Influence of anharmonicity on superconductivity

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The method of functional differentiation is used to obtain equations for the Green function of electrons in a superconductor making full allowance for anharmonic interactions. It is shown that these equations are formally identical with the well-known Eliashberg equations. The main difference is that the equations allowing for the lattice anharmonicty have to be modified by replacing the spectral density of the one-phonon Green function occurring in the Éliashberg equation with the dynamic part of a function representing the correlation between this density and the ion concentration. The results obtained demonstrate that allowance for the anharmonicity alters the superconducting properties of a metal for the following reasons: 1) the existence of the Debye–Waller factors in the ionic potential; 2) a change in the spectral density of the one-phonon Green function because of the occurrence of phonon–phonon interactions; 3) many-phonon process; 4) interference effects between one- and many-phonon processes. An analysis is made of the superconductivity of PdH and of the influence of the anharmonicity on the critical temperature T_c of this compound. It is shown that in this case the greatest influence of the anharmonicity on T_c is due to the Debye–Waller factors and due to a change in the spectral density of the one-phonon Green function. These two effects reduce the electron–phonon coupling constant of palladium hydride. The effect is greater in PdH than in PdD because of the greater amplitude of the zero-point vibrations of the H atoms. This gives rise to an anomalous isotopic effect in PdH(D).

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§1. INTRODUCTION

Superconducting properties of metals are usually considered ignoring anharmonic effects in the lattice dynamics and in the electron–phonon interaction. The reason for this is simple. It is well known that changes in the physical properties of metals due to the anharmonicity are proportional (to an order of magnitude) to the square of the ratio of the amplitude of thermal vibrations u_T of atoms for the interatomic distance a. This ratio is usually much less than unity even close to the melting point. The transitions to the superconducting state occur in metals at such very low temperatures that in most cases the effects associated with the ratio u_T^2/a^2 can be ignored completely.

However, recent years have seen indications of the importance of the low-temperature anharmonicity in a number of superconducting systems. This applies particularly to compounds with the A-15 structure. In many of these compounds there is a structure transition from the cubic to the tetragonal phase near the superconducting temperature.[1,2] Neutron investigations[3] have shown that this structural transition softens the phonon modes extending over considerable part of the Brillouin zone. The appearance of these soft modes increases greatly the amplitude of thermal vibrations and gives rise to low-temperature anharmonicity effects in such systems. The importance of the anharmonicity effects in the superconducting properties of compounds of the A-15 type has recently been stressed by Testardi.[4] The existence of low-temperature anharmonicity in other superconducting compounds with soft phonon modes is pointed out also elsewhere.[5]

Palladium hydride is another example of the considerable influence of anharmonicity on the superconducting properties and particularly on the critical transition temperature T_c.[6] Specifically, this compound exhibits an anomalous isotopic effect.[7,8] The critical temperature of PdD is 2°K higher than that of PdH. This is practically impossible to explain within the harmonic approximation framework. Ganguly[9] put forward a hypothesis of the possibility of explaining this anomalous isotopic effect in PdH by the influence of the anharmonicity associated with vibrations of the light hydrogen atom.

Even a partly consistent theoretical treatment of the influence of anharmonicity on the superconducting properties of metals is not yet available. Apart from Ganguly's paper,[9] one can mention also a short note by Hui and Allen.[10] In both cases a study is made of the influence of anharmonicity on the electron–phonon interaction and, consequently, also on T_c. As in a harmonic crystal, only the one-phonon scattering is considered but allowance is made for the change in the phonon frequencies because of anharmonicity. The results of these papers can easily be understood by adopting the McMillan formula[11] for the electron–phonon coupling:

$$\lambda=C/M\langle\omega^2\rangle. \tag{1}$$

The phonon–phonon interaction in an anharmonic crystal alters the phonon frequencies.[12] This circumstance then changes the value of $\langle\omega^2\rangle$ which occurs in the denominator of Eq. (1) describing the electron–phonon coupling constant. Moreover, if the anharmonic interaction results in hardening of the original phonon spectrum of a harmonic cyrstal, the value of $\langle\omega^2\rangle$ rises and the coupling constant λ correspondingly decreases. This is the conclusion reached by Ganguly[9] and by Hui and Allen.[10]

Clearly, a discussion of the electron–phonon interaction in an anharmonic crystal allowing only for the one-phonon process of scattering of electrons by renormalized anharmonic phonons[9,10] is not self-consistent. It is well known[13] that a change in the elec-

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tron–phonon interaction in an anharmonic crystal occurs not only because of a change in the phonon frequencies but also because of many-phonon scattering processes and also because of the appearance of the Debye–Waller factors in the ionic potential. All these processes are of the same order in respect of anharmonicity and are proportional to the ratio u_T^2/a^2.

One should also mention a further fairly interesting problem in which it is very important to allow correctly for the influence of anharmonicity on superconductivity. Kumar[14] and Ngai[15] considered the effectiveness of two-phonon processes as possible superconductivity mechanisms in semimetals and degenerate semiconductors. Since these processes are also proportional to the ratio u_T^2/a^2, Kumar proposed to increase their effectiveness by pumping with external ultrasound so as to make the ratio u_T^2/a^2 larger. Ngai pointed out that these processes are likely to be effective in systems with soft phonon modes, which are indeed characterized by large values of the ratio u_T^2/a^2.

The importance of complete allowance for the anharmonic interactions in these problems is self-evident if only from the following observation. Some years ago Sham and Ziman[13] put forward the hypothesis that an increase in the electron–phonon interaction because of many-phonon processes may be compensated completely by a weakening of this interaction associated with the appearance of the Debye–Waller factors in the ionic potential. Grimvall[16] considered this problem in detail in the case of the electrical resistance of metals at high temperatures. However, there is no complete solution to this problem even in respect of the electrical resistance.

All these problems have not only been ignored in the theory of superconducitivity but have not even been correctly formulated. We shall begin by deriving the exact equations for superconductivity allowing for anharmonicity in the electron–phonon interaction in all orders. We shall show that in fact such equations are analogous to the Éliashberg equations[17] for the electron–phonon interaction if the spectral density of the one-phonon Green functions is replaced with the spectral density of the dynamic part of a function describing correlation between this density and the concentration of ions. Similar equations for a harmonic crystal with defects were obtained earlier by one of the present authors.[18] In recent years the correlation function of the concentration of ions in anharmonic crystals has been investigated intensively both theoretically and experimentally by slow neutron scattering.[19] The equations derived by us make it possible to utilize fully both theoretical and experimental data obtained in studies of the scattering of slow neutrons in considering the influence of anharmonicity on superconductivity.

The present paper is organized as follows. In §2 we shall obtain the exact superconductivity equations allowing fully for the anharmonicity in the electron–phonon interaction. Next in §3, we shall analyze our equations and simplify them for "dirty" superconductors with a short electron mean free path. In §4 we shall study superconducting properties of the PdH(D) system and consider qualitatively the influence of anharmonicity of these properties.

§2. DERIVATION OF SUPERCONDUCTIVITY EQUATIONS FOR AN ANHARMONIC CRYSTAL

We shall write the complete electron–ion Hamiltonian of a crystal in the form

$$\begin{aligned} H=&\int\left(-\frac{\nabla^2}{2m}-\mu\right)\psi^+(\mathbf{r})\tau_3\psi(\mathbf{r})\,d\mathbf{r}\\ &+\frac{1}{2}\int V_{ee}(\mathbf{r},\mathbf{r}')\psi^+(\mathbf{r})\tau_3\psi(\mathbf{r})\psi^+(\mathbf{r}')\tau_3\psi(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'\\ &+\int V_{ei}(\mathbf{r},\mathbf{r}')\rho_i(\mathbf{r}')\psi^+(\mathbf{r})\tau_3\psi(\mathbf{r})\,d\mathbf{r}\,d\mathbf{r}'+\frac{1}{2}\int V_{ii}(\mathbf{r},\mathbf{r}')\rho_i(\mathbf{r})\rho_i(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'. \end{aligned} \tag{2}$$

We have introduced here the operator of the ion concentration

$$\rho_i(\mathbf{r})=\sum_n\delta(\mathbf{r}-\mathbf{R}_n), \tag{3}$$

where $\mathbf{R}_n$ is the coordinate of the ion position.

