

# Effect of impurity modes with quasilocal and local frequencies on the temperature of a superconducting transition

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An isotropic irregular superconductor is considered. It is assumed that  $\lambda$ —the effective interaction parameter determining the pairing of electrons—is smaller than or of the order of 0.5. The system of Eliashberg integral equations is solved for  $T \rightarrow T_c$ . A simple analytic expression is obtained for  $T_c$ . A detailed analysis is given of the nature of the variation of the critical temperature in superconductors containing impurity atoms. Its dependence on parameters describing the phonon spectrum of the impurity system is investigated. It turns out that the presence in the phonon spectrum of impurity modes with quasilocal and with local frequencies can lead both to relatively small, and also to quite appreciable changes in  $T_c$ . The former case is typical for a situation when the impurity atom is a practically isotopic defect. If the impurity atom is very heavy ( $M_1 \gg M_0$ ), the corresponding relative correction  $\delta T_c$  to  $T_c$  is negative, and  $\delta T_c \sim \ln(M_0/M_1)$ . For a light defect the factor  $\delta T_c$  is, generally speaking, positive, but  $\delta T_c \lesssim c$ . The latter case is realized when the impurity atom is coupled to the atoms of the matrix in an anomalously weak ( $\gamma_1 \ll \gamma_0$ ) or an anomalously strong ( $\gamma_1 \gg \gamma_0$ ) manner. A sharp reduction in the effective force constant  $\gamma_1$  for an impurity atom leads to an increase in  $\delta T_c$ :  $\delta T_c \sim c\gamma_0/\gamma_1 (\lambda - \mu^{(0)})$ . In the opposite case an increase in the value of  $\gamma_1$  results in the appearance of a negative correction to  $T_c$ , and  $\delta T_c \sim c/(\lambda - \mu^{(0)})$ . A comparison with experimental data is carried out. For a number of solutions a qualitative description is given of the variation of  $T_c$  due to the presence of impurities. The quantitative agreement between the calculated and the experimental values of  $\delta T_c$  is satisfactory.

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## 1. INTRODUCTION

The study of the nature of the variation of the temperature  $T_c$  characterizing the transition of metals into the superconducting state as the number of nonmagnetic impurity atoms is varied forms the content of a number of papers. Usually the investigation is carried out within the framework of the BCS theory, i.e., it is assumed that the interaction responsible for the appearance of the superconducting state is a nonretarded one. In the simplest approximation when the metal is assumed to be isotropic and only the elastic scattering of electrons by defects is taken into account, it turns out that the value of  $T_c$  does not change (cf., for example, [1]). Among the factors that lead to a variation of  $T_c$  the following have been investigated.

Markowitz and Kadanoff<sup>[2]</sup> have investigated the isotropization, caused by the elastic scattering of electrons by defects, of an anisotropic energy gap in a real regular crystal. According to the usual estimates isotropization gives rise to a very insignificant reduction of  $T_c$ . Moskalenko and Palistrant<sup>[3]</sup> had set themselves the aim of determining the role played by impurities in superconductors by assuming the existence of several energy gaps. However, the model with several energy gaps is, generally speaking, inapplicable to nontransition metals, where in accordance with the experimental data of<sup>[4]</sup> the anisotropy of the gap does not exceed 30–40%, and it is also inapplicable to transition metals even with a very small content of impurity atoms<sup>[4]</sup>. Bar'yakhtar et al<sup>[5]</sup> have investigated the effect on  $T_c$  of the modifications of the electron spectrum near singularities due to the presence of impurities. Maksimov<sup>[6]</sup> has calculated the renormalization due to impurities of the effective interaction parameter  $\lambda$  which gives rise to the pairing of electrons. The difference was taken into account in the scattering amplitudes between the atoms of the basic lattice and the impurity atoms, and also, to some extent,

the special nature of the oscillations of the group of atoms singled out near the impurity. The values obtained for the difference  $\lambda(c) - \lambda(c=0)$ , where  $c$  is the concentration of the impurities, is of order  $c\lambda(c=0)$ .

