\{\frac{\Delta'}{(\omega'^2-\Delta'^2)^{1/2}}\right\}K_-^{\mathrm{ph}}(\omega,\omega'), \tag{4}$$

where $K_\pm^{\mathrm{ph}}(\omega,\omega')$ represents the phonon part of the interaction kernel and U is the pseudo-Coulomb potential, which includes interactions between electrons outside the energy interval $\omega<|\omega_c|$ around the Fermi surface.

Let us now assume that for a pure metal the solutions of Eqs. (3) and (4), $\Delta_0(\omega)$ and $Z_0(\omega)$, are known. These

[9] For example, in Al with 1% Mg the residual resistivity $\rho_r=2.2\times10^{-7}$ Ω cm, corresponding to $l_r/\xi_0(\mathrm{Al})\simeq 0.2$ and $\tau_r\omega_D\simeq 2$. The value of ρ_r is taken from Ref. 10.

[10] A. Channin, E. A. Lynton, and B. Serin, Phys. Rev. **114**, 719 (1959).

[11] D. P. Seraphim, C. Chion, and D. J. Quinn, Acta Met. **9**, 861 (1961).

[12] G. M. Éliashberg, Zh. Eksperim. i Teor. Fiz. **38**, 966 (1960) [English transl.: Soviet Phys.—JETP **11**, 696 (1960)].

[13] For a discussion of this point I would like to thank Professor H. Suhl.

[14] J. M. Rowell, W. L. McMillan, and P. W. Anderson, Phys. Rev. Letters **14**, 633 (1965); see also J. G. Adler, J. E. Jackson, and B. S. Chandrasekhar, *ibid.* **16**, 53 (1966). The possibility of observing localized modes in dilute lead alloys with the help of the tunneling technique was first suggested by A. A. Maradudin, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 726.

[15] J. R. Schrieffer, *Theory of Superconductivity* (W. A. Benjamin, Inc., New York, 1964), p. 148.

solutions are determined by the interaction kernels of the pure metal, i.e., by U_0 and by the kernel functions $K_{\pm 0}^{\rm ph}$ which are conveniently written in the form

$$K_{\pm 0}^{\rm ph}(\omega,\omega')=\sum_\kappa \lambda_0^\kappa \int_0^\infty d\omega_0 g_\kappa(\omega_0)\frac{\omega_0}{2} \times\left(\frac{1}{\omega_0+\omega'+\omega-i0^+}\pm\frac{1}{\omega_0+\omega'-\omega-i0^+}\right), \quad (5)$$

where the phonon distribution g_κ of branch κ is given by the Lorentzian

$$g_\kappa(\omega)=\frac{\omega_2^\kappa/\pi}{(\omega+\omega_1^\kappa)^2+(\omega_2^\kappa)^2}, \quad (6a)$$

and where the el-ph interaction constant λ_0^κ is given by

$$\lambda_0^\kappa=2\alpha_\kappa^2(\omega_1^\kappa)/\omega_1^\kappa, \quad (6b)$$

with the following expression for the frequency-dependent el-ph interaction parameter[16]:

$$\alpha_\kappa^2(\omega)=\frac{N(0)q_D^3\omega_1^\kappa}{6\pi^2 k_F^2\omega} \times\left\{\sum_{\mathbf{K}}\frac{d\Omega_q}{4\pi}\frac{|g_{|\mathbf{K}+\mathbf{q}|}^\kappa|^2}{|\mathbf{q}+\mathbf{K}|}H(2k_F-|\mathbf{q}+\mathbf{K}|)\right\}_{\omega_\kappa(q)=\omega}. \quad (7)$$

Here k_F is the Fermi momentum, q_D is the Debye wave number, g_k^κ is the matrix element for the electron-phonon interaction, $\mathbf{K}$ is a reciprocal lattice vector, and $H(x)$ is Heaviside's unit step function: $H(x)=0$ if $x<0$, $H(x)=1$ if $x>0$. Equation (5) represents a convenient form of the phonon-induced interaction since the integration is readily carried out:

$$K_{\pm 0}^{\rm ph}(\omega,\omega')=\sum_\kappa \frac{\lambda_0^\kappa}{2}(\omega_1^\kappa-i\omega_2^\kappa) \times\left(\frac{1}{\omega_1^\kappa+\omega'+\omega-i\omega_2^\kappa}\pm\frac{1}{\omega_1^\kappa+\omega'-\omega-i\omega_2^\kappa}\right). \quad (8)$$

This form of the kernel has been derived by Anderson and Morel[3] from the time dependence of the retarded phonon-induced interaction. It is an excellent approximation to the kernel functions used by other authors[17–19] for the calculation of the tunneling density of states of lead.

A perturbation of the interaction kernel of the pure metal caused by impurities, other point defects, or by a homogeneous deformation of the lattice will change the gap function and the renormalization parameter. As for point defects, their impurity-mode distribution is often sharply peaked.[20] Then, it is a good approximation for the calculation of the impurity-gap parameter Δ_{10} and for the transition temperature change δT_c to assume an Einstein distribution, $g(\omega_{11})=\delta(\omega=\omega_{11})$. For the calculation of the energy dependence of the impurity-gap function, $\Delta_1(\omega)$, it is, however, important to take the "spreading" of the impurity-mode distribution into account. To this end, either the Einstein results $\Delta_1(\omega,\omega_{11})$ and $Z_1(\omega,\omega_{11})$ are integrated over $g(\omega_{11})$—the integral equations for Δ_1 and Z_1 are linear[21]—or the impurity kernel $K_1(\omega,\omega')$ is derived from a Lorentzian distribution of impurity modes. With the impurity-mode distribution given by $\delta(\omega-\omega_{11})$, the perturbation of the phonon-induced interaction has the form

$$K_\pm^{\rm ph}-K_{\pm 0}^{\rm ph}=K_{\pm 1}^{\rm ph}(\omega,\omega')=\frac{\lambda_1\omega_{11}}{2} \times\left(\frac{1}{\omega_{11}+\omega'+\omega-i0^+}\pm\frac{1}{\omega_{11}+\omega'-\omega-i0^+}\right) -\frac{N_1}{N_0}K_{\pm 0}^{\rm ph}(\omega,\omega'), \quad (9)$$

where N_1 and N_0 are the number of impurity atoms and host atoms per cubic centimeter, respectively. The second term in Eq. (9) is omitted if the impurity atoms occupy interstitial sites. The electron–impurity-mode coupling constant λ_1 depends linearly on N_1. Only for the special case of light impurity atoms arranged in a periodic lattice can λ_1 be evaluated from Eq. (9).[22] In general, λ_1 must be considered as an unknown parameter. The perturbation of the Coulomb interaction is given by

$$U_1=U-U^2=A\frac{\delta N(0)}{N(0)}+B\frac{\delta k_F}{k_F}, \quad (10)$$

[16] D. J. Scalapino, Y. Wada, and J. C. Swihart, Phys. Rev. Letters **4**, 102 (1965).
[17] J. M. Rowell, P. W. Anderson, and D. E. Thomas, Phys. Rev. Letters **10**, 334 (1963).
[18] J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters **10**, 336 (1963).
[19] W. L. McMillan and J. M. Rowell, Phys. Rev. Letters **14**, 108 (1965).

[20] For localized modes (light impurity atoms), ω_{11} is larger than the cutoff frequency of the host lattice and an Einstein distribution is a good approximation to the localized mode distribution. The distribution for resonant modes can also be sharply peaked, provided $M_1-M_0\gg M_0$ (M_0 = mass of host atoms, M_1 = mass of impurity atoms) as can be seen from the theoretical work of R. Brout and W. Visscher [Phys. Rev. Letters **9**, 54 (1962)].
[21] D. J. Scalapino and P. W. Anderson, Phys. Rev. **133**, A921 (1963).
[22] One finds

$$|g_q|^2=\left(\frac{4\pi e^2}{q^2}\right)^2\frac{1}{2\omega_1(q)}\frac{Z_1^2N_1}{M_1}S^2(q,r_0).$$

Here Z_1 is the charge of an impurity atom and $\omega_1(q)$ is the frequency of the longitudinal branch of the impurity phonon band. The function $S^2(q,r_0)$ accounts for the screening of the electron–impurity-mode interaction. If the interaction is screened by $\exp(-r/r_0)$,

$$S(q,r_0)=\int_0^\infty \exp\left(-\frac{r}{r_0}\right)\left(\cos qr-\frac{\sin qr}{qr}\right)\left(1+\frac{r}{r_0}\right)(dr/r).$$

where

$$A=\left[\frac{2}{a}-\frac{a}{(1+a^2)}\right]U_0, \quad B=\frac{2a}{\mu}\left[\frac{a^2}{\mu(1+a)^2}-2\right]U_0,$$

$$a^2=\frac{\pi e^2 N(0)}{k_F{}^2}, \qquad \mu=\frac{a^2}{2}\log\left[1+\left(\frac{1}{a^2}\right)\right].$$

Since a^2 is of the order of 0.4 for superconducting metals, $A>0$ and $B<0$.