For convenience, we shall describe superconducting properties not by means of the usual electron creation and annihilation operators but by introducing

$$\psi(x)=\begin{vmatrix}\psi_\uparrow(x)\\ \psi_\downarrow^+(x)\end{vmatrix},\quad \psi^+(x)=|\psi_\uparrow^+(x),\psi_\downarrow(x)|. \tag{4}$$

The downward-pointing arrow in the operator $\psi_\downarrow(x)$ denotes the spin direction. The quantity τ_3 is the usual Pauli matrix.

We shall obtain the superconductivity equations by functional differentiation and with this in mind we shall introduce the following external sources in the Hamiltonian

$$\int\psi^+(x)\tau_3\psi(x)U(x)\,dx+\int\rho_i(x)J(x)\,dx. \tag{5}$$

We shall write the equation for the operator $\psi(x)$:

$$\begin{aligned} &\left[i\frac{\partial}{\partial t}+\left(\frac{\nabla^2}{2m}+\mu\right)\tau_3-U(x)\tau_3\right]\psi(x)\\ &=\int V_{ei}(\mathbf{r},\mathbf{r}')\rho_i(\mathbf{r}',t)\tau_3\psi(x)\,d\mathbf{r}'+\int V_{ee}(\mathbf{r},\mathbf{r}')\psi^+(x')\tau_3\psi(x)\,d\mathbf{r}', \end{aligned} \tag{6}$$

where $x=\mathbf{r},t$. Introducing the matrix thermodynamic Green function, defined in the time interval $-1/T<t<1/T$ (T is the temperature),

$$G(x,x')=-i\langle T\psi(x)\psi^+(x')\rangle, \tag{7}$$

we obtain the following equation for this function

$$\begin{aligned} &\left[i\frac{\partial}{\partial t}I+\left(\frac{\nabla^2}{2m}+\mu\right)\tau_3-U(x)\tau_3\right]G(x,x')\\ &=-i\int d\mathbf{r}''\,V_{ei}(\mathbf{r},\mathbf{r}'')\langle T\rho_i(\mathbf{r}'',t)\tau_3\psi(x)\psi^+(x')\rangle\\ &-i\int d\mathbf{r}''\,V_{ee}(\mathbf{r},\mathbf{r}'')\langle T\psi^+(x'')\tau_3\psi(x'')\tau_3\psi(x)\psi^+(x')\rangle+\delta(x-x')I. \end{aligned} \tag{8}$$

Here, I is a unit matrix.

We shall rewrite Eq. (8) by means of the functional derivatives:

$$\Big[i\frac{\partial}{\partial t}I+\Big(\frac{\nabla^2}{2m}+\mu\Big)\tau_3-U(x)\tau_3-\tau_3\int d\mathbf{r}_1\,V_{ee}(\mathbf{r},\mathbf{r}')\langle\psi^+(x_1)\tau_3\psi(x_1)\rangle$$
$$-\tau_3\int d\mathbf{r}_1\,V_{ei}(\mathbf{r},\mathbf{r}_1)\langle\rho_i(x_1)\rangle-i\tau_3\int d\mathbf{r}_1\,V_{ee}(\mathbf{r},\mathbf{r}_1)\frac{\delta}{\delta U(\mathbf{r}_1,t)} \tag{9}$$
$$-i\tau_3\int d\mathbf{r}_1\,V_{ei}(\mathbf{r},\mathbf{r}_1)\frac{\delta}{\delta J(\mathbf{r}_1,t)}\Big]G(x,x')=I\delta(x-x').$$

We can easily show that

$$\langle\psi^+(x_1)\tau_3\psi(x_1)\rangle=\rho_e(x_1),$$

where $\rho_e(\mathbf{r}_1)$ is the density of electrons at the point $\mathbf{r}_1$.

We shall introduce $V(x)$ for the total Hartree field acting on electrons:

$$V(x)=U(x)+\int d\mathbf{r}_1\,V_{ee}(\mathbf{r},\mathbf{r}_1)\langle\rho_e(\mathbf{r}_1)\rangle+\int d\mathbf{r}_1\,V_{ei}(\mathbf{r},\mathbf{r}_1)\langle\rho_i(\mathbf{r}_1)\rangle \tag{10}$$

and we shall rewrite Eq. (9) in terms of the functional derivative of $V(x)$:

$$\Big[i\frac{\partial}{\partial t}I+\Big(\frac{\nabla^2}{2m}+\mu\Big)\tau_3-U(x)\tau_3$$
$$-i\tau_3\int dx''\,d\mathbf{r}_1\,V_{ec}(\mathbf{r},\mathbf{r}_1)\frac{\delta V(x'')}{\delta U(\mathbf{r}_1,t)}\frac{\delta}{\delta V(x'')} \tag{11}$$
$$-i\tau_3\int dx''\,d\mathbf{r}_1\,V_{ei}(\mathbf{r},\mathbf{r}_1)\frac{\delta V(x'')}{\delta J(\mathbf{r}_1,t)}\frac{\delta}{\delta V(x'')}\Big]G(x,x')=I\delta(x-x').$$

Equation (11) for the Green function $G(x,x')$ can be written in the generally accepted form employing the matrix for the self-energy part $\Sigma(x,x'')$:

$$\Big[i\frac{\partial}{\partial t}I+\Big(\frac{\nabla^2}{2m}+\mu\Big)\tau_3-V(x)\tau_3\Big]G(x,x')$$
$$-\int dx''\,\Sigma(x,x'')G(x'',x')=I\delta(x-x'). \tag{12}$$

Comparing Eqs. (11) and (12), we find that

$$\int dx''\,\Sigma(x,x'')G(x'',x')=i\tau_3\int dx''\,d\mathbf{r}_1\Big[V_{ee}(\mathbf{r},\mathbf{r}_1)\frac{\delta V(x'')}{\delta U(\mathbf{r}_1,t)}$$
$$+V_{ei}(\mathbf{r},\mathbf{r}_1)\frac{\delta V(x'')}{\delta J(\mathbf{r}_1,t)}\Big]\frac{\delta}{\delta V(x'')}G(x,x').$$

Multiplying this equation by $G^{-1}(x',x'')$ and integrating with respect to x', we find that

$$\Sigma(x,x'')=i\int dx_1\,dx_2\,W(x,x_1)\tau_3\Gamma(x_2,x'',x_1), \tag{13}$$

where we employ the following notation for the effective electron–electron interaction

$$W(x,x_1)=\int d\mathbf{r}'\Big[V_{ee}(\mathbf{r},\mathbf{r}')\frac{\delta V(x_1)}{\delta U(\mathbf{r}',t)}+V_{ei}(\mathbf{r},\mathbf{r}')\frac{\delta V(x_1)}{\delta J(\mathbf{r}',t)}\Big], \tag{14a}$$

and also for the matrix vertex part

$$\Gamma(x_2,x'',x_1)=\tau_3\frac{\delta G^{-1}(x_2,x'')}{\delta V(x_1)}. \tag{14b}$$