A consistent theory of irregular superconductors must be constructed taking into account the effects of retardation and of the damping of the quasiparticles. Equations of the Eliashberg type<sup>[7,8]</sup> for superconductors with impurity atoms have been obtained by Maximov<sup>[6]</sup>. Below in Sec. 2 these equations are solved for  $T = T_c$  in the case of an isotropic superconductor with intermediate coupling under general assumptions concerning the nature of the electron-phonon interaction and the shape of the phonon spectrum. A simple analytic expression is obtained for  $T_c$ . In Sec. 3 with the aid of this expression a special analysis is given of the manner in which  $T_c$  varies when specific impurity modes are present in the vibrational spectrum of the superconductor: a local and a quasilocal mode. Theoretically the possibility of the existence of the aforementioned modes in weak solutions has been predicted by I. Lifshitz<sup>[9]</sup> and by Yu. Kagan and Iosilevskii<sup>[10]</sup>. Experimentally these modes have been directly discovered in a number of metals for the first time in the course of measurements of the spectra of the inelastic coherent<sup>[11]</sup> and incoherent<sup>[12,13]</sup> scattering of slow neutrons, and also, for example, as a result of the reduction of data on the low temperature measurements of specific heat<sup>[13-15]</sup>, resistance<sup>[16,17]</sup>, tunnel characteristics (cf., for example, [18]). We note that the effect of quasilocal and local modes on  $T_c$  has been investigated theoretically earlier by Appel<sup>[19]</sup>. The results of the present paper are compared to his results.

In the last, fourth section an investigation of the experimental data is carried out within the framework of the theory developed here in order to obtain directly the variation of  $T_c$  produced by specific impurity modes. Use has been made of the results of measurements of the low

temperature specific heat of impurity superconductors. We recall that in the case of such measurements it turns out to be possible along with  $T_C$  to determine the manner of the variation of the density of normal electron states on the Fermi surface  $N$  and the Debye temperature  $\Theta_D$ .

## 2. GENERAL RELATIONS

As our point of departure we take the system of the Eliashberg integral equations for an isotropic irregular superconductor which determine the renormalization parameter for the electron mass  $Z$  and the parameter for the energy gap  $\Delta$ <sup>[8, 6]</sup>. We restrict ourselves to the examination of the situation when all the characteristic phonon frequencies  $\omega_0$  significantly exceed the value of the superconducting transition temperature  $T_C$ . We also assume that the effective parameter  $\lambda$  is smaller than or of the order of 0.5. Then, as can be shown, in order to find  $T_C$  it is sufficient to solve an equation of the form

$$\varphi(\omega) = \int_0^\infty d\omega' \operatorname{th} \frac{\omega'}{2T_C} \frac{\varphi(\omega')}{\omega'} \left[ \nu I(\omega, \omega') - \frac{\mu \theta(\epsilon_F - \omega')}{\operatorname{Re} Z(\omega')} \right], \quad (1)$$

where

$$\nu = \frac{\lambda}{1+\lambda}, \quad \lambda = 2 \int_0^\infty \frac{d\omega}{\omega} S(\omega), \quad (2)$$

$$\varphi(\omega) = \operatorname{Re} \Delta(\omega) \operatorname{Re} Z(\omega) / \operatorname{Re} \Delta(0) \operatorname{Re} Z(0),$$

$$I(\omega, \omega') = \frac{1}{\lambda} \int_0^\infty d\omega'' S(\omega'') \left[ \frac{1}{\omega' + \omega + \omega''} + \frac{1}{\omega' - \omega + \omega''} \right].$$

In (1) we have denoted by  $\mu$  the matrix element of the screened Coulomb interaction averaged over the Fermi surface and multiplied by the value of the density of normal electron states at the Fermi level,  $\theta$  is the unit function. The general expression for  $S$  is given in<sup>[6]</sup>.

We note that the kernel of the integral equation (1) has a logarithmic singularity as  $\omega \rightarrow 0$ . The correction terms  $\Delta I$  which have not been taken into account explicitly in the expression for the kernel do not have such a singularity. If we take into account the specific nature of the frequency dependence of  $\Delta I$ , then it turns out that this leads to the appearance in the equation for  $T_C$  of terms of order  $\nu$ ,  $\mu$  and  $3T_C/\omega_0$  in the factor multiplying the exponential.

For the solution of (1) we utilize an approach close to the one described in<sup>[20]</sup>. We go over from Eq. (1) to the following system of equations:

$$\varphi(\omega) = I(\omega, 0) + [I(\omega, 0) - 1] \kappa + \nu \int_0^\infty \frac{d\omega'}{\omega'} [I(\omega, \omega') - I(\omega, 0)I(0, \omega')] \varphi(\omega'), \quad (3)$$

$$\kappa = \mu \int_0^\infty \frac{d\omega}{\omega} \operatorname{th} \frac{\omega}{2T_C} \frac{\varphi(\omega)}{\operatorname{Re} Z(\omega)}, \quad (4)$$

$$1 = \nu \int_0^\infty \frac{d\omega}{\omega} \varphi(\omega) \operatorname{th} \frac{\omega}{2T_C} I(0, \omega) - \kappa. \quad (5)$$

We make some comments regarding the relations (3)–(5). Firstly, the kernel of (3) no longer has a logarithmic singularity as  $\omega \rightarrow 0$ . Secondly, the inhomogeneous term in (3) in fact corresponds to the well-known trial function of Morel-Anderson<sup>[21]</sup> (cf., in addition,<sup>[22]</sup>).