With Eqs. (9) and (10) the perturbation calculation proceeds by writing the interaction kernel of the impure metal in the form

$$K_{\pm}(\omega,\omega')=K_{\pm 0}(\omega,\omega')+\epsilon K_{\pm 1}(\omega,\omega'), \tag{11}$$

where ϵ is a smallness parameter, corresponding to the impurity concentration, and where $K_+=K_+{}^{\rm ph}-U$, $K_-=K_-{}^{\rm ph}$. The gap function $\Delta(\omega)$ and the renormalization parameter $Z(\omega)$ of the impure metal are also written in this form. If one substitutes Eq. (11) into Eqs. (3) and (4), one finds equations for $\Delta_1(\omega)$ and $Z_1(\omega)$[23]:

$$\Delta_1(\omega)=F(\omega)+\frac{1}{Z_0(\omega)}\int_{\Delta_{00}}^{\omega_c}d\omega' \times\mathrm{Re}\left\{\frac{\Delta_1'-\Delta_{10}}{(\omega'^2-\Delta_0'^2)^{1/2}}\right\}K_{+0}(\omega,\omega'), \tag{12}$$

where

$$F(\omega)=\frac{1}{Z_0(\omega)}\left\{\int_{\Delta_{00}}^{\omega_c}d\omega'\,\mathrm{Re}\left\{\frac{\Delta_0'}{(\omega'^2-\Delta_0'^2)^{1/2}}\right\}K_{+1}(\omega,\omega')+\int_{\Delta_{00}}^{\omega_c}d\omega'\,\mathrm{Re}\left\{\frac{\Delta_{10}}{(\omega'^2-\Delta_0'^2)^{1/2}}\right\}K_{+0}(\omega,\omega')+\int_{\Delta_{00}}^{\omega_c}d\omega'\frac{\Delta_{10}\Delta_{00}}{(\omega'^2-\Delta_{00}^2)^{3/2}} \times[\Delta_{00}K_{+0}(\omega,\omega')-\omega' K_{+0}(\omega,\Delta_{00})]-Z_1(\omega)\Delta_0(\omega)\right\} \tag{13}$$

and

$$Z_1(\omega)=-\frac{1}{\omega}\left\{\int_{\Delta_{00}}^{\omega_c}d\omega'\,\mathrm{Re}\left\{\frac{\omega'}{(\omega'^2-\Delta'^2)^{1/2}}\right\}K_{-1}(\omega,\omega')+\int_{\Delta_{00}}^{\omega_c}d\omega\frac{\Delta_{10}\Delta_{00}\omega'}{(\omega'^2-\Delta_{00}^2)^{3/2}} \times[K_{-0}(\omega,\omega')-K_{-0}(\omega,\Delta_{00})]\right\}. \tag{14}$$

These equations are correct for small impurity concentrations, independent of the strength of the electron-phonon interaction in the host metal. Equation (12) is a linear inhomogeneous integral equation for the impurity gap function. The inhomogeneous part $F(\omega)$ can be presented in closed form, if one assumes a Lorentzian phonon distribution for the host lattice (Appendix I). For a more realistic phonon spectrum, e.g., a superposition of two Lorentzians, the first term of $F(\omega)$ must be calculated numerically. The two equations for $\Delta_1(\omega)$ and $Z_1(\omega)$ are merely coupled via the impurity gap parameter Δ_{10}.

[23] From hereon the perturbation of gap function and renormalization parameter will be denoted as $\Delta_1(\omega)$ and $Z_1(\omega)$, respectively.

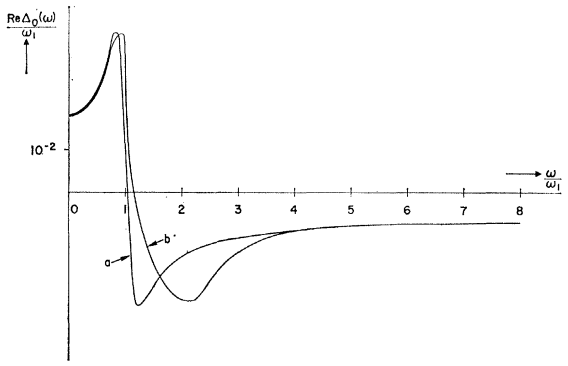

FIG. 1. Real part of the energy-gap function of a pure metal characterized by a Lorentzian phonon distribution centered at $\omega=\omega_1$ and having half-width $\omega_2=0.2\omega_1$. Curve (a) represents the approximate solution of the gap equation given by Eq. (15). Curve (b) is the exact solution, ignoring renormalization. The parameters of the interaction kernel are given by $\lambda_0=0.35$ and $U_0=0.1$.

III. SOLUTION OF THE IMPURITY-GAP EQUATION (WEAK COUPLING)

In the case, where $\Delta_{00}\ll\omega_1{}^{\kappa}$, the quantity Δ_0' under the square root in Eq. (12) may be replaced by Δ_{00}. Then the two equations for the real and imaginary part of $\Delta_1(\omega)$ decouple, and the mathematical problem consists of solving the linear inhomogeneous integral equation for $\mathrm{Re}\{\Delta_1(\omega)\}$. To this end, a successive interaction procedure is applied which results in the Neumann series.[24] The first term of this series, corresponding to the zeroth-order solution for $\mathrm{Re}\{\Delta_1(\omega)\}$, is the homogeneous part $F(\omega)$ which consists of four

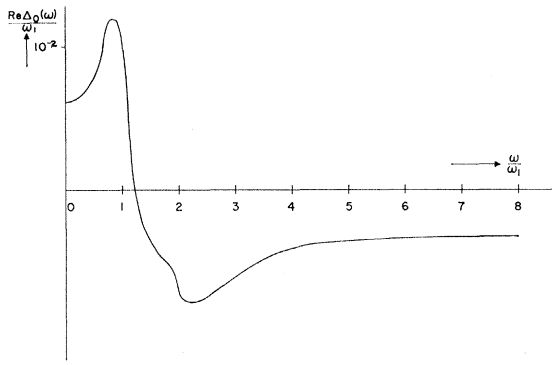

FIG. 2. Real part of the energy-gap function of the pure metal, including renormalization. For the parameter values of the interaction kernel, see Fig. 1.