The effective electron–electron interaction $W(x,x_1)$ is calculated in the same manner as in an earlier paper by one of the present authors[20] dealing with a harmonic crystal. Introducing the electron polarization operator $\Pi(x,x')$,

$$\Pi(x,x')=\frac{\delta\langle\rho_e(x)\rangle}{\delta V(x')},$$

and the function of the reciprocal permittivity $\epsilon^{-1}(x,x')$,

$$\varepsilon^{-1}(x,x')=\delta(x-x')+\int dx''\,d\mathbf{r}_1\,V_{ee}(\mathbf{r},\mathbf{r}_1)\Pi(x,x'')\varepsilon^{-1}(x'',x'), \tag{15}$$

we find that laborious but simple calculations yield

$$W(x,x_1)=\int dx_3\,V_{ei}(\mathbf{r},\mathbf{r}_3)\varepsilon^{-1}(x_1,x_3)$$
$$+\int dx_2\,dx_3\,d\mathbf{r}'\,d\mathbf{r}''\,V_{ei}(\mathbf{r}_2,\mathbf{r}')\varepsilon^{-1}(x,x_2)V_{ei}(\mathbf{r}_3,\mathbf{r}'')\varepsilon^{-1}(x_3,x_1)D(\mathbf{r}'t_2,\mathbf{r}''t_1). \tag{16}$$

The first term in Eq. (16) represents simply the screened Coulomb electron–electron interaction. The second term represents the interaction of electrons with dynamic vibrations of ions. We shall describe these variations by introducing the thermodynamic Green function:

$$D(x,x')=-i\langle T(\rho_i(x)-\langle\rho_i(x)\rangle)(\rho_i(x')-\langle\rho_i(x')\rangle)\rangle. \tag{17}$$

The Fourier component of this function $D(r,r',i\omega_n)$ has the spectral representation

$$D(r,r',i\omega_n)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dz\frac{\Phi(\mathbf{r},\mathbf{r}',z)}{i\omega_n-z}. \tag{18}$$

The spectral density $\Phi(\mathbf{r},\mathbf{r}',z)$ can be expressed in terms of the dynamic part of a function $S'(\mathbf{r},\mathbf{r}',\omega)$ describing the correlation between this density and ion concentration:

$$\Phi(\mathbf{r},\mathbf{r}',\omega)=[n(\omega)+1]^{-1}S'(r,r',\omega), \tag{19}$$

where $n(\omega)$ is the Bose function

$$n(\omega)=\frac{1}{e^{\omega/T}-1}.$$

Then, the total correlation function $S'(\mathbf{r},\mathbf{r}',\omega)$ is described by

$$S(\mathbf{r},\mathbf{r}',\omega)=\int_{-\infty}^{\infty}dt\,e^{i\omega(t-t')}\langle\rho_i(\mathbf{r},t)\rho_i(\mathbf{r}',t')\rangle. \tag{20}$$

Integration in Eq. (20) is carried out over the usual time between $-\infty$ and $+\infty$ and the angular brackets represent thermodynamic averaging.

The function $S(\mathbf{r},\mathbf{r}',\omega)$ was first introduced by Van Hove[21] and it is central to the description of any scattering processes in condensed media. The dynamic part of the correlation function $S'(\mathbf{r},\mathbf{r}',\omega)$ is related to the total correlation function $S(\mathbf{r},\mathbf{r}',\omega)$ by

$$S'(\mathbf{r},\mathbf{r}',\omega)=S(\mathbf{r},\mathbf{r}',\omega)-\langle\rho_i(\mathbf{r},t)\rangle\langle\rho_i(\mathbf{r}',t')\rangle\delta(\omega).$$

§3. INVESTIGATION OF SUPERCONDUCTIVITY EQUATIONS OF AN ANHARMONIC CRYSTAL

Before analyzing our new equations, we shall note that a complete treatment would require derivation, from the electron–ion Hamiltonian (2), also an equation for the Green function $D(x,x')$. We shall see later that in the harmonic approximation this function reduces to the usual one-phonon Green function. The relevant equations for a normal metal are obtained in the harmonic approximation in an earlier paper of one of the present authors.[20] Meissner,[22] Gillis,[23] and Plakida[24] made attempts to obtain equations for this function allowing for the anharmonic interactions. However, the resultant equations were so complex that any detailed analysis was practically impossible. Therefore, we shall calculate the function $D(x, x')$ using a phenomenological Hamiltonian allowing for the anharmonic interactions up to the fourth order in respect of the ion displacement. This approach to the calculation of $D(x, x')$ is used widely in studies of the scattering of neutrons in anharmonic crystals.

We shall begin by rewriting the above equations in a somewhat more convenient form:

$$G^{-1}(x, x') = G_0^{-1}(x, x') - \Sigma(x, x'),$$

where the function $G_0(x, x')$ satisfies

$$\left\{ i\frac{\partial}{\partial t} I + \left(\frac{\nabla^2}{2m} + \mu \right) \tau_3 - \tau_3 \int d\mathbf{r}_1 [V_{ee}(\mathbf{r}, \mathbf{r}_1) \langle \rho_e(\mathbf{r}_1) \rangle + V_{ei}(\mathbf{r}, \mathbf{r}_1) \langle \rho_i(\mathbf{r}_1) \rangle] \right\} G_0(x, x') = I\delta(x - x'). \tag{21}$$

The Green function $G_0(x, x')$ can be expressed in terms of the Bloch wave functions $\varphi_{\mathbf{k}}(x)$ of an electron in a periodic field:

$$G_0(x, x') = iT \sum_{\omega_n} \sum_{\mathbf{k}} \frac{\varphi_{\mathbf{k}}(x) \varphi_{\mathbf{k}}^*(x')}{i\omega_n - \varepsilon_{\mathbf{k}}} e^{-i\omega_n(t - t')}. \tag{22}$$

The Bloch wave functions $\varphi_{\mathbf{k}}(x)$ should naturally be deduced in a self-consistent manner from Eq. (21) but we shall not consider this problem because detailed calculations would take us outside the scope of the present paper.

We shall write the self-energy part $\Sigma(x, x')$ as a sum of two terms:

$$\Sigma(x, x') = \Sigma_{\text{Coul}}(x, x') + \Sigma_{\text{phon}}(x, x'). \tag{13a}$$

The first term in this sum, $\Sigma_{\text{Coul}}(x, x')$ is due to the Coulomb electron–electron interaction. The second term $\Sigma_{\text{phon}}(x, x')$ can be written, in accordance with Eqs. (13) and (15) in the form

$$\Sigma_{\text{phon}}(x, x') = -i \int dx_1\, dx_2\, dx_3\, dx_4\, d\mathbf{r}'\, d\mathbf{r}''\, V_{ei}(\mathbf{r}_3, \mathbf{r}') \varepsilon^{-1}(x, x_3) V_{ei}(\mathbf{r}_4, \mathbf{r}'') \times \varepsilon^{-1}(x_4, x_1) D(\mathbf{r}'t_3, \mathbf{r}''t_1) \tau_3 G(x, x_2) \tau_3 \Gamma(x_2, x', x_1). \tag{23}$$

A complete calculation of the superconducting properties of a metal with exact allowance for the Coulomb electron–electron interaction is not yet possible. Strictly speaking, the absence of a small parameter in the Coulomb interaction prevents a consistent calculation of the properties of even a normal metal. However, it is well known that the direct contribution of the Coulomb interaction to the superconducting properties of a metal is largely suppressed because of the considerable difference between the energies of electron excitations (these are of the order of the Fermi energy, i.e., ~2-5 eV) and phonon energies (~0.01–0.1 eV). Therefore, we shall follow the usual procedure of replacing $\Sigma_{\text{Coul}}(x, x')$ with the simplest approximation of the Coulomb pseudopotential and we shall describe the vertex part $\Gamma(x_2, x', x_1)$ by the simplest approximation which follows from Eq. (15):

$$\Gamma(x_2, x', x_1) = I\delta(x_2 - x')\delta(x_2 - x_1).$$

A detailed discussion of the problem of correctness in these approximations is given in the book by Bulaevskiĭ *et al.*[25] Since we are interested mainly in the influence of anharmonicity and this is concentrated in the function $D(x, x')$, our approximations will have little effect on the problem in hand.