By utilizing the system (3)–(5) it is not difficult to obtain an expression for  $T_C$  in the form

$$T_C = 1.14\omega_0 \exp \{ -1/(g - \bar{\mu}_*) \}, \quad (6)$$

where

$$\omega_c = \exp \langle \ln \omega \rangle, \quad g = \frac{\nu}{1 + \eta\nu/2},$$

$$\bar{\mu}_* = \frac{\mu_*}{1 + \lambda}, \quad \mu_* = \frac{\mu}{1 + \mu \ln(\epsilon_F/\omega_c)},$$

$$\eta = \left\langle \left\langle \frac{\omega^2}{\omega^2 - \omega'^2} \ln \frac{\omega^2}{\omega'^2} \right\rangle \right\rangle_{\omega, \omega'}. \quad (7)$$

The symbol  $\langle \dots \rangle$  is to be interpreted as follows:

$$\langle f \rangle_\omega = \int_0^\infty \frac{d\omega}{\omega} S(\omega) f(\omega) / \int_0^\infty \frac{d\omega}{\omega} S(\omega). \quad (8)$$

We emphasize that Eqs. (6)–(8) have been obtained for an irregular isotropic superconductor with intermediate coupling. In deriving these expressions no assumptions were made, generally speaking, concerning the nature of the electron-phonon interaction and the shape of the phonon spectrum.

By using an electronic computer we have made estimates of the accuracy of formula (6) for  $T_C$ . The vibrational spectrum was assumed to be in turn a Debye spectrum and of the form of a sum of two Lorentz terms with characteristic peak frequencies that did not differ much from each other. In evaluating the function for the electron-phonon interaction the electron-ion potential was chosen in the form of a screened Coulomb potential. It turned out that the coefficients in the numerator of the index of the exponential in (6) multiplying  $\nu^2$  and  $\nu\mu$  are respectively smaller than 0.5 and 1. The coefficients of  $\mu\nu^2$  and of  $\nu\mu^2$  in the denominator do not exceed unity. (In<sup>[23]</sup>, where the phonon spectrum has been approximated by a single Einstein peak, similar results have been obtained). In the models mentioned above  $\eta$  is practically equal to unity.

Taking the foregoing into account it can be easily seen that relation (6) for  $T_C$  bears a strong resemblance to the well-known empirical formula due to McMillan<sup>[24]</sup>. For  $\eta \approx 1$  and  $\lambda \gg \mu_*$  we have

$$T_C \approx \frac{\omega_c}{1.45} \exp \left( -\frac{1 + \lambda}{\lambda - \mu_*(1 + 0.5\lambda)} \right). \quad (9)$$

We state the desired expression for that part of  $T_C$  which is due to the presence of impurity atoms. We take the impurity concentration  $c$  to be a small quantity. We then have

$$\delta T_C = \frac{T_C(c) - T_C(c=0)}{T_C(c=0)} = \frac{g_0^2}{(g_0 - \bar{\mu}_*^{(c)})^2} \left\{ \left( \frac{\lambda_1}{\lambda_0^2} - \frac{\mu_* \bar{\mu}_*^{(c)}}{\mu_0^2 g_0^2} \right) \mu_1 \right. \\ \left. + \left\langle \left\langle \frac{1}{1 - \omega^2/\omega'^2} - \frac{\mu_*^{(0)}}{g_0} \right\rangle \ln \frac{\omega^2}{\omega'^2} \frac{S_1(\omega)}{S_0(\omega)} \right\rangle_{\omega, \omega'} \right\}, \quad (10)$$

where

$$\lambda_1 = \lambda(c) - \lambda(c=0), \quad \mu_1 \approx (N_1/N(c=0) - F(\delta k_F)) \mu_0, \\ S_1 = S(c) - S(c=0), \quad N_1 = N(c) - N(c=0) \quad (11)$$