[24] G. Hamel, *Integralgleichungen* (Julius Springer-Verlag, Berlin, 1949), p. 25.

terms, $F_i(\omega)$, where i denotes successively the four terms on the right side of Eq. (13). For the phonon-induced interaction given by Eq. (8), the last three of the four terms are readily calculated. The function $F_1(\omega)$, however, contains $\Delta_0(\omega)$ which in case of a single Lorentzian phonon spectrum can be approximated by a simple function, so F_1 can also be presented in a closed form. Then $K_{\pm 0}^{\rm ph}$ consists of a single term and $\Delta_0(\omega)$ can be approximated by the function

$$\Delta_0(\omega)=(\Delta_{00}+\Delta_{0C})U(\omega)-\Delta_{0C}, \tag{15}$$

where

$$U(\omega)=\frac{\omega_1-i\omega_2}{2}\left(\frac{1}{\omega_1+\omega-i\omega_2}+\frac{1}{\omega_1-\omega-i\omega_2}\right), \tag{16}$$

and where Δ_{00} and Δ_{0C} can be considered as adjustable parameters (the index $\kappa=1$ has been omitted). For $Z_0(\omega)=1$ and for $(\omega_2/\omega_1)^2\ll 1$, one finds by substituting $\Delta_0(\omega)$ into the gap equation for the pure metal:

$$\Delta_{00}=2\omega_1\exp\left(-\frac{1+\frac{1}{2}\lambda_0}{\lambda_0-U_0}\right) \tag{17}$$

and

$$\Delta_{0C}=\Delta_{00}U_0\frac{\log(2\omega_1/\Delta_{00})}{1+U_0\log(\omega_c/\omega_1)}. \tag{18}$$

The validity of these results has been checked by solving numerically the nonlinear integral equation for the pure metal. This result and that given by Eqs. (15) through (18) are compared in Fig. 1. For $Z_0(\omega)\neq 1$, which takes into account the renormalization of quasiparticle energies caused by electron-phonon interactions, the energy-gap function is shown in Fig. 2. The ratio Δ_{0C}/Δ_{00} is also given by Eq. (18). However, the value of Δ_{00} is much smaller than that found by ignoring the renormalization. With the help of Eq. (15), an analytical expression is found for $F_1(\omega)$. This result and those for the other parts of $F(\omega)$ are given in Appendix I; formulas for the renormalization parameters $Z_0(\omega)$ and $Z_1(\omega)$ are found in Appendix II. The results are readily generalized to the more general case of a multipeaked phonon spectrum. If one knows the inhomogeneous part of the impurity gap, Eq. (12), the Neumann series is found by numerical integration. The first few approximations to the impurity-gap function are given by

$$\Delta_1^{(0)}(\omega)=F(\omega,\Delta_{10}^{(0)}), \tag{19}$$

$$\Delta_1^{(1)}(\omega)=F(\omega,\Delta_{10}^{(1)})+\frac{1}{Z_0(\omega)}\int_{\Delta_{00}}^{\omega_c}d\omega' \times\frac{[\mathrm{Re}\{F_1(\omega',\Delta_{10}^{(1)})\}-\Delta_{10}^{(1)}]}{(\omega'^2-\Delta_{00}^2)^{1/2}}K_{+0}(\omega,\omega'). \tag{20}$$

The impurity-gap parameter Δ_{10} is in zeroth order determined by $\mathrm{Re}\{F(\omega=\Delta_{00})\}$; the first-order result is found with one numerical integration, etc. To study the dependence of the impurity-gap parameter on the Einstein frequency ω_{11}, the phonon spectrum of the host lattice is characterized by a Lorentzian distribution. This assumption allows for an analytic calculation of $F(\omega)$. It is sufficient for this purpose, since it is primarily the interference of $\Delta_0(\omega')$ with $K_{+1}(\omega,\omega')$ which determines the characteristic dependence of Δ_{10} on ω_{11} shown in Fig. 3. A two-Lorentzian phonon spectrum of the host lattice would not significantly alter the ω_{11} dependence of the impurity-gap parameter. The result for the first few approximations to Δ_{10}, shown in Fig. 3, are calculated under the assumption that the electron-phonon interaction constant per atom of the host lattice is equal to that for an impurity atom and that the pseudo-Coulomb potential remains unchanged.

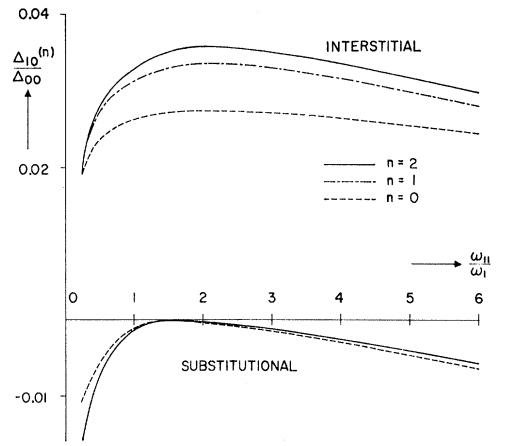

FIG. 3. Impurity-gap parameter as a function of the impurity-mode frequency ω_{11}, taking into account renormalization. The index n denotes the order of approximation in which the impurity-gap equation has been solved by iteration. The interaction kernel of the impurities is characterized by $\lambda_1/\lambda_0=N_1/N_0=U_1/U_0=0.01$. For the interaction kernel of the host lattice see Fig. 1.

The effect of a localized mode, centered at $\omega_{11}=2\omega_1$ and caused by interstitial impurities, on the shape

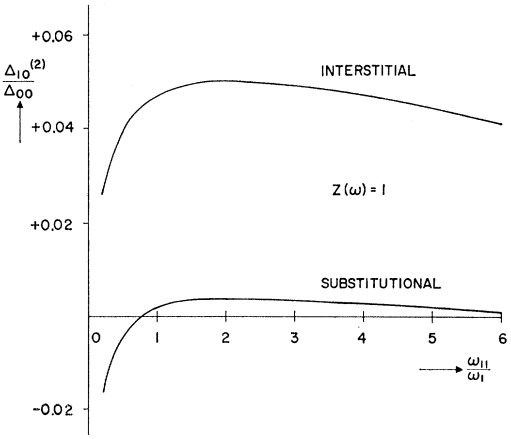

FIG. 4. Impurity-gap parameter as a function of the impurity-mode frequency ω_{11}, ignoring renormalization. For the parameters of the interaction kernel see Fig. 3.

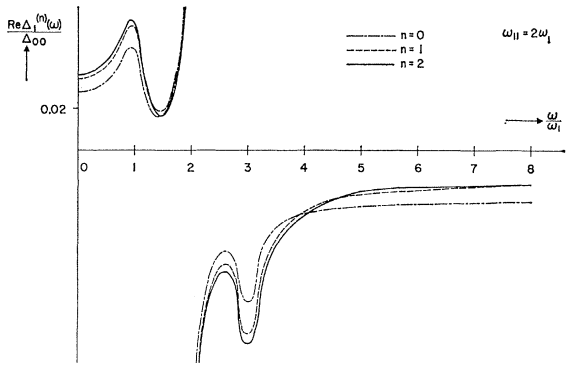

FIG. 5. Real part of the impurity-gap function for localized modes (light interstitial impurity atoms) $\omega_{11}=2\omega_1$. For the parameters of the interaction kernel see Fig. 3.

of the impurity-gap function is shown in Fig. 5. The renormalization is properly taken into account. At $\omega=\omega_{11}+\Delta_{00}$, the impurity-gap function has a square root singularity when ω comes from *below*, because of $\mathrm{Re}\{K_{+1}(\omega,\omega')\}$ in $F_1(\omega)$ and because of $\mathrm{Re}\{K_{-1}(\omega,\omega')\}$ in $\mathrm{Re}\{Z_1(\omega)\}$. It also has a square root singularity when ω comes from *above*, because of $\mathrm{Im}\{K_{+1}(\omega,\omega')\}$ in $F_1(\omega)$ and because of $\mathrm{Im}\{K_{-1}(\omega,\omega')\}$ in $\mathrm{Im}\{Z_1(\omega)\}$. Figure 5 demonstrates the good convergence of the Neumann series for all values of ω. Structure in the impurity-gap function is seen at ω_{11} and $\omega_{11}\pm\omega_1$.

IV. IMPURITY-GAP FUNCTION FOR DILUTE Pb-In ALLOYS

In strong-coupling superconductors such as lead, the condition $\Delta_{00}\ll\omega_1^{\kappa}$ is, at least for the transverse acoustical branch, not fulfilled. In calculating the impurity-gap function for $Pb_{0.97}In_{0.03}$ we have, however, made the approximation that Δ_0' under the square root of Eq. (12) can be replaced by Δ_{00}. Renormalization is properly taken into account. The spectral dependence of the el-ph interaction is known for this alloy system.[14] For the calculation of the energy dependence of the impurity-gap function $\Delta_1(\omega)$, the following assumptions are made for the interaction kernels of the pure and impure metal, respectively:

1. For lead, the phonon-induced interaction is given by Eq. (8). The corresponding phonon density of states is that chosen by other authors[18,19] for the calculation of the tunneling density of states. It consists of two Lorentzians, one for transverse and one for longitudinal modes, centered at $\omega_1^1=4.4$ MeV and at $\omega_1^2=8.5$ MeV, respectively, with half-widths $\omega_2^1=0.75$ MeV and $\omega_2^2=0.5$ MeV, respectively. The coupling consists λ_0^1 and λ_0^2 are given by Eq. (6b), with average values of the electron-phonon interaction parameter given by McMillan and Rowell,[19] $\alpha_1^2=1.11$ MeV and $\alpha_2^2=1.34$ MeV. The Coulomb pseudopotential $U_0=0.11$.