In the case of pure superconducting metals the transition to the representation in terms of the Bloch function $\varphi_{\mathbf{k}}(x)$ makes the self-energy part $\Sigma(x, x')$ a fairly complex function of the energy and momentum k. It is well known that the retarding nature of the electron–phonon interaction results in concentration of the function $\Sigma(i\omega_n, k)$ mainly near the Fermi surface so that this function depends only on the direction of the vector $\mathbf{k}_F$ ($\mathbf{k}_F$ is the vector defining the Fermi surface). In "dirty" superconductors the scattering by impurities results in averaging of all the quantities over the angles and the self-energy part becomes, as in an isotropic superconductor, solely a function of $i\omega_n$. In this case the function $\Sigma(i\omega_n, \epsilon_F)$ is described by the following equation:

$$\Sigma(i\omega_n, \varepsilon_F) = T \sum_{\omega_{n'}} \int_{-\infty}^{\infty} d\varepsilon' \tau_3 [i\omega_n I - \varepsilon' \tau_3 - \Sigma(i\omega_{n'}, \varepsilon_F)]^{-1} \tau_3 R(\varepsilon_F, \varepsilon', i\omega_{n'} - i\omega_n) + T \sum_{\omega_{n'}} \mu \int_{-\varepsilon_F}^{\varepsilon_F} d\varepsilon' \tau_3 [i\omega_n I - \varepsilon' \tau_3 - \Sigma(\varepsilon', i\omega_{n'})] \tau_3. \tag{24}$$

In Eq. (24), μ is the averaged Coulomb interaction and $R(\epsilon_F, \epsilon', i\omega_{n'} - i\omega_n)$ is the averaged electron–electron interaction, which is due to the dynamic vibrations of ions. Following Eqs. (13), (16), and (23), the latter quantity can be written in the following form

$$R(\varepsilon_F, \varepsilon', i\omega_n - i\omega_{n'}) = \frac{1}{N(\varepsilon_F)} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{d\mathbf{k}}{(2\pi)^3} \times \sum_{\mathbf{g}_1 \mathbf{g}_2 \mathbf{g}_3 \mathbf{g}_4} \varepsilon^{-1}(\mathbf{q}+\mathbf{g}_1, \mathbf{q}+\mathbf{g}_2) V_{ei}(\mathbf{q}+\mathbf{g}_2) \varepsilon^{-1}(\mathbf{q}+\mathbf{g}_3, \mathbf{q}+\mathbf{g}_4) V_{ei}(\mathbf{q}+\mathbf{g}_3) \times D(\mathbf{q}+\mathbf{g}_2, \mathbf{q}+\mathbf{g}_3, i\omega_n - i\omega_{n'}) A(\mathbf{q}+\mathbf{g}_1, \mathbf{k}) A^*(\mathbf{q}+\mathbf{g}_4, \mathbf{k}) \times A(\mathbf{q}+\mathbf{g}_2, \mathbf{k}) A^*(\mathbf{q}+\mathbf{g}_3, \mathbf{k}) \delta(\varepsilon_F - \varepsilon_{\mathbf{k}}) \delta(\varepsilon' - \varepsilon_{\mathbf{k}+\mathbf{q}}). \tag{25}$$

In Eq. (25), $\mathbf{g}_1$, $\mathbf{g}_2$, $\mathbf{g}_3$, and $\mathbf{g}_4$ are the reciprocal lattice vectors, $N(\epsilon_F)$ is the density of electron states on the Fermi surface, $\epsilon_{\mathbf{k}}$ and $\epsilon_{\mathbf{k}+\mathbf{q}}$ are the energies of Bloch electrons with momenta $\mathbf{k}$ and $\mathbf{k}+\mathbf{q}$. The quantity $A(\mathbf{q}+\mathbf{g}, \mathbf{k})$ is the form factor for the scattering of Bloch electrons, given by

$$A(\mathbf{q}+\mathbf{g}, \mathbf{k}) = \frac{1}{\Omega_0} \int d\mathbf{r}\, \varphi_{\mathbf{k}+\mathbf{q}}^*(\mathbf{r}) e^{i(\mathbf{q}+\mathbf{g})\mathbf{r}} \varphi_{\mathbf{k}}(\mathbf{r}).$$

The function $\epsilon^{-1}(\mathbf{q}+\mathbf{g}, \mathbf{q}+\mathbf{g}_1)$ is the matrix of the reciprocal permittivity and $D(\mathbf{q}+\mathbf{g}, \mathbf{q}+\mathbf{g}_1, i\omega_n - i\omega_{n'})$ is the Fourier component of the function describing the dynamic vibrations of ions. The quantity $V_{ei}(\mathbf{q}+\mathbf{g})$ is the matrix element of the interaction of an electron with the ionic potential of a unit lattice, given by

$$V_{ei}(\mathbf{q}+\mathbf{g}) = \sum_{\varkappa} e^{i\mathbf{g}\varkappa} V_{ei}(\mathbf{q}+\mathbf{g}, \varkappa), \tag{26}$$

where $\varkappa$ is the radius vector of an atom in a given cell. The summation in Eq. (26) is carried out over all the positions of atoms in one unit cell.

Applying the spectral representation (18) of the function $D(\mathbf{q}+\mathbf{g}, \mathbf{q}+\mathbf{g}_1, i\omega_n - i\omega_{n'})$ and expressing the analytic continuation of the function $\Sigma(i\omega_n, \epsilon_F)$ in the form

$$\Sigma(\omega)=[1-(Z(\omega)]\omega I+Z(\omega)\Delta(\omega)\tau_2,$$

we can reduce Eq. (24) for the functions $Z(\omega)$ and $\Delta(\omega)$ to expressions which are formally identical with the usual Éliashberg equations

$$\begin{gathered} Z(\omega)\Delta(\omega)=\int_0^\infty d\omega' \operatorname{Re}\Delta(\omega')\int_0^\infty d\omega'' S(\omega'')\Big\{[f(-\omega')+N(\omega'')] \\ \times K_+(\omega',\omega'',\omega)-[f(\omega')+N(\omega'')]K_+(-\omega',\omega'',\omega) \\ -\mu\int_0^{\varepsilon_F} d\omega' \operatorname{Re}\Delta(\omega')[1-2f(\omega')]\Big\} \\ \times[1-Z(\omega)]\omega=\int_0^\infty d\omega'\int_0^\infty d\omega'' S(\omega'') \\ \times\{[f(-\omega')+N(\omega'')]K_-(\omega',\omega'',\omega)+[f(\omega')+N(\omega'')]K_-(\omega',\omega'',\omega)\}. \end{gathered} \tag{27}$$

Here, $f(\omega)$ and $N(\omega)$ are the Fermi and Bose distribution functions,

$$K_\pm(\omega',\omega'',\omega)=\frac{1}{\omega'+\omega''+\omega+i\delta}\pm\frac{1}{\omega'+\omega''-\omega-i\delta}.$$

In the system (27) we shall consider only the critical temperatures.