We note that explicit representations for the function  $S_1(\omega)$  in metals with impurity replacement atoms have been obtained by Yu. Kagan and one of the present authors in<sup>[25, 26]</sup>, and in metals with implanted impurity atoms and with vacancies – in<sup>[27]</sup>. The change in the mass  $M$  and in the pseudopotentials  $V$  was taken into account exactly. The change in the force constants  $\gamma$  of the interaction between the atoms was described approximately. For example, in the case of replacement impurity atoms we have

$$\frac{\lambda_1}{c\lambda_0} = \frac{((V_1^2))}{((V_0^2))} - 1 + \left( 2 + \beta \frac{\gamma_1}{\gamma_0} \right) \left( \frac{\gamma_0}{\gamma_1} - 1 \right) \frac{((V_1^2))}{((V_0^2))} + \frac{N_1}{cN(c=0)} \quad (12)$$

where the symbol  $((\dots))$  is defined by the relation

$$((f)) = \int_0^{2k_F} dq \frac{q^2 f}{\omega_q^2}, \quad \beta < 1.$$

(Both here and in future we denote by the indices 0 and 1 quantities which refer respectively to atoms of the basic lattice and to impurity atoms).

The expression for the first term in (10) practically coincides with the expression obtained by Maksimov<sup>[6]</sup>. This term is associated with the impurity renormalization of  $\lambda$  and  $\mu$ . Its value is determined by the values of the parameters  $V_1/V_0$ ,  $N_1/N_0$  and  $\gamma_1/\gamma_0$ . The second term in (10) appeared as a result of taking into account the frequency dependence of  $\Delta$  in the course of finding  $T_C$ . It is a function of the parameters  $V_1/V_0$ ,  $N_1/N_0$ ,  $M_1/M_0$  and  $\gamma_1/\gamma_0$ . In the usual situation the principal term in (10) is the first term. However, if specific impurity modes (quasilocal or local) appear in the lattice and the frequency dependence of  $\Delta$  changes appreciably, then the first and the second terms turn out to be of the same order of magnitude.

### 3. DISCUSSION OF RESULTS

For the sake of definiteness we assume that the impurity atoms are situated at the lattice points of the matrix. We make an analysis of the specific manner in which the quantity  $T_C$  varies. We consider several cases.

$$1) ((V_1^2)) \neq ((V_0^2)), \quad N_1 \neq 0, \quad M_1 = M_0, \quad \gamma_1 = \gamma_0$$

In this case  $\delta T_C$  is determined only by the first term in (10). We note the following. Maximov has noted<sup>[6]</sup> that  $\lambda_1 \sim \Delta\rho(\Theta_D)$  where  $\Delta\rho(\Theta_D)$  is the temperature dependent part of the impurity resistance in the classical temperature limit<sup>[25]</sup>. As direct calculations have shown (cf., for example<sup>[18]</sup>), for a qualitative description of the experimentally observed behavior of  $\Delta\rho(\Theta_D)$  in the nontransition metals in the case of impurity atoms replacing the original ones one can usually neglect in the corresponding equations the term of type F and simultaneously assume that  $V_1\alpha Z_1$  and  $N\alpha(Z/\Omega)^{1/3}$ , where  $Z_1$  is the effective charge of the  $i$ -th ion, while  $Z$  and  $\Omega$  are the "average" charge and volume. The foregoing enables us to assume that in the nontransition metals the sign of  $\lambda_1$ , and consequently also the sign of the correction to  $\delta T_C$  under discussion are determined by the sign of the difference  $Z_1 - Z_0$ .

$$2) ((V_1^2)) = ((V_0^2)), \quad N_1 = 0, \quad M_1 \neq M_0, \quad \gamma_1 = \gamma_0$$

In considering the qualitative aspects of the phenomenon we choose the following model. We assume that the vibrational spectrum of the regular lattice is described by a single Einstein mode. The frequency of this mode  $\omega_0$  is determined by the average phonon frequency  $\omega_C^{(0)}$ . In the presence of "foreign" atoms in accordance with<sup>[25]</sup> we have

$$S(\omega) = N(c) \left[ (1-c) \frac{((V_0^2))}{M_0} \delta(\omega^2 - \omega_0^2) + c \frac{((V_1^2))}{M_1} \delta(\omega^2 - \omega_1^2) \right], \quad (13)$$

where  $\omega_1^2/\omega_0^2 = M_0/M_1$ .

We note that the representation of  $S$  in the form (13) in a situation when the frequencies  $\omega_0$  and  $\omega_1$  differ appreciably is, strictly speaking, valid only in the case of a very small number of impurity atoms<sup>[28]</sup>.