2. The perturbation of the phonon-induced interaction is derived from a Lorentzian distribution of impurity modes centered at $\omega_{11}=9.5$ MeV and with half-width $\omega_{12}=0.25$ MeV. The coupling constant $\alpha^2(\omega)=1.34$ MeV. This choice of the coupling constant corresponds to the observation of Rowell, McMillan, and Anderson,[14] who found by the inversion of the energy-gap function of the impure metal that the electron–impurity-mode coupling constant $\alpha^2(\omega_{11})$ is of the same magnitude as that for pure lead. The authors do not quote a value for the Coulomb pseudopotential in $Pb_{0.97}In_{0.03}$. Therefore, the change of the Coulomb pseudopotential of lead due to alloying with indium has been determined by fitting the calculated value of the transition-temperature change δT_c (valence effect, see Sec. VI) to the experimental value of Gamari-Seale and Coles.[25] The result is $U_1=0.007$. If it were also possible to determine U_1 accurately from an inversion of the gap equation of the impure metal, the valence effect δT_c could be predicted.

The results for the second-order approximation of the impurity-gap function are shown in Figs. 6(a) and 6(b). The impurity-gap parameter is given by $\Delta_{10}^{(2)}/\Delta_{00}=-0.010$; the calculated change of the transition temperature is smaller, $\delta T_c/T_c=-0.0058$. The energy dependence of the impurity-gap function exhibits structure at $\omega_{11}+\Delta_{00}$ and at $\omega_{11}+\omega_1^{\kappa}+\Delta_{00}$. At these frequencies, also the tunneling density of states of the impure metal, which is readily calculated with the energy-dependent gap function $\Delta_0(\omega)+\Delta_1(\omega)$,[15] has additional structure [see Fig. 6(c)].

V. PERTURBATION CALCULATIONS OF THE IMPURITY EFFECT ON THE TRANSITION TEMPERATURE

The integral equation for the energy-gap function at nonzero temperature has been derived by different authors.[26,27] The presumptions, namely, a spherical energy band and the random-phase approximation for the effective el-el interaction, are the same as those for the energy-gap equation (3) at zero temperature. Near the transition temperature, where $(T_c-T)/T_c\ll 1$, the integral equation for the energy-gap function can be linearized because in the denominator square root, $(\omega'^2-\Delta'^2)^{1/2}$, the Δ'^2 term can be ignored. Then, the linearized integral equation is given by

$$\Delta(\omega)=\frac{1}{Z(\omega)}\int_0^{\omega_c}d\omega'\,\mathrm{Re}\Delta(\omega')\Big[f(-\omega')K_+^{\mathrm{ph}}(\omega,\omega')-f(\omega')K_+^{\mathrm{ph}}(\omega,-\omega')-U\tanh\frac{\beta\omega'}{2}\Big]+\frac{i\pi}{Z(\omega)}\int_0^{\omega_c}d\omega'\times\mathrm{Re}\Big\{\frac{\Delta(\omega+\omega')}{\omega+\omega'}+\frac{\Delta(\omega-\omega')}{\omega-\omega'}\Big\}\frac{\sum_{\kappa}\alpha_{\kappa}^2(\omega')g_{\kappa}(\omega')}{\exp(\beta\omega')-1},\quad(21)$$

[25] H. Gamari-Seale and B. R. Coles, Proc. Phys. Soc. (London) **86**, 1199 (1965).
[26] V. Ambegaokar and L. Tewordt, Phys. Rev. **134**, A805 (1964).
[27] Y. Wada, Phys. Rev. **135**, A1481 (1964).

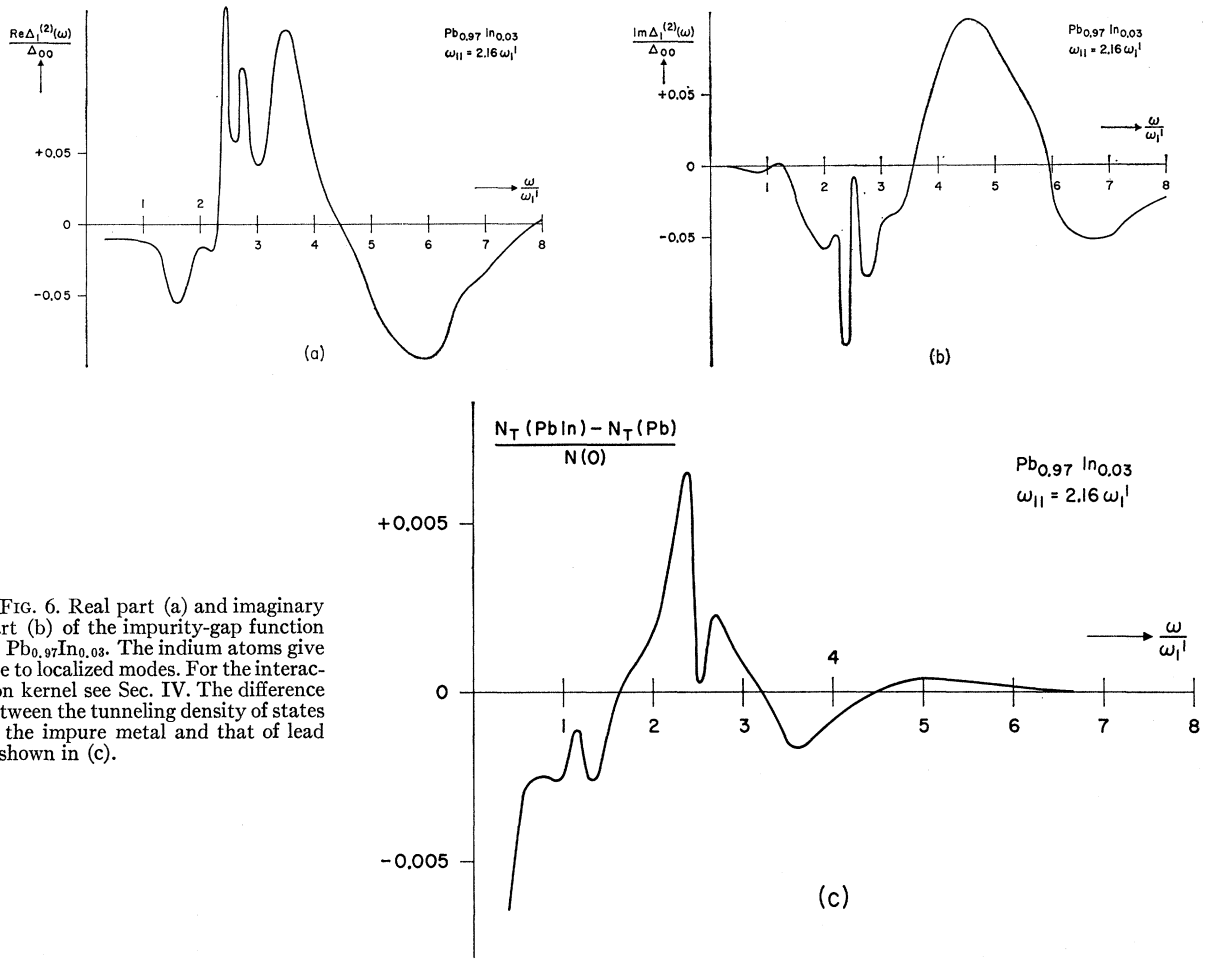

FIG. 6. Real part (a) and imaginary part (b) of the impurity-gap function of $Pb_{0.97}In_{0.03}$. The indium atoms give rise to localized modes. For the interaction kernel see Sec. IV. The difference between the tunneling density of states of the impure metal and that of lead is shown in (c).