The only real difference between the system (27) and the usual Éliashberg equations is the definition of the function $S(\omega)$. It follows from Eqs. (18) and (25) for an anharmonic crystal that this function is

$$\begin{gathered} S(\omega)=\frac{1}{N(\varepsilon_F)}\int\frac{d\mathbf{q}}{(2\pi)^3}\frac{d\mathbf{k}}{(2\pi)^3}\sum_{\mathbf{g}_1\mathbf{g}_2\mathbf{g}_3\mathbf{g}_4}\varepsilon^{-1}(\mathbf{q}+\mathbf{g}_1,\mathbf{q}+\mathbf{g}_2) \\ \times V_{ei}(\mathbf{q}+\mathbf{g}_2)\varepsilon^{-1}(\mathbf{q}+\mathbf{g}_3,\mathbf{q}+\mathbf{g}_4)V_{ei}(\mathbf{q}+\mathbf{g}_4)\Phi(\mathbf{q}+\mathbf{g}_2,\mathbf{q}+\mathbf{g}_4,\omega) \\ \times A(\mathbf{q}+\mathbf{g}_1,\mathbf{k})A^*(\mathbf{q}+\mathbf{g}_3,\mathbf{k})\delta(\varepsilon_F-\varepsilon_{\mathbf{k}})\delta(\varepsilon_F-\varepsilon_{\mathbf{k}+\mathbf{q}}). \end{gathered} \tag{28}$$

The spectral density $\Phi(\mathbf{q}+\mathbf{g}, \mathbf{q}+\mathbf{g}_1, \omega)$ will be determined by calculating the Green functions of ion displacements $D(\mathbf{Q}_1, \mathbf{Q}_2, t)$, which can be written in the following form on the basis of Eqs. (3), (16), and (17):

$$\begin{gathered} D(\mathbf{Q}_1,\mathbf{Q}_2,t)=-i\sum_{n,n'}\exp\{-i\mathbf{Q}_1\mathbf{R}_n+i\mathbf{Q}_2\mathbf{R}_{n'}\} \\ \langle\times T(\exp\{-i\mathbf{Q}_1\mathbf{u}_n(t)\}-\langle\exp\{-i\mathbf{Q}_1\mathbf{u}_n(t)\}\rangle) \\ \times(\exp\{i\mathbf{Q}_2\mathbf{u}_{n'}(0)\}-\langle\exp\{i\mathbf{Q}_2\mathbf{u}_{n'}(0)\}\rangle)\rangle. \end{gathered} \tag{29}$$

We have introduced here the following description of dynamic displacements of ions $\mathbf{u}_n(t)$ from the equilibrium position:

$$\mathbf{R}_n(t)=\mathbf{R}_n+\mathbf{u}_n(t).$$

Employing an expansion in terms of cumulants,[26] this function can be represented as

$$\begin{gathered} D(\mathbf{Q}_1,\mathbf{Q}_2,t)=-i\sum_{n,n'}\exp\{-i\mathbf{Q}_1\mathbf{R}_n+i\mathbf{Q}_2\mathbf{R}_{n'}\} \\ \times\langle\exp\{-i\mathbf{Q}_1\mathbf{u}_n(t)\}\rangle\langle\exp\{i\mathbf{Q}_2\mathbf{u}_{n'}(0)\}\rangle \\ \times\{\exp[\langle T(\exp\{-i\mathbf{Q}_1\mathbf{u}_n(t)\}-1)(\exp\{i\mathbf{Q}_2\mathbf{u}_{n'}(0)\}-1)\rangle]_L-1\}. \end{gathered} \tag{30}$$

Here, the index L means that we have to consider only the coupled diagrams in the calculation of thermodynamic averages.

The function $D(\mathbf{Q}_1, \mathbf{Q}_2, t)$ for a harmonic crystal can be calculated exactly[27]:

$$\begin{gathered} D(\mathbf{Q}_1,\mathbf{Q}_2,t)=-i\sum_{n,n'}\exp(-i\mathbf{Q}_1\mathbf{R}_n+i\mathbf{Q}_2\mathbf{R}_{n'})\exp(-W_{\mathbf{Q}_1}-W_{\mathbf{Q}_2}) \\ \times\{\exp[\langle T\mathbf{Q}_1\mathbf{u}_n(t)\mathbf{Q}_2\mathbf{u}_{n'}(0)\rangle]-1\}, \end{gathered} \tag{31}$$

where the expression

$$\exp(-W_{\mathbf{Q}_1})=\langle\exp(-i\mathbf{Q}_1\mathbf{u}_n(t)\rangle=\exp[-{}^1/_2Q_{1\alpha}Q_{1\beta}\langle u_n^\alpha(t)u_n^\beta(t)\rangle] \tag{32}$$

is simply the usual Debye-Waller factor.

Expanding the exponential function in the last factor in Eq. (30), we find successively the contributions made to $D(\mathbf{Q}_1, \mathbf{Q}_2, t)$ by one-phonon, two-phonon, and other processes. In describing superconductivity in harmonic crystals at low temperatures we can ignore both many-phonon processes and the Debye-Waller factors so that the function $D(\mathbf{Q}_1, \mathbf{Q}_2, t)$ reduces to the usual one-phonon Green function

$$\begin{gathered} D(\mathbf{Q}_1,\mathbf{Q}_2,t)=D_1(\mathbf{Q}_1,\mathbf{Q}_2,t) \\ =-i\sum_{n,n'}\exp[-i\mathbf{Q}_1\mathbf{R}_n+i\mathbf{Q}_2\mathbf{R}_{n'}]\langle T\mathbf{Q}_1\mathbf{u}_n(t)\mathbf{Q}_2\mathbf{u}_{n'}(0)\rangle. \end{gathered}$$

The spectral density of the function $D_1(\mathbf{Q}_1, \mathbf{Q}_2, t)$ has the simple form

$$\Phi(\mathbf{q}+\mathbf{g},\mathbf{q}+\mathbf{g}_1,\omega)=\sum_\lambda\frac{(\mathbf{q}+\mathbf{g})^\alpha e_{\mathbf{q}\lambda}^\alpha(\mathbf{q}+\mathbf{g}_1)^\beta e_{\mathbf{q}\lambda}^\beta}{M\omega_{\mathbf{q}\lambda}}\delta(\omega-\omega_{\mathbf{q}\lambda}). \tag{33}$$

Here, M is the mass of an ion, $\mathbf{e}_{\mathbf{q}\lambda}$ is the polarization vector, and $\omega_{\mathbf{q}\lambda}$ is the phonon frequency. In this case the function $S(\omega)$ reduces to the usual expression employed in descriptions of superconductivity in harmonic crystals.