We substitute (13) into (10). We obtain

$$\delta T_C = c \frac{g_0^2}{(g_0 - \bar{\mu}^{(0)})^2} \left[ 1 + \left( \frac{1}{1 - M_0/M_1} - \frac{\mu^{(0)}}{g_0} \right) \ln \frac{M_0}{M_1} \right] \quad (14)$$

(in the general case, if  $M_1 \gg M_0$  or  $M_1 \ll M_0$ , (14) is valid with an accuracy up to numerical coefficients).

The introduction into the lattice of massive impurity

atoms ( $M_1 \gg M_0$ ) produces in an obvious manner a reduction in the magnitude of  $T_C$ . The possible scale of the change is  $\ln(M_0/M_1)$ . Let the lattice contain light impurity atoms ( $M_1 \ll M_0$ ). If one starts with the BCS relation for  $T_C$ :  $T_C \sim \Theta_D e^{-1/\lambda}$ , then since for the isotopic defect  $\lambda(c \neq 0) = \lambda(c = 0)$  and  $\Theta_D \propto M^{-1/2}$ , where  $M = (1 - c)M_0 + cM_1$  we find that the presence of light defects gives rise to an appreciable increase of  $T_C$ . On the other hand, in accordance with (14),  $T_C$ , generally speaking, decreases, although to a very inconsiderable extent:  $\delta T_C \lesssim c$ .

$$3) ((V_1^2)) = ((V_0^2)), \quad N_1 = 0, \quad M_1 = M_0, \quad \gamma_1 \neq \gamma_0$$

Let us make use of the simplest model. We again neglect the dispersion of the phonon frequencies and assume that the correction to the dynamic matrix of the force constants is  $\Delta\Phi_{nn'} = c_n \delta_{nn'} \gamma_1$ . Then  $S(\omega)$  is determined by Eq. (13), where  $\omega_1^2/\omega_0^2 = \gamma_1/\gamma_0$ . If the effective force constants  $\gamma_0$  and  $\gamma_1$  differ considerably, then we have

$$\delta T_C \approx c \left[ \left( 2 \frac{\gamma_0}{\gamma_1} - \beta \frac{\gamma_1}{\gamma_0} \right) \frac{1}{\lambda_0} + \frac{\gamma_0}{\gamma_1} \left( \frac{1}{1 - \gamma_1/\gamma_0} - \frac{\mu^{(0)}}{g_0} \right) \ln \frac{\gamma_1}{\gamma_0} \right]. \quad (15)$$

Consequently, the appearance in the lattice of anomalously weakly bound impurity atoms ( $\gamma_1 \ll \gamma_0$ ) should lead to an appreciable increase in  $T_C$ . In the opposite case, when  $\gamma_1 \gg \gamma_0$ ,  $T_C$  decreases.

We compare the results obtained above with the results of the work of Appel<sup>[19]</sup>. Above we have obtained an expression for  $\delta T_C$  for an isotropic irregular superconductor with intermediate coupling using a description of the characteristic function of the electron-phonon interaction  $\alpha^2$  and of the function describing the density of the phonon states  $\psi(S = \alpha^2\psi)$  without introducing a model. Appel solved equations of the Éliashberg type only for a problem involving a model. It was assumed that the function  $\psi$  for a regular crystal is a Lorentz function. The correction to  $\psi$  proportional to  $c$  was chosen in the form of a  $\delta$ -function. The principal conclusions in<sup>[19]</sup> were made on the basis of numerical calculations. It is essential that in that case  $\alpha^2$  was taken to be arbitrary. But in actual fact this is not so (cf., for example, (13)). For the aforementioned reason Appel in<sup>[19]</sup> obtained an incorrect result for the light isotopic defect and in fact an incorrect picture is presented when  $\gamma_0$  and  $\gamma_1$  differ appreciably.

### 4. COMPARISON WITH EXPERIMENT

There are many experimental papers in which the effect of nonmagnetic impurity atoms on the magnitude of  $T_C$  has been analyzed. We note, first of all, a detailed study<sup>[29]</sup> of the variation of  $T_C$  with changing content of the impurity atoms ( $c \approx 0.01 - 0.3$  atomic %) in displacement solutions of Al with Ag, Mg, Zn, Ge, Sn and of In with Cd, Ga, Tl, Sn, Pb, Bi, and also an investigation<sup>[30]</sup> of weak solutions of Sn. A direct comparison with the results of Lynton, Serin and Chanin is difficult for a number of reasons. However, rough estimates according to formula (12) lead, generally speaking, to a correct description of the observed sign for relatively large values of  $c$  ( $\delta T_C > 0$  for  $\delta Z > 0$  and conversely).