where $f(\omega')$ is the Fermi-Dirac function and where $\beta=1/kT$. The renormalization parameter is independent of $\Delta(\omega')$ and is given by the quadrature

$$[1-Z(\omega)]\omega=\int_0^{\omega_c} d\omega' \times[f(-\omega')K_-^{\rm ph}(\omega,\omega')+f(\omega')K_-^{\rm ph}(\omega,-\omega')] -i2\pi\int_0^{\omega_c}\frac{d\omega'}{\exp(\beta\omega')-1}\sum_\kappa \alpha_\kappa^2(\omega')g_\kappa(\omega'). \quad (22)$$

The solution of Eq. (21) for $\beta=\beta_c$ represents the exact energy-gap function at the transition temperature T_c. The latter plays the role of an eigenvalue parameter in a Fredholm integral equation of the second kind. The eigenvalue, i.e., T_c for which Eq. (21) has a solution depends on the interaction kernel. A small change of the kernel leads to a small change of the eigenvalue parameter for which the linearized gap equation has a solution. Here, we are interested in the effect of impurities on T_c, not in their effect on the energy-gap function. The calculation of an exact formula for δT_c proceeds with the following perturbation procedure. The real part of the kernel in Eq. (21) is written in the form:

$$\Re(\omega,\omega';\beta)=\Re_0(\omega,\omega';\beta)+\Re_1(\omega,\omega';\beta), \quad (23)$$

where

$$\Re_0(\omega,\omega';\beta)={\rm Re}\left\{\frac{1}{Z_0(\omega)}\left[f(-\omega)K_{+0}^{\rm ph}(\omega,\omega') -f(\omega')K_{+0}^{\rm ph}(\omega,-\omega')-U_0\tanh\left(\frac{\beta\omega'}{2}\right)\right]\right\}, \quad (24)$$

and where

$$\Re_1(\omega,\omega';\beta)={\rm Re}\left\{\frac{1}{Z_0(\omega)}\left[f(-\omega)K_{+1}^{\rm ph}(\omega,\omega') -f(\omega')K_{+1}^{\rm ph}(\omega,-\omega')-U\tanh\left(\frac{\beta\omega'}{2}\right)\right]\right\}-{\rm Re}\left\{\frac{Z_1(\omega)}{Z_0(\omega)}\right\} \times{\rm Re}\{\Re_0(\omega,\omega';\beta)\}+{\rm Im}\left\{\frac{Z_1(\omega)}{Z_0(\omega)}\right\}{\rm Im}\{\Re(\omega,\omega';\beta)\}. \quad (25)$$

The renormalization parameter of the pure metal, $Z_0(\omega)$, is given by Eq. (22) with $K_-^{\rm ph}=K_{-0}^{\rm ph}$. The change of the renormalization parameter due to the electron–impurity-

mode interaction is in good approximation given by

$$Z_1(\omega)=-(1/\omega)\int_0^{\omega_c} d\omega' \times[f(-\omega')K_{-1}^{\rm ph}(\omega,\omega')-f(\omega')K_{-1}^{\rm ph}(\omega,-\omega')]. \quad (26)$$

The perturbation of the interaction kernel $\mathfrak{K}_1$ causes a change of the transition temperature from T_c to $T_c+\delta T_c$. Therefore, near the transition temperature the kernel of the impure metal is written as

$$\mathfrak{K}(\omega,\omega';\beta)=\mathfrak{K}_0(\omega,\omega';\beta)+(\beta-\beta_c)\times\left(\frac{d\mathfrak{K}_0(\omega,\omega';\beta)}{d\beta}\right)_{\beta=\beta_c}+\mathfrak{K}_1(\omega,\omega';\beta_c). \quad (27)$$

This expression is inserted into the real part of Eq. (33) and one finds the impurity-gap equation at $T_c+\delta T_c$,

$$\mathrm{Re}\{\Delta_1(\omega)\}-\int_0^{\omega_c}\mathrm{Re}\{\Delta_1(\omega')\}\mathfrak{K}_0(\omega,\omega';\beta_c)=\delta\beta_c\int_0^{\omega_c}\mathrm{Re}\{\Delta_0(\omega')\}\left(\frac{d\mathfrak{K}_0(\omega,\omega';\beta)}{d\beta}\right)_{\beta=\beta_c}+\int_0^{\omega_c}\mathrm{Re}\{\Delta_0(\omega')\}\mathfrak{K}_1(\omega,\omega';\beta_c)d\omega', \quad (28)$$

where $k\delta\beta_c=(T_c+\delta T_c)^{-1}-T_c^{-1}$. The left-hand side of of this equation is of the same form as the real part of the homogeneous Eq. (21.) Therefore, according to a well-known theorem for inhomogeneous Fredholm equations of the second kind, the inhomogeneous integral Eq. (28) has a solution only if the right side of this equation is orthogonal to the solution $\mathrm{Re}\{\tilde{\Delta}_0(\omega)\}$ of the transposed equation,

$$\mathrm{Re}\{\tilde{\Delta}_0(\omega)\}=\int_0^{\omega_c} d\omega'\,\mathrm{Re}\{\tilde{\Delta}_0(\omega')\}\mathfrak{K}_0(\omega',\omega;\beta_c). \quad (29)$$

Assuming that this equation has a nontrivial solution, we find from the orthogonality condition the following expression for the change of the transition temperature

$$\delta\beta_c=-\int_0^{\omega_c} d\omega'\,\mathrm{Re}\{\tilde{\Delta}_0(\omega')\}\int_0^{\omega_c} d\omega''\,\mathrm{Re}\{\Delta_0(\omega'')\}\mathfrak{K}_1(\omega',\omega'';\beta_c)\Big/\int_0^{\omega_c} d\omega''\,\mathrm{Re}\{\tilde{\Delta}_0(\omega')\}\int_0^{\omega_c} d\omega'' \times\mathrm{Re}\{\Delta_0(\omega'')\}\left(\frac{d\mathfrak{K}_0(\omega',\omega'';\beta)}{d\beta}\right)_{\beta=\beta_c}. \quad (30)$$

VI. RESULTS FOR THE TRANSITION-TEMPERATURE CHANGE

First, δT_c has been calculated as a function of the impurity-mode frequency ω_{11} for a single Lorentzian-phonon distribution of the host lattice superimposed with an Einstein distribution of impurity modes. For this model the impurity-gap parameter Δ_{10} has been calculated in Sec. II. It also provides a qualitative picture for the ω_{11} dependence of δT_c and Δ_{10} for a more realistic phonon model. The formula for δT_c contains the solution of the gap equation and of the transposed gap equation of the host lattice at T_c. For weak-coupling superconductors, the shape of $\Delta_0(\omega,T_c)$ is the same as that of the zero-temperature gap function (Fig. 2),[16] the same is true for $\tilde{\Delta}_0(\omega,T_c)$. The equation for δT_c contains, besides the gap functions, the transition temperature of the pure metal. The value of T_c is taken from the BCS relation $\gamma kT_c=2\Delta_{00}$, where Δ_{00} is the exact gap parameter of the pure metal and where $\gamma=3.5$. Since, in general, γ depends on the strength of the phonon-induced el-el interaction, we have evaluated the dependence of $\delta T_c/T_c$ on γ for $3\leq\gamma\leq4$ and found it to be smaller than 3%, independent of whether or not renormalization is taken into account. The results for $\delta T_c/T_c$ are plotted in Fig. 7. It is assumed that the electron–impurity-mode coupling constant is equal to the electron-phonon interaction of the host lattice.

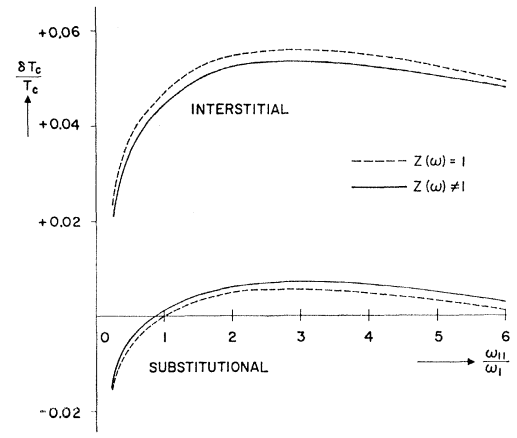

FIG. 7. Relative change of the transition temperature as a function of the impurity-mode frequency ω_{11}, taking into account and ignoring renormalization, respectively. For the parameters of the interaction kernel see Figs. 1 and 3.