The expression (31) for the function $D(\mathbf{Q}_1, \mathbf{Q}_2, t)$ does not apply to an anharmonic crystal. Moreover, in such a crystal we cannot even separate clearly one-phonon processes, two-phonon processes, etc., because in this case there are always interference effects.[27,28]

In calculating the function $D(\mathbf{Q}_1, \mathbf{Q}_2, t)$ we shall confine ourselves to the simplest one- and two-phonon processes and to the interference between them. With this in mind, we shall expand the exponential functions in Eq. (29) to within terms of the fourth order in $\mathbf{u}_n$:

$$\begin{gathered} \langle T(\exp\{-i\mathbf{Q}_1\mathbf{u}_n(t)\}-1)(\exp\{i\mathbf{Q}_2\mathbf{u}_{n'}(0)\}-1)\rangle \\ =\langle T[1-{}^1/_2 i\mathbf{Q}_1\mathbf{u}_n(t)][\mathbf{Q}_1\mathbf{u}_n(t)][\mathbf{Q}_2\mathbf{u}_{n'}(0)][1+{}^1/_2 i\mathbf{Q}_2\mathbf{u}_{n'}(0)]\rangle. \end{gathered}$$

Finally, the Green function $D(\mathbf{Q}_1, \mathbf{Q}_2, t)$ can be expressed in the following form in this approximation:

$$D(\mathbf{Q}_1,\mathbf{Q}_2,t)=D_1(\mathbf{Q}_1,\mathbf{Q}_2,t)+D_2(\mathbf{Q}_1,\mathbf{Q}_2,t)+D_{int}(\mathbf{Q}_1,\mathbf{Q}_2,t). \tag{34}$$

Here, $D_1(\mathbf{Q}_1, \mathbf{Q}_2, t)$ is the one-phonon Green function:

$$\begin{gathered} D_1(\mathbf{Q}_1,\mathbf{Q}_2,t)=-i\sum_{n,n'}\exp(-i\mathbf{Q}_1\mathbf{R}_n+i\mathbf{Q}_2\mathbf{R}_{n'}) \\ \times\exp(-W_{\mathbf{Q}_1}-W_{\mathbf{Q}_2})\langle T\mathbf{Q}_1\mathbf{u}_n(t)\mathbf{Q}_2\mathbf{u}_{n'}(0)\rangle, \end{gathered} \tag{35}$$

$D_2(\mathbf{Q}_1,\mathbf{Q}_2,t)$ is the two-phonon Green function:

$$D_2(\mathbf{Q}_1,\mathbf{Q}_2,t)=-\frac{1}{4}i\sum_{n,n'}\exp(-i\mathbf{Q}_1\mathbf{R}_n+i\mathbf{Q}_2\mathbf{R}_{n'})$$
$$\times\exp(-W_{\mathbf{Q}_1}-W_{\mathbf{Q}_2})\langle T\mathbf{Q}_1\mathbf{u}_n(t)\,\mathbf{Q}_1\mathbf{u}_n(t)\,\mathbf{Q}_2\mathbf{u}_{n'}(0)\,\mathbf{Q}_2\mathbf{u}_{n'}(0)\rangle \tag{36}$$

and the function D_{int} describes interference processes

$$D_{int}(\mathbf{Q}_1,\mathbf{Q}_2,t)=-\frac{1}{2}\sum_{n,n'}\exp(-i\mathbf{Q}_1\mathbf{R}_n+i\mathbf{Q}_2\mathbf{R}_{n'})$$
$$\times\exp(-W_{\mathbf{Q}_1}-W_{\mathbf{Q}_2})\,[\langle T\mathbf{Q}_1\mathbf{u}_n(t)\,\mathbf{Q}_1\mathbf{u}_n(t)\,\mathbf{Q}_2\mathbf{u}_{n'}(0)\rangle$$
$$-\langle T\mathbf{Q}_1\mathbf{u}_n(t)\,\mathbf{Q}_2\mathbf{u}_{n'}(0)\,\mathbf{Q}_2\mathbf{u}_{n'}(0)\rangle]. \tag{37}$$

The function $S(\omega)$, describing superconducting properties, can then also be written in the form

$$S(\omega)=S_1(\omega)+S_2(\omega)+S_{int}(\omega). \tag{38}$$

The functions $D_1(\mathbf{Q}_1,\mathbf{Q}_2,t)$, $D_2(\mathbf{Q}_1,\mathbf{Q}_2,t)$, and $D_{\text{int}}(\mathbf{Q}_1,\mathbf{Q}_2,t)$ should be calculated allowing for the anharmonic interactions. In the description of neutron scattering in an anharmonic crystal we have to know these functions only for $\mathbf{Q}_1=\mathbf{Q}_2$. Such functions have been calculated on many occasions[26-29] using a phenomenological phonon Hamiltonian allowing for third- and fourth-order anharmonicity. These calculations are given in the most detailed form by Glyde.[29] We can readily extend these results to the more general case $\mathbf{Q}_1\neq\mathbf{Q}_2$ and we then obtain the following expressions for the Fourier components of these functions applicable to crystals with one atom per unit cell:

$$D_1(\mathbf{Q}_1,\mathbf{Q}_2,\omega)=\sum_{\mathbf{q}\lambda}\frac{Q_1{}^{\alpha}e_{\mathbf{q}\lambda}{}^{\alpha}\exp(-W_{\mathbf{Q}_1})}{(2M\omega_{\mathbf{q}\lambda})^{1/2}}\frac{Q_2{}^{\beta}e_{\mathbf{q}\lambda}{}^{\beta}\exp(-W_{\mathbf{Q}_2})}{(2M\omega_{\mathbf{q}\lambda})^{1/2}}$$
$$\times d_1(\mathbf{q}\lambda,\omega)\sum_{\mathbf{g}_1}\Delta(\mathbf{Q}_1-\mathbf{q}-\mathbf{g}_1)\sum_{\mathbf{g}_2}\Delta(\mathbf{Q}_2-\mathbf{q}-\mathbf{g}_2), \tag{39}$$

$$D_2(\mathbf{Q}_1,\mathbf{Q}_2,\omega)=\frac{1}{2}\sum_{\mathbf{q}_1\lambda_1\mathbf{q}_2\lambda_2}\frac{|Q_1e_{\mathbf{q}_1\lambda_1}|^2}{2M\omega_{\mathbf{q}_1\lambda_1}}\frac{|Q_2e_{\mathbf{q}_2\lambda_2}|^2}{2M\omega_{\mathbf{q}_2\lambda_2}}$$
$$\times d_2(\mathbf{q}_1\lambda_1,\mathbf{q}_2\lambda_2,\omega)\sum_{\mathbf{g}_1}\Delta(\mathbf{Q}_1-(\mathbf{q}_1+\mathbf{q}_2)-\mathbf{g}_1)\sum_{\mathbf{g}_2}\Delta(\mathbf{Q}_2-(\mathbf{q}_1+\mathbf{q}_2)-\mathbf{g}_2), \tag{40}$$

$$D_{int}(\mathbf{Q}_1,\mathbf{Q}_2,\omega)=-\frac{1}{2}i\sum_{\mathbf{q}_1\lambda_1\mathbf{q}_2\lambda_2\mathbf{q}_3\lambda_3}\frac{Q_1{}^{\alpha}e^{\alpha}_{\mathbf{q}_1\lambda_1}}{(2M\omega_{\mathbf{q}_1\lambda_1})^{1/2}}$$
$$\times\frac{Q_1{}^{\beta}e^{\beta}_{\mathbf{q}_2\lambda_2}}{(2M\omega_{\mathbf{q}_2\lambda_2})^{1/2}}\frac{Q_2{}^{\gamma}e^{\gamma}_{\mathbf{q}_3\lambda_3}}{(2M\omega_{\mathbf{q}_3\lambda_3})^{1/2}}d_1(\mathbf{q}_3\lambda_3,\omega)\,d_2(\mathbf{q}_1\lambda_1,\mathbf{q}_2\lambda_2,\omega)$$
$$\times V_3(-\mathbf{q}_1\lambda_1,-\mathbf{q}_2\lambda_2,\mathbf{q}_3\lambda_3)\sum_{\mathbf{g}_1}\Delta(\mathbf{Q}_1-(\mathbf{q}_1+\mathbf{q}_3)-\mathbf{g}_1)$$
$$\times\sum_{\mathbf{g}_2}\Delta(\mathbf{Q}_2-\mathbf{q}_3-\mathbf{g}_2)+\frac{1}{2}i\sum_{\mathbf{q}_1\lambda_1\mathbf{q}_2\lambda_2\mathbf{q}_3\lambda_3}\frac{Q_1{}^{\alpha}e^{\alpha}_{\mathbf{q}_1\lambda_1}}{(2M\omega_{\mathbf{q}_1\lambda_1})^{1/2}}$$
$$\times\frac{Q_2{}^{\beta}e^{\beta}_{\mathbf{q}_2\lambda_2}}{(2M\omega_{\mathbf{q}_2\lambda_2})^{1/2}}\frac{Q_2{}^{\gamma}e^{\gamma}_{\mathbf{q}_3\lambda_3}}{(2M\omega_{\mathbf{q}_3\lambda_3})^{1/2}}d_1(\mathbf{q}_1\lambda_1,\omega)\,d_2(\mathbf{q}_2\lambda_2,\mathbf{q}_3\lambda_3,\omega)\,V_3(\mathbf{q}_1\lambda_1,\mathbf{q}_2\lambda_2,-\mathbf{q}_3\lambda_3)$$
$$\times\sum_{\mathbf{g}_1}\Delta(\mathbf{Q}_1-\mathbf{q}_1-\mathbf{g}_1)\sum_{\mathbf{g}_2}\Delta(\mathbf{Q}_2-(\mathbf{q}_2+\mathbf{q}_3)-\mathbf{g}_2). \tag{41}$$