In recent years a series of papers has been published in which data are given on the measurement of low temperature specific heat. It is essential that the experiments were carried out using samples with a relatively large content of impurity atoms, i.e., of the order of several atomic percent over a sufficiently wide temperature range (1-10 K). This enabled one to obtain together

with  $T_C(c)$  simultaneously  $N(c)$  and  $\Theta_D(c)$  and enables one in principle to separate out the contribution to  $T_C$  due to the impurity isotropization of the gap. In particular, impurity superconductors were investigated characterized by high values of  $T_C$ : InSn<sup>[31]</sup>, PbIn<sup>[32]</sup>, VTa<sup>[15]</sup>, VW<sup>[33]</sup>, VHF<sup>[34]</sup>, VTi<sup>[35]</sup>, VNb, NbV, TaV<sup>[36]</sup>, TaNb<sup>[37]</sup>, NbMo<sup>[38]</sup>, TaRe<sup>[39]</sup>, and also ZrHf<sup>[40]</sup> and MoRe<sup>[41]</sup>.

Of course, a comparison of the theory presented above with data for a superconductor with strong coupling (Pb) and for superconductors numbered among the transition metals is, strictly speaking, incorrect. Nevertheless, taking into account the closeness of Eq. (6) to McMillan's empirical formula it is natural to assume that on the whole the above scheme is also applicable here, at least if one restricts oneself to the qualitative aspect of the phenomenon. In particular this applies to the part  $\delta T_C$  related to the perturbation of the phonon spectrum due to the presence of impurities and to the renormalization of  $\lambda$  because of this perturbation.

In order to establish the specific properties and the magnitude of the above mentioned corrections to  $\delta T_C$  we have carried out, for the alloys investigated in<sup>[31-41]</sup>, calculations on the basis of relations (10), (12), and (13). The values of  $\lambda_0$  were taken from McMillan's paper<sup>[24]</sup>. Since for Pb his data for  $\lambda_0$  differ appreciably from the data of Kakitani<sup>[22]</sup>,  $\lambda_0$  was taken to be equal to 1.12 and 1.55. The factors  $\mu$  and  $\mu_*^{(0)}$  were taken from<sup>[21, 24]</sup> (for Zr we have taken  $\mu_*^{(0)} = 0.11$  and 0.17). The value of  $N_i$  was taken from experimental results. Since the Debye temperatures of the solution and of the matrix are known one can make an estimate of  $\gamma_1/\gamma_0$  by utilizing the formula<sup>[26]</sup>

$$\frac{\gamma_1}{\gamma_0} = 1 - \frac{D}{1 + \alpha D}, \quad D = \frac{\Theta_D(c) - \Theta_D(c=0)}{c\Theta_D(c=0)} + \frac{1}{2} \left( \frac{M_i}{M_0} - 1 \right)$$

where  $\alpha$  is a constant (for example, for a lattice of the body centered cubic type  $\alpha = 0.16$ ). For alloys based on vanadium the factor  $((V_i^2)/(V_0^2))$  was determined on the basis of the data of<sup>[24]</sup> and on data on residual resistance  $\rho_0$ , in the remaining cases this factor was taken to be proportional to  $(Z_i/Z_0)^2$ , where  $Z$  is the charge of the ion (in fact this corresponds to the choice of  $V$  in the form of a screened Coulomb potential).

A significant role in (16) is also played by another term  $\delta T^{(A)}$  which takes into account the effect on  $T_C$  of the impurity isotropization of the energy gap. If we take into account only the isotropization of the gap then using the data on the measure of the mean square anisotropy of the gap<sup>[4]</sup> we found (cf.,<sup>[2]</sup>) that for alloys based on V, Ta and Pb the value of  $\delta T^{(A)}$  is approximately by an order of magnitude smaller than the values of  $\delta T_C$  observed experimentally. Moreover, for the systems under consideration<sup>[31-41]</sup> the initial samples of V, Nb, Ta, Mo and Zr are characterized by the ratio  $\rho(\Theta_D)/\rho_0 \sim 10-20$ , i.e., they are already quite impure. Taking the foregoing into account we have in what follows neglected the contribution to  $\delta T_C$  due to the isotropization of the energy gap of the superconductor.