Second, δT_c has been evaluated for substitutional lead alloys as a function of the impurity-mode frequency ω_{11}, the associated coupling parameter $\alpha^2(\omega_{11})$, and the change of the pseudo-Coulomb potential U_1.

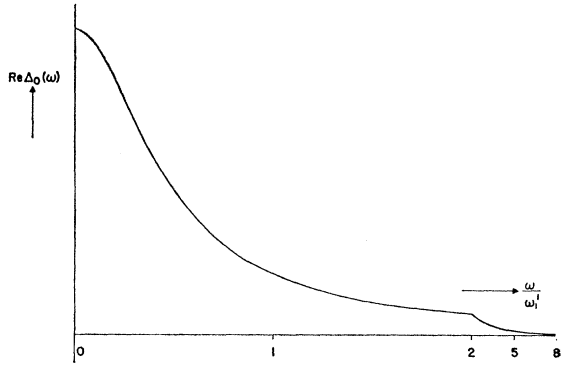

FIG. 8. Solution of the transposed energy-gap equation for lead at $T=T_c$; arbitrary units.

This calculation of δT_c is exact within the framework of the Éliashberg electron-phonon model of an isotropic superconductor, which is independent of the strength of the el-ph interaction. The phonon distribution of lead and the el-ph coupling constants for longitudinal and transverse phonons are taken from tunneling data.[18,19] The corresponding result for the solution of the transposed gap equation is shown in Fig. 8. In Fig. 9 some of the results for δT_c are shown which are useful for a comparison with the experimental data of Gamari-Seale and Coles.[25] These authors have measured δT_c for dilute alloys of lead with In, Sn, and Sb of the fifth row of the periodic system and with Hg, Tl, and Bi of the sixth row. They account for the gap anisotropy of lead[28] and for the corresponding mean-free-path effect on T_c with the help of the formula derived by Markowitz and Kadanoff.[7] The valence effect is then obtained from the relation $\delta T_c=(\delta T_c)_{\text{exp}}-(\delta T_c)_{\text{anis}}$. The experimental results for δT_c are found in the last column of Table I. In the first case of dilute lead-indium alloys, the observed tunneling density of states has led, via the inversion of the gap equation,[14] to the determination of the phonon distribution in the impure metal and, thereby, to the following numbers for the impurity parameters: $\omega_{11}=9.5$ MeV, $\alpha^2(\omega_{11})=1.34$ MeV. The third parameter U_1 which depends on the change of the electronic structure, is obtained by fitting the theoretical value for δT_c to the experimental value of Gamari-Seale and Coles. This procedure may be applied to a metal such as lead which has a nearly-free-electron Fermi surface. In the vicinity of the Fermi energy, the value of the density of states is not much different from that for free electrons. The slope of the density of states curve is, however, negative and, below the Fermi energy, Anderson and Gold[29] find a peak in this curve. This irregular dependence of the density of states is unimportant for small impurity concentrations. Each indium atom contributes only three conduction electrons for accommodation inside the Fermi surface, instead of four of a Pb atom. Therefore, δk_F is negative and, since B in Eq. (10) is positive, the second term in the expression for U_1 is positive ($a^2=0.38$ for lead[3]). The first term of U_1 [in Eq. (10)] is positive if $\delta N(0)>0$; this is the case if the free-electron Fermi surface shrinks. For Bloch electrons, the change of $N(0)$ with alloying is not merely determined by the change of k_F, or of the conduction electron density, but also by the effect of the impurity potential on the energy of a Bloch state, $E(\mathbf{k})=E_0(\mathbf{k})+N_1(\mathbf{k}|U(\mathbf{r})|\mathbf{k})$, where $E_0(\mathbf{k})$, is the periodic potential caused by an impurity atom. For free electrons, the matrix element is independent of $\mathbf{k}$ (wave vector) and the density of states remains unchanged. Here it is assumed that the change in the electron concentration, or k_F, is determined by the

TABLE I. δT_c (valence effect) for substitutional lead alloys; ω_{11}=impurity-mode frequency, $\alpha^2(\omega_{11})$=electron–impurity-mode coupling parameter, U_1=change of the pseudo-Coulomb potential.

Impurity	$\omega_{11}/\omega_1{}^1$	$\alpha^2(\omega_{11})$ in MeV	U_1	δT_c in m°K/at.%
In	2.16	1.34	+0.0023	−0.010
Sn	2.16	1.34	+0.0011	+0.016
Sb	2.16	1.34	−0.0046	+0.140
Hg	···	···	0	0
Tl	···	···	+0.0040	−0.012
Bi	···	···	−0.0176	+0.053
TlBi	···	···	−0.0057	+0.017

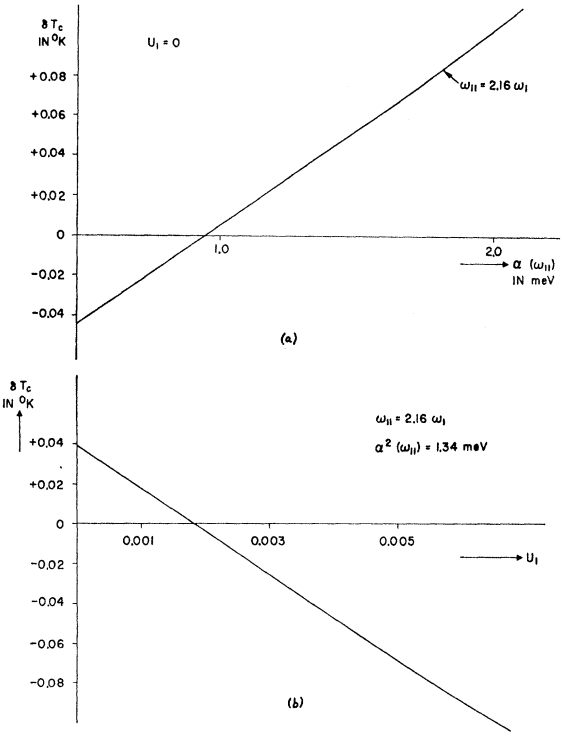

FIG. 9. The valence effect on the transition temperature δT_c for dilute lead alloys as a function of (a) the electron–impurity-mode coupling $\alpha(\omega_{11})$, and (b) of the change in the Coulomb pseudopotential U_1.

[28] A. J. Bennett, Phys. Rev. **140**, A1902 (1965).

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

TABLE II. Estimated value of the change of the density of states, found with the pseudo-Coulomb potential U_1 (Table I) which fits theoretical and experimental results of δT_c.

Impurity	U_1	$\delta k_F/k_F$	$\delta N(0)/N(0)$
In	+0.0023	−0.0033	+0.0022
Sn	+0.0011	0	+0.0036
Sb	−0.0046	+0.0033	−0.0096
Hg	0	−0.0066	−0.0110
Tl	+0.0040	−0.0033	+0.0077
Bi	−0.0176	+0.0033	−0.0518
TlBi	−0.0057	0	−0.0185

valency of the impurity atoms; $\delta N(0)$ is then considered as an adjustable parameter to fit experimental and theoretical values of δT_c. The results of this procedure, which has been described for Pb-In alloys, are given in Table II. Since for Pb-In the experimental value of ω_{11} is in agreement with the theoretical one found under the presumption that the interatomic force constants remain unchanged by substitution,[14] we assume that the impurity frequencies for Sn and Sb are also given by the mass ratios (which are $\simeq M_{\mathrm{In}}/M_{\mathrm{Pb}}$). Then, with $\alpha^2(\omega_{11})$ equal to the el-ph coupling of lead phonons of that frequency, one finds the values for U_1 given in Table I. For the impurity atoms of the same row as lead, namely Hg, Tl, and Bi, the change of the el-ph interaction $\alpha^2(\omega)g(\omega)$ of lead is ignored and the experimental results for δT_c are entirely attributed to the modification of the pseudo-Coulomb potential.