In these expressions $\Delta(\mathbf{Q}-\mathbf{q}-\mathbf{g})$ is the delta function describing the conservation of momentum to within a reciprocal lattice vector, and $V_3(\mathbf{q}_1\lambda_1,\mathbf{q}_2\lambda_2,\mathbf{q}_3\lambda_3)$ is the anharmonic three-phonon interaction constant. The functions $d_1(\mathbf{q}\lambda,\omega)$ and $d_2(\mathbf{q}_1\lambda_1,\mathbf{q}_2\lambda_2,\omega)$ are, respectively, the one- and two-phonon Green functions. When allowance is made for the anharmonic interactions, the one-phonon Green function can be expressed in the form

$$d_1(\mathbf{q}\lambda,\omega)=\frac{2\omega_{\mathbf{q}\lambda}}{\omega^2-\omega_{\mathbf{q}\lambda}{}^2-\Pi_{\mathbf{q}\lambda}(\omega)}, \tag{42}$$

where $\Pi_{\mathbf{q}\lambda}(\omega)$ is the polarization phonon operator, the simplest expressions for which have been obtained by several authors[26-29] allowing for the three-phonon interactions in the second order of the perturbation theory and for the four-phonon interactions in the first order.

In the investigations mentioned in Introduction[9,10] an allowance for the influence of anharmonicity of superconductivity is essentially limited to changes in the one-particle Green function alone. We can see from our expressions that this is quite inconsistent. One should allow, to the same extent, for changes associated with the Debye-Waller factors $\exp(-W_Q)$, which occur in the function $D_1(\mathbf{Q}_1,\mathbf{Q}_2,t)$ and also the changes associated with with the functions $D_2(\mathbf{Q}_1,\mathbf{Q}_2,t)$ and $D_{\text{int}}(\mathbf{Q}_1,\mathbf{Q}_2,t)$.

We have ignored the Debye-Waller factors in the calculation of $D_2(\mathbf{Q}_1,\mathbf{Q}_2,t)$ and $D_{\text{int}}(\mathbf{Q}_1,\mathbf{Q}_2,t)$, Moreover, it is sufficient to find these functions by using the one- and two-particle Green functions (occurring in them) in the harmonic approximation. Allowance for anharmonicity may give rise to coupled two-phonon states,[30,31] which—in their turn—may become hybridized with one-particle optical phonons. All these processes may influence also superconductivity. Such refinements of two-particle Green functions are clearly of little importance in the case of weak anharmonicity. Allowance for bound states, compared with the harmonic approximation for the two-phonon Green function, alters slightly the quantities averaged over the whole spectrum. For example, such changes in the electron-phonon coupling are of the order of $(E_c-2\omega_0)/2\omega_0$, where E_c is the energy of a coupled two-phonon state and ω_0 is the energy of one phonon.

In the case of crystals whose anharmonicity is associated with the existence of soft phonon modes of frequencies $\omega_{\mathbf{q}}$ of the order of the critical superconducting temperature T_c, for example the A-15 compounds, an analytic solution of the superconductivity equations (27) is practically impossible, as shown in our earlier paper.[32]

An interesting case, which has the advantage that it can be considered within the framework of analytic solution of the equations of superconductivity, is the superconductivity of PdH, whose anharmonicity is associated with the zero-point vibrations of the light hydrogen atoms. In this case all the characteristic phonon frequencies $\omega_{\mathbf{q}}$ are higher than T_c and we can use an analytic expression for T_c found by us earlier.[32]

§4. SUPERCONDUCTIVITY OF PdH(D) COMPOUNDS AND THE ANOMALOUS ISOTOPIC EFFECT

The critical temperature of the superconducting transition given by the system (27) can be described as follows[25,32]:

$$T_c=1{,}14\omega_{\log}e^{-A}\exp\left[-\frac{1+\lambda}{\lambda-\mu^*(1+\alpha)}\right]. \tag{43}$$

In this expression λ is the electron–phonon coupling constant:

$$\lambda=2\int_0^\infty d\omega\frac{S(\omega)}{\omega}.$$

The quantity $\omega_{\log}$ is the logarithmic mean frequency of the phonon spectrum:

$$\omega_{\log}=\frac{2}{\lambda}\int_0^\infty d\omega\frac{S(\omega)}{\omega}\ln\omega,$$

and μ^+ is the Coulomb pseudopotential

$$\mu^+=\frac{\mu}{1+\mu\ln(\varepsilon_F/\omega_{\log})},\quad \alpha=\frac{\lambda}{1+\lambda}A.$$

The quantity A is defined as follows:

$$A=\frac{2}{\lambda^2}\int_0^\infty d\omega_1\frac{S(\omega_1)}{\omega_1}\ln\left(\frac{\omega_1^2}{\omega_{\log}^2}\right)\int_0^\infty d\omega_2 S(\omega_2)\left(\frac{1}{\omega_2+\omega_1}-\frac{1}{\omega_2-\omega_1}\right).$$

The lattice dynamics of the compounds PdH(D) is characterized by the existence of two modes with very different frequencies[33]: these are the acoustic vibration modes of characteristic frequency $\omega_{ac}\sim 200\,^\circ\mathrm{K}$ and the optical vibrations with $\omega_{opt}\sim 650\,^\circ\mathrm{K}$. In view of the large difference between the masses of the Pd and H atoms, essentially only the Pd atoms participate in the acoustic vibrations and the H atoms in the optical vibrations. Consequently, the electron–phonon coupling constant can be written in the form

$$\lambda=2\int_0^{\omega_c} d\omega\frac{S(\omega)}{\omega}+2\int_{\omega_c}^\infty d\omega\frac{S(\omega)}{\omega}=\lambda_{Pd}+\lambda_H. \tag{44}$$

Here, ω_c is some frequency lying in the gap between the acoustic and optical vibrations $\omega_{ac}<\omega_c<\omega_{opt}$, where the constants λ_{Pd} and λ_H represent the interaction of electrons with the vibrations of the Pd and H atoms. In the harmonic approximation they can be described in the form suggested by McMillan[11]:

$$\lambda_{Pd}=\frac{C_{Pd}}{M_{Pd}\langle\omega_{ac}^2\rangle},\quad \lambda_H=\frac{C_H}{M_H\langle\omega_{opt}^2\rangle} \tag{45}$$

and in this approximation the two constants are independent of the atomic masses but are affected only by the magnitude of the electron–ion interaction and by the force constants of the acoustic and optical vibrations.