The values of  $\gamma_1/\gamma_0$ ,  $M_0\gamma_1/M_1\gamma_0$ ,  $\delta T_C$  and  $\delta T_C(\mu=0)$  are given in the table.

Firstly, examining the data in the table which determine the relationship between the effective frequencies  $\omega_0$  and  $\omega_1$  one can conclude that in the majority of alloys under consideration the phonon spectrum is sharply deformed. We note the following circumstance. In alloys of nontransition metals (InSn, PbIn) the difference be-

tween  $\gamma_1$  and  $\gamma_0$  usually does not exceed 20-30%. But in alloys of transition metals, as can be seen from the table,  $\gamma_1$  and  $\gamma_0$  can differ by more than 100%.

Secondly, as can be seen from the table, for all the alloys one observes agreement with respect to sign and order of magnitude of the calculated and the experimental values of  $\delta T_C$ . The agreement is better for the alloys InSn and PbIn when the concept of an effective screened Coulomb potential is, generally speaking, justified, and also in the case of alloys of transition elements for which the values of  $\rho_0$  are known.

Thirdly, we examine directly how  $\delta T_C$  varies when in the superconductors investigated in<sup>[31-41]</sup> modes exist with quasilocal and local frequencies. Suppose that a quasilocal mode exists in a superconductor. Then, if the impurities are close to isotopic (VTa and VNb), the modification of the phonon spectrum leads to a decrease in  $T_C$ . For VTa the corresponding correction to  $\delta T_C$  is of the order of 30% and for VNb it is  $\sim 10\%$ . For the systems VHF, VTi, MoRe and VW with an anomalously large difference between  $\gamma_0$  and  $\gamma_1$  the variation of  $\delta T_C$  due to the deformation of the phonon spectrum has a more pronounced character, with the corrections to  $\delta T_C$  due to the deformation of the phonon and the electron spectra being of the same order of magnitude.

Suppose that a local mode is present in a superconductor. For an isotopic impurity (PbIn) the correction to  $\delta T_C$  due to the deformation of the phonon spectrum is positive and amounts to 30%. In the case of NbV, where  $\gamma_1/\gamma_0 > 1$ , the situation is completely determined by the deformation of the phonon spectrum.

We note that within the framework of the theory developed above it turns out to be possible to understand the nature of the variation of  $\delta T_C$  in weak solutions VTa and VW. Here the picture is as follows: the relative change in the density of electron states in VTa is by a factor of two greater than in the system VW, but the relative change in  $\delta T_C$  is approximately by a factor of 1.2 larger in VW. It turns out to be possible to explain the observed behavior in these alloys by the fact that in VTa the force constants vary but little, while in VW their strength is doubled.

Thus, the presence in superconductors of isotopic impurities (both of heavy and light masses) and the deformation of the phonon spectrum produced by them, generally speaking, have a small effect on the magnitude of the change in  $T_C$ . Nevertheless, even for a qualitative description of the variation of  $\delta T_C$  it is necessary to take

Composition	c, %	$\frac{\gamma_1}{\gamma_0}$	$\frac{\gamma_1 M_0}{\gamma_0 M_1}$	$\delta T_{exp}$	$\delta T_{calc}$	
					$\mu \neq 0$	$\mu = 0$
VTa <sup>[15]</sup>	3.55	1.3	0.35	-0.13	-0.14	-0.17
VW <sup>[33]</sup>	5.2	2	0.55	-0.22	-0.16	-0.29
VHF <sup>[34]</sup>	0.9	0.6	0.17	-0.01	-0.002	0.005
VNb <sup>[36]</sup>	15	1.2	0.70	-0.17	-0.28	-0.29
VTi <sup>[35]</sup>	5	0.4	0.42	-0.31	-0.48	-0.49
NbV <sup>[38]</sup>	10	1.54	2.80	-0.16	-0.09	-0.05
NbMo <sup>[38]</sup>	10	0.98	1	-0.37	-0.28	-0.51
TaV <sup>[36]</sup>	10	0.62	2.34	-0.17	-0.05	-0.02
TaNb <sup>[37]</sup>	3.7	0.97	1.89	-0.02	-0.03	+0.03
TaRe <sup>[39]</sup>	2.5	3.48	3.39	-0.20	-0.13	-0.14
MoRe <sup>[41]</sup>	5	0.61	0.32	+0.50	+0.67	0.61
ZrHf <sup>[40]</sup>	9.5	1.75	0.89	-0.29	-0.16	-0.31
InSn <sup>[31]</sup>	5.03	1.02	0.98	0.13	0.11	0.10
PbIn <sup>[32]</sup>	10	0.94	1.71	-0.02	-0.03	-0.025

\*For the calculation the value  $\mu_*^{(0)} = 0.17$  was utilized.