VII. SUMMARY

We have derived formulas for the valence effect of nonmagnetic impurities on energy gap and transition temperature of isotropic superconductors, valid in the framework of the Éliashberg electron-phonon model of superconductivity. The results go beyond the relation for the valence effect found from the BCS theory,[30] since the frequency dependence of the phonon-induced electron-electron interaction and its modification through impurity modes can accurately be taken into account. To this end, one must know: (a) The electron-phonon interaction of the host lattice, $\alpha^2(\omega)g(\omega)$, and the repulsive Coulomb potential U_0. (b) The impurity-mode distribution $g(\omega_{11})$, the inelastic electron-impurity coupling parameter $\alpha^2(\omega_{11})$, and the change of the Coulomb interaction, U_1. From (a) one can construct the interaction kernel which determines $\Delta_0(\omega)$ and $Z_0(\omega)$ through two *nonlinear* integral equations. If one knows $\Delta_0(\omega)$ and $Z_0(\omega)$, the change of the gap function caused by impurities $\Delta_1(\omega)$ is given by an *inhomogeneous linear* integral equation. The solution of this equation is easier to find, using the well-known iteration procedure of Neumann,[24] than that of the nonlinear integral equations for the impure metal. Furthermore, the integral equation for $\Delta_1(\omega)$ has a form similar to that of a Fredholm integral equation of the second type. Therefore, Fredholm's orthogonality theorem can be applied to the impurity-gap equation near the transition temperature, in order to find an exact formula for δT_c. This formula has been applied to a number of dilute lead alloys for which $\Delta_0(\omega)$ and $Z_0(\omega)$ are known for which experimental results for the valence effect have been found by Gamari-Seale and Coles. For this purpose, $g(\omega_{11})$ can be approximated by an Einstein distribution. In the case of Pb-In alloys, two of the three impurity parameters, ω_{11} and $\alpha^2(\omega_{11})$, are known from tunneling data; the third, U_1 is found by fitting theoretical and experimental values of δT_c. For the other alloy systems we make a reasonable *ad hoc* assumption about $\alpha^2(\omega_{11})$ to compare theory and experiment. It is evident that further experimental information is necessary, such as the change of the tunneling density of states with alloying, which determines the impurity-gap function $\Delta_1(\omega)$ and the change of the electronic specific heat—the relative change of the electron density of states at the Fermi surface with alloying is not affected by the electron-phonon interaction—to allow for a clear-cut comparison between theory and experiment in these cases.

Finally, let us mention some points of interest for this comparison. In calculating $\Delta_1(\omega)$ and δT_c, one must know the correct values of the gap function $\Delta_0(\omega)$ and of T_c, both of which are completely determined by $\alpha^2(\omega)g(\omega)$ and U_0 of the pure metal.

The impurity-gap parameter Δ_{10} and δT_c depend strongly on the impurity-mode frequency ω_{11} if it is smaller than the cutoff frequency of the phonon spectrum of the host lattice (Figs. 3 and 7). For larger values of ω_{11}, corresponding to localized impurity modes, Δ_{10} and δT_c depend only slightly on ω_{11}. Therefore, a possible increase of the transition temperature due to localized modes is limited by the electron–impurity-mode interaction constant $\alpha^2(\omega_{11})$. Because of the inelastic nature of the interaction,[22] one expects $\alpha^2(\omega_{11})$ to increase with decreasing mass ratio m/M_i (m=electron mass, M_i=impurity mass).

In comparing the relative change of the transition temperature, $\delta T_c/T_c$, with that of the gap parameter, Δ_{10}/Δ_{00} (calculated in second order), we find that, for a Lorentzian-phonon spectrum of the host lattice superimposed with an Einstein distribution of impurity modes, there is agreement within 10% if renormalization is ignored. When it is taken into account, the difference becomes larger, ~30%. This large difference, which is also found for Pb-In, cannot be, for the most part, attributed to the difference between $\Delta_{10}^{(2)}$ and the exact value of Δ_{10}, because of rapid convergence; furthermore, ΔT_c is exact. Instead, it is caused by the fact that the ratio T_c/Δ_0 of the pure metal depends on

[30] $\frac{\delta T_c}{T_c}=\frac{\delta\omega_1}{\omega_1}+\frac{1}{N(0)V}\left(\frac{\delta V}{V}+\frac{\delta N}{N}\right)$.

Short of detailed information on the el-ph interaction in an impure metal, this equation can be useful in discussing the valence effect as has been shown by D. M. Ginsberg [Phys. Rev. **136**, A1167 (1964); **138**, A1409 (1965)] for dilute Sn and In alloys.

the strength of the phonon-induced electron-electron interaction, in particular when renormalization is taken into account. The decrease of the ratio $2\Delta_0/kT_c$ for a strong-coupling superconductor such as pure lead when high-frequency impurity modes are introduced can be qualitatively understood in terms of the change of T_c/θ, where θ is a characteristic temperature which may correspond to ω_1[1]. The gross effect of the impurity modes is to increase θ without a corresponding increase of the electron-phonon interaction. Therefore, the effective coupling measured by T_c/θ will decrease and hence the ratio $2\Delta_0/kT_c$ will decrease towards the weak-coupling ratio 3.5.

ACKNOWLEDGMENTS

It is a pleasure to thank Professor W. Kohn for many stimulating and constructive discussions. I would also like to thank Dr. B. Ross and H. Appel for their help with some of the mathematical problems.

APPENDIX I: INHOMOGENEOUS PART OF THE IMPURITY-GAP FUNCTION ($T=0$)

The inhomogeneous part $F(\omega)$ for a Lorentzian phonon distribution of the host lattice, centered at ω_1 and having half-width ω_2, and for an Einstein distribution of the impurity modes, centered at ω_{11}, is given by

$$\mathrm{Re}\{F_1(\omega)\}=\frac{\lambda_1\omega_{11}}{2|Z_0|^2}\Big\{\frac{(\Delta_{00}+\Delta_{0C})\,\mathrm{Re}\{Z_0\}}{2}[f(\omega,\omega_1)+f(-\omega,\omega_1)+f(\omega,-\omega_1)+f(-\omega,-\omega_1)]-\Delta_{0C}\,\mathrm{Re}\{Z_0\}$$
$$\times\Big[J_0(\omega_{11}+\omega)+J_0(\omega_{11}-\omega)-\frac{2U_1}{\lambda_1\omega_{11}U_0}\Big]+\frac{\pi H(\omega-\omega_{11}-\Delta_{00})\,\mathrm{Im}\{Z_0\}}{[(\omega-\omega_{11})^2-\Delta_{00}^2]^{1/2}}\Big[\frac{(\Delta_{00}+\Delta_{0C})}{2}\,\mathrm{Re}\{U(\omega-\omega_{11})\}-\Delta_{0C}\Big]\Big\}, \quad \text{(A1)}$$

where

$$f(\omega,\omega_1)=[1/(\omega_1-\omega-\omega_{11})^2+\omega_2^2]\{\omega_2^2[J_0(\omega_{11}+\omega)-K_1(\omega_1)]+(\omega_1-\omega_{11}-\omega)$$
$$\times[\omega_1 J_0(\omega_{11}+\omega)-\omega_1 K_1(\omega_1)-(\omega_1^2+\omega_2^2)K_0(\omega_1)]\},$$

and where the parameter integrals J_0, K_0, K_1 are defined below:

$$\mathrm{Re}\{F_2(\omega)\}=\frac{\lambda_0\Delta_{10}}{2|Z_0|^2}\Big\{\mathrm{Re}\{Z_0\}\Big[g(\omega)+g(-\omega)-\frac{2U_0}{\lambda_0}\log(2\omega_c/\Delta_{00})\Big]-\omega_2\,\mathrm{Im}\{Z_0\}$$
$$\times[\omega K_0(\omega_1+\omega)-\omega K_0(\omega_1-\omega)+K_1(\omega_1+\omega)+K_1(\omega_1-\omega)]\Big\}, \quad \text{(A2)}$$

where

$$g(\omega)=[\omega_1(\omega_1+\omega)+\omega_2^2][K_0(\omega_1+\omega)+\omega_1 K_1(\omega_1+\omega)],$$

$$\mathrm{Re}\{F_3(\omega)\}=\frac{\lambda_0\Delta_{10}}{2|Z_0|^2}\{\mathrm{Re}\{Z_0\}[h(\omega)+h(-\omega)-2U_0/\lambda_0]-\omega_2\,\mathrm{Im}\{Z_0\}[k(\omega)+k(-\omega)]+O(\Delta_{00}^2/\omega_1^2)\}, \quad \text{(A3)}$$

where

$$h(\omega)=\frac{\omega_1(\omega_1+\omega)+\omega_2^2}{(\omega_1+\omega)^2+\omega_2^2}, \quad k(\omega)=\frac{\omega}{(\omega_1+\omega)+\omega_2^2};$$

$$\mathrm{Re}\{F_4(\omega)\}=-\frac{1}{|Z_0|^2}[\mathrm{Re}\{Z_0\}(\mathrm{Re}\{Z_0\}\,\mathrm{Re}\{Z_1\}+\mathrm{Im}\{Z_0\}\,\mathrm{Im}\{Z_1\})$$
$$+\mathrm{Im}\{Z_0\}(\mathrm{Im}\{Z_0\}\,\mathrm{Re}\{Z_1\}-\mathrm{Re}\{Z_0\}\,\mathrm{Im}\{Z_1\})]. \quad \text{(A4)}$$