An important feature which distinguishes PdH from many other transition-metal hydrides is the smallness of the force constants responsible for the optical vibrations, compared with the acoustic force constants. The force constants can be described by the quantity $\gamma=M\langle\omega^2\rangle$. In the case of PdH the ratio of the force constants is $\gamma_{ac}/\gamma_{opt}\sim 5$. It is clear from Eq. (45) that the smallness of the force constants of the optical vibrations tends to increase the constant representing the coupling with the vibrations of the H atoms. The relative values of the constants λ_{Pd} and λ_H are governed not only by the force constants γ_{ac} and γ_{opt}, but also by the electron–ion interaction represented by the constants C_{Pd} and C_H. When $C_{Pd}\sim C_H$, we find—in accordance with the ratio of the force constants—that $\lambda_H\sim 5\lambda_{Pd}$. In fact, the relationship between λ_{Pd} and λ_H of PdH is still not known and the published estimates are highly contradictory.[6]

In quantitative estimates of the dependence of T_c on the masses of the H and D isotopes it is absolutely essential to know the ratio of λ_{Pd} to λ_H and, therefore, we shall confine ourselves to the qualitative analysis of the situation. Since PdH is a superconductor with weak coupling, we can calculate T_c confining our attention to the effects of anharmonicity in the electron–phonon coupling constants λ. The preexponential factors $\omega_{\log}$ and e^{-A} can be calculated in the harmonic approximation. We then find that

$$T_c=\frac{\bar\omega}{1.43}\exp\left[-\frac{1+\lambda+\delta\lambda}{\lambda+\delta\lambda-\mu^+}\right], \tag{46}$$

$$\bar\omega=\omega_{ac}^{a}\omega_{opt}^{b}\exp(\lambda_{Pd}\lambda_H/\lambda^2),$$
$$a=\frac{\lambda_{Pd}}{\lambda}\left(1+\frac{\lambda_H}{\lambda}\right),\quad b=\left(\frac{\lambda_H}{\lambda}\right)^2, \tag{47}$$

where the values of λ_{Pd} and λ_H are given by Eq. (45).

The change $\delta\lambda$ in the electron–phonon coupling constant can be expressed in the form

$$\delta\lambda=2\int_0^\infty\frac{d\omega}{\omega}[S(\omega)-S_0(\omega)]=\delta\lambda_1+\delta\lambda_2+\delta\lambda_3+\delta\lambda_4, \tag{48}$$

where $S_0(\omega)$ is calculated in the harmonic approximation using Eq. (33) for the spectral density of the function $D(\mathbf{Q}_1,\mathbf{Q}_2,\omega)$. The four contributions to $\delta\lambda$ represent the following processes. The term $\delta\lambda_1$ appears because of the presence of the Debye-Waller factor in the one-phonon Green function, $\delta\lambda_2$ is due to the difference between the one-phonon Green function for an anharmonic crystal and that obtained in the harmonic approximation, $\delta\lambda_3$ is the contribution of two-phonon processes, and $\delta\lambda_4$ is a contribution of the interference processes.

The application of Eqs. (39)–(41) makes it possible to estimate these contributions considering only the anharmonicity of the optical vibrations of light atoms. It must be mentioned particularly that in the calculation of the coupling constant and its changes in accordance with Eqs. (44) and (46) there is no need to calculate the spectral density of the functions $D(\mathbf{Q}_1,\mathbf{Q}_2,\omega)$ because

$$\lambda=\int_0^\infty d\omega\frac{S(\omega)}{\omega}$$

can be expressed directly in terms of the D function at a zero frequency. Applying the approximation of almost-free electrons, we easily obtain the expressions for two of these terms:

$$\delta\lambda_1=-\frac{N(\varepsilon_F)}{M_H^2\omega_{opt}^3}\int_0^{2k_F}\frac{dq}{2k_F^2}q^5\tilde V_H^2(q)\approx-\frac{(2k_F)^2}{M_H\omega_{opt}}\lambda_H, \tag{49}$$

$$\delta\lambda_3=\frac{N(\varepsilon_F)}{4M_H^2\omega_{opt}^3}\int_0^{2k_F}\frac{dq}{2k_F^2}q^5\tilde V_H^2(q)\approx\frac{(2k_F)^2}{4M_H\omega_{opt}}\lambda_H. \tag{50}$$

In the above expressions $\tilde V_H(q)$ represents the screened potential of the interaction of an electron with a H atom.

It is clear from Eqs. (49) and (50) that in the case of an optical dispersion-free mode the contribution of the Debye-Waller factor is negative and four times as large as the contribution of two-phonon processes. We can show that in the same approximations there is no contribution from interference processes and $\delta\lambda_4 = 0$.

The factor $(2k_F)/M_H\omega_{\text{opt}}$ occurring in Eqs. (49) and (50) in front of the constant λ_H is the square of the ratio of the distance between electrons to the amplitude of zero-point vibrations. In the adopted approximations, we find that $\delta\lambda_2$ can be described by

$$\delta\lambda_2 = -\frac{N(\varepsilon_F)}{M_H\omega_{\text{opt}}^2}\int_0^{2k_F}\frac{dq}{2k_F^2}\,q^5\bar{V}_H(q)\,\frac{\Pi_{\text{opt}}(q,0)}{\omega_{\text{opt}}^2}. \qquad (51)$$

In this expression, $\Pi_{\text{opt}}(q,0)$ is the polarization operator for the optical vibrations.

We shall begin by rewriting Eq. (51) on the basis of the theorem of averages:

$$\delta\lambda_2 = -\Pi_{\bar{q}}(0)\lambda_H/\omega_{\text{opt}}^2 .$$

The sign of the change in the coupling constant $\delta\lambda_2$ depends on the sign of the polarization operator. The third-order anharmonicity is known to make a negative contribution to $\Pi_{\bar{q}}(0)$ and the contribution of the four-order anharmonicity is positive.[26-29] It is known from the experimental results[33] that the shift of the phonon frequencies in PdH because of anharmonicity increases these frequencies. The shift can be written in the form

$$\bar{\omega}_{q\lambda}^2 = \omega_{q\lambda}^2\left(1 + \mathrm{Re}\,\Pi_{q\lambda}(\omega_{q\lambda})/\omega_{q\lambda}^2\right).$$

The experimental results[33] show that $\mathrm{Re}\Pi_{q\lambda}(\omega_{q\lambda})/\omega_{q\lambda}^2$ is of the order of 0.1. Since $\Pi_{q\lambda}(\omega)$ is a decreasing function of the frequency ω, the ratio $\Pi_{\bar{q}}(0)/\omega_{q\lambda}^2$ is at least not smaller than 0.1 and it is positive.

Thus, the most important processes which alter the electron–phonon coupling constant and reduce it because of anharmonicity are the Debye-Waller factor and renormalization of phonon frequencies. The order of magnitude is such that if we allow only for the fourth-order anharmonicity, we find that

$$\Pi_{\bar{q}}(0) = \frac{1}{M_H\omega_{\text{opt}}}\frac{\bar{V}_4}{\omega_{\text{opt}}^2},$$

where $\bar{V}_4$ is the average anharmonicity constant. A calculation of the actual relationship between the values of $\delta\lambda_1$ and $\delta\lambda_2$ requires a more accurate knowledge of the force constants and interionic potentials in the compoung PdH. It is important to note that the reduction in the coupling constant for PdH is greater than for PdD because the amplitude of the zero-point vibrations $u_H^2 = 1/M_H\omega_{\text{opt}}$ of the H atoms is greater than that of the deuterium atoms. In the final analysis, this aspect is responsible for the anomalous isotopic effect exhibited by PdH(D).

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