\*\*For the calculation it was assumed that  $\lambda = 1.55$ .

into account the difference in the masses of the atoms.

If in the impurity system the effective force constants  $\gamma_0$  and  $\gamma_1$  differ strongly, then the quasilocal and the local modes arising because of this change in the force constants have a large effect on  $T_C$ . The renormalization of  $\lambda$  due to the interaction of an electron with such a type of quasilocal modes leads to an appreciable increase in  $T_C$ , while an interaction with local modes leads to a decrease in  $T_C$ .

In the weak solutions based on transition metals discussed in Sec. 4 the value of  $\delta T_C$  is determined to an equal extent by the renormalization of the density of electron states  $N$  and of the parameter  $\lambda$  of the electron-phonon interaction (due to the variation of the force constants). In isoelectronic solutions the change in  $T_C$  directly due to the deformation of the phonon spectrum turns out to be essential.

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## APPENDIX

In the papers of Markowitz and Kadanoff<sup>[2]</sup> and Maximov<sup>[6]</sup>, where the variation of  $T_C$  was investigated in crystals with impurity atoms, in the derivation of equations for  $Z$  and  $\Delta$  electron and phonon Green's functions were used averaged over the impurity configurations being formed. Evidently such an investigation is an approximate one. Below we show how it is possible to obtain the desired equations for  $Z$  and  $\Delta$  in a more rigorous manner on the assumption that the pseudopotentials  $V_1$  and  $V_0$  do not differ appreciably.

We restrict ourselves to the situation when the superconducting crystal contains one impurity atom. The thermodynamic electron Green's function constructed by utilizing two-component spinors<sup>[42]</sup> satisfies the equation

$$G_{kk'} = \bar{G}_{kk'} + \bar{G}_{kk} \Sigma_{k_1 k_2}^L G_{k_1 k_2 k'}, \quad (A.1)$$

where

$$\bar{G}_{kk'}^{(0)} = \frac{1}{V_1(k_1, k_2)} \frac{D_{nm}}{V_m(k_2, k)} + \frac{G_{kk'}}{V_m(k_1, k)} - \Sigma_{kk}^{(0)} \delta_{kk'} \quad (A.2)$$

The function  $\bar{G}$  is a solution of the equation

$$\bar{G}_{kk'} = G_{0, kk} \delta_{kk'} + G_{0, kk} \Sigma_{k_1 k_2}'' G_{k_1 k_2 k'}. \quad (A.3)$$

The polarization operator associated with elastic scattering of an electron by static impurities has the form

$$\Sigma_{kk}'' = \frac{1}{\Delta V_{kk'}} + \frac{1}{\Delta V_{kk_1}} G_{0, k_1 k_1} + \frac{1}{\Delta V_{k_1 k'}} + \dots \quad (A.4)$$

$D_{nm}$  denotes the phonon Green's function of an irregular crystal in the coordinate representation;  $G_0$  and  $\Sigma^{(0)}$  are the electron Green's function and the polarization operator for a regular superconductor;  $\Delta V = V_1 - V_0$ .

We assume that  $\Delta V/\epsilon_F \ll 1$ . Then in the expression for  $\Sigma$  (cf. below) we can neglect terms of the order of  $\Delta V^2/\epsilon_F$  and  $V_n V_m \Delta V/\epsilon_F$  compared with terms proportional respectively to  $\Delta V^2$  and  $V_n V_m$ . We also take into account that  $\Delta V_{kk} = 0$  due to the condition of electric neutrality. As a result we have for the function diagonal with respect to the quasimomentum indices of  $G$

$$G_{kk} = G_{kk}^{(0)} + G_{kk}^{(0)} \Sigma_{kk} G_{kk}, \quad (A.5)$$

where  $G^{(0)}$  is the Green's function for a free electron,

$$\Sigma_{kk} = \frac{1}{\Delta V_{kk_1}} \frac{G_{k_1 k_1}}{V_1(k_1, k_1)} + \frac{D_{nm}}{V_n(k_1, k_1)} \frac{G_{k_1 k_1}}{V_m(k_1, k)} + \frac{G_{kk'}}{V_m(k_1, k')} \quad (A.6)$$

Utilizing relations (A.5) and (A.6) one can obtain in the usual manner equations of the Eliashberg type which agree in their form with the equations appearing in<sup>[6]</sup>.

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