The imaginary part of $F(\omega)$ is found from Eqs. (A1) through (A4) by interchanging $\mathrm{Re}\{Z_0\}$ with $-\mathrm{Im}\{Z_0\}$ and $\mathrm{Im}\{Z_0\}$ with $\mathrm{Re}\{Z_0\}$. The integrals $J_0(\omega)$ and $K_n(\omega)$ are defined by

$$J_0(\omega)=\int_{\Delta_{00}}^{\infty}\frac{d\omega'}{(\omega'^2-\Delta_{00}^2)^{1/2}(\omega+\omega')}, \quad \text{(A5)}$$

$$K_n(\omega)=\int_{\Delta_{00}}^{\infty}\frac{\omega'^n d\omega'}{(\omega'^2-\Delta_{00}^2)^{1/2}[(\omega+\omega')^2+\omega_2^2]}. \quad \text{(A6)}$$

The quadrature of Eq. (A5) gives

$$J_0(\omega)=\pm\frac{1}{(\omega^2-\Delta_{00}^2)^{1/2}}$$
$$\times\log\Big[\frac{|\omega|+\Delta_{00}+(\omega^2-\Delta_{00}^2)^{1/2}}{|\omega|+\Delta_{00}+(\omega^2-\Delta_{00}^2)^{1/2}}\Big], \quad \text{if } |\omega|\geq\Delta_{00} \quad \text{(A7)}$$

where the sign + indicates $\omega\geq\Delta_{00}$ and the sign − in-

dicates $\omega \leq -\Delta_{00}$,

$$J_0(\omega)=\frac{2}{(\Delta_{00}^2-\omega^2)^{1/2}}\arctan\left(\frac{\Delta_{00}-\omega}{\Delta_{00}+\omega}\right)^{1/2},$$
$$\text{if } -\Delta_{00}\leq\omega\leq+\Delta_{00}. \quad \text{(A8)}$$

The quadrature of Eq. (A6) gives

$$K_0(\omega)=-\frac{\beta_2}{2\omega_2(\beta_1^2+\beta_2^2)}\times\log\{[(\beta_1+\omega)^2+(\beta_2-\omega_2)^2]/\Delta_{00}^2\}-\frac{\beta_1}{\omega_2(\beta_1^2+\beta_2^2)}[\arctan(\omega_2/\beta_1)-\pi H(-\omega)],$$

$$K_1(\sigma)=\frac{\beta_1\omega_2+\beta_2\omega}{2\omega_2(\beta_1^2+\beta_2^2)}\times\log\{[(\beta_1+\omega)^2+(\beta_2-\omega_2)^2]/\Delta_{00}^2\}+\frac{\beta_1\omega-\beta_2\omega_2}{\omega_2(\beta_1^2+\beta_2^2)}[\arctan(\omega_2/\beta_1)-\pi H(-\omega)],$$

where

$$\beta_{1(2)}=\{(1/2)[(\omega^2-\omega_2^2-\Delta_{00}^2)^2+4\omega^2\omega_2^2]^{1/2}\pm\tfrac{1}{2}(\omega^2-\omega_2^2+\Delta_{00}^2)^{1/2}\}^{1/2},$$

and where $H(\omega)$ is Heaviside's unit step function.

For a more realistic phonon spectrum of the host lattice, consisting of a superposition of two Lorentzians, one for longitudinal phonons and one for transverse phonons, the right side of Eq. (A1) is calculated numerically using the given theoretical or experimental values for the gap function of the host lattice. The corresponding equations for (A2)–(A4) are simply given by linear combinations of expressions of the above form.

APPENDIX II: RENORMALIZATION PARAMETERS

These parameters for a Lorentzian phonon spectrum of the host lattice and an Einstein distribution of the impurity modes are, respectively, given by

$$\mathrm{Re}\{Z_0(\omega)\}=1-(\lambda_0/2\omega)\{(\omega_2^2-\omega_1^2-\omega_1\omega)K_1(\omega_1+\omega)-(\omega_2^2-\omega_1^2+\omega_1\omega)K_1(\omega_1-\omega)-\omega_1[(\omega_1+\omega)^2+\omega_2^2]K_0(\omega_1+\omega)+\omega_1[(\omega_1-\omega)^2+\omega_2^2]K_0(\omega_1-\omega)\}, \quad \text{(A9)}$$

$$\mathrm{Im}\{Z_0(\omega)\}=-(\lambda_0\omega_2/2\omega)\{(2\omega_1+\omega)K_1(\omega_1+\omega)-(2\omega_1-\omega)K_1(\omega_1-\omega)+[(\omega_1+\omega)^2+\omega_2^2]K_0(\omega_1+\omega)-[(\omega_1-\omega)^2+\omega_2^2]K_0(\omega_1-\omega)\}, \quad \text{(A10)}$$

$$\mathrm{Re}\{Z_1(\omega)\}=-(1/2\omega)\{\lambda_1\omega_{11}[(\omega_{11}+\omega)J_0(\omega_{11}+\omega)+(\omega_{11}-\omega)J_0(\omega_{11}-\omega)]+\Delta_{10}\Delta_{00}\lambda_0[\omega_1L_1(\omega_1+\omega)-\omega_1L_1(\omega_1-\omega)+(\omega_2^2+\omega_1(\omega_1+\omega))L_0(\omega_1+\omega)-(\omega_2^2+\omega_1(\omega_1-\omega))L_0(\omega_1-\omega)]\}, \quad \text{(A11)}$$

$$\mathrm{Im}\{Z_1(\omega)\}=-(1/2\omega)\left\{\pi\lambda_1\omega_{11}\frac{(\omega_{11}-\omega)H(\omega-\omega_{11}-\Delta_{00})}{[(\omega-\omega_{11})^2-\Delta_{00}^2]^{1/2}}+\Delta_{10}\Delta_{00}\lambda_0\omega_2[L_1(\omega_1-\omega)-L_1(\omega_1+\omega)-\omega L_0(\omega_1+\omega)-\omega L_0(\omega_1-\omega)]\right\}. \quad \text{(A12)}$$

The integrals $L_n(\omega)$ of Sec. III can be expressed in terms of the $K_n(\omega)$,

$$L_0(\omega)=(1/N)\{2\omega[1-(\omega^2+\omega_2^2)]K_0(\omega)-(\omega^2+\omega_2^2+\Delta_{00}^2)K_1(\omega)\}, \quad \text{(A13)}$$

$$L_1(\omega)=(1/N)\{(\omega^2+\omega_2^2+\Delta_{00}^2)[(\omega^2+\omega_2^2)-1]K_0(\omega)+2\omega\Delta_{00}^2K_1(\omega)\}, \quad \text{(A14)}$$

where

$$N=[(\omega+\Delta_{00})^2+\omega_2^2][(\omega-\Delta_{00})^2+\omega_2^2\ ].$$

For a more realistic phonon spectrum of the host lattice, characterized by a superposition of Lorentzians, the renormalization parameters are simply given by linear combinations of expressions of the above form.