Indirect Interaction Involving Impurity States in Superconductors*

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A new theoretical mechanism of the observed increase in transition temperature T_c in some superconductors containing magnetic-element inpurities in low concentration (e.g. Fe in Ti etc.) has been suggested. In the concentration region of interest, these systems do not show the existence of any net localized magnetic moment. In the proposed mechanism, we have invoked indirect Coulomb and exchange-type interactions involving BCS pairs and impurity electron pairs in the singlet states interacting through empty impurity states. The resulting interaction between BCS pairs is attractive. The theoretical expression for T_c, inclusive of the present (attractive) and earlier (repulsive) interactions, gives the right dependence as observed experimentally. The estimated strength of the interaction parameter J turns out to be of the order of 0.5 eV. Such mechanisms seem to be important for systems containing impurities which provide empty orbital states as visualized above.

I. INTRODUCTION

IN recent years there has been a considerable amount of experimental and theoretical work on the variation of the transition temperature T_c of superconductors with the concentration of magnetic-element impurities.[1] Matthias and his co-workers[2] have reported that the magnetic impurities usually lower the transition temperature in that the conduction-electron–magnetic-ion interaction in general prevents the antiparallel spin correlation in the superconducting state. However, in certain systems namely solid solutions of Ti with Fe, Co, Cr, Mn, Ru, etc. and Zr with Co, Rh, Ir, etc., where no net localized magnetic moment has been observed experimentally, T_c is increased in the low-concentration regions.[3,4] Further, Matthias *et al.*[3] have clearly demonstrated experimentally that the observed increase in T_c in the systems noted above is not due to increase in the number of valency electrons only. Thus it appears that the conduction-electron–impurity-ion interaction may be responsible for the observed increase in T_c.

Earlier theoretical attempts[5,6] although very successful in explaining the decrease in T_c and other superconducting properties have not been able to provide a satisfactory explanation for the observed increase in T_c. Other notable contributions are those of Akhiezer and Akhiezer,[7] and Vonsovskii and Svirskii.[8] However, the latter authors differ from the former ones in that they consider the localized impurity-electron spins to be uncoupled rather than ferro- or antiferro-magnetically coupled as considered by the Akhiezers.[7] Furthermore, Vonsovskii and Svirskii have considered a generalized exchange model by taking into account the changes of the multiplicity of the impurity d or f shells induced by the conduction electrons and they obtained an attractive interaction between the triplet Cooper pairs only. However, there is no experimental support for the existence of triplet Cooper pairs in superconductors.[9] So far, to the authors' knowledge, no theory has been advanced to explain the increase in T_c.

In this paper, as an attempt to explain the increase of T_c, we suggest an indirect mechanism which takes into account the fact that in the systems of present interest, there exists no net localized magnetic moment. The interaction is envisaged through the Coulomb and exchange type interactions between the conduction electrons and impurity electrons via unoccupired localized impurity states. In particular, we consider the interactions which also take into account the changes in the multiplicity of the impurity d shell induced by the conduction electrons because of the exchange type interaction.

In Sec. II, we consider the Hamiltonian containing the usual one-electron terms and the appropriate two-particle conduction-electron–impurity-electron interaction terms. The resulting interaction between the Bardeen, Cooper and Schrieffer (BCS)[10] pairs over and above the usual BCS-type interaction[10] is obtained by making use of a suitable canonical transformation which eliminates two-particle conduction-electron–impurity-electron interaction terms in the first order. In Sec. III, following the BCS[10] formalism, an explicit expression for the increase in T_c as a power series in impurity concentration is derived arising from the interaction envisaged in Sec. II. The final expression for

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the change in transition temperature as a function of impurity concentration incorporates two types of possible interactions, namely, the indirect interaction of Sec. II and the purely orbital scattering of conduction electrons by impurity potentials as done by Suhl and Matthias.[5] In Sec. III, the above results are applied to a typical system (viz. Fe in Ti) and a fairly good agreement is obtained with the experimentally observed dependence of T_c on impurity concentration. Finally, the interaction mechanism considered in Sec. II is discussed in relation to similar mechanisms already shown to be important in case of polarization of the d band in transition metals, of the f band in metals close to or in the rare-earth series, of spin waves etc.[11]

II. INTERACTION HAMILTONIAN

We consider the superconductors containing the magnetic-element impurities as a system of conduction electrons interacting with the localized impurity electrons via generalized Coulomb and exchange type interactions. The impurities, for simplicity, are assumed to consist of two localized electrons in the singlet state. In the present section, the effect of their contributions to the increase in the density of conduction electrons and the change in the periodic crystal field is not considered. Thus, the Hamiltonian for the system can be written in the occupation-number representation as

$$H=H_0+H_{\rm int}, \tag{2.1}$$

where

$$H_0=\sum_{\mathbf{k}\sigma}\epsilon_{\mathbf{k}\sigma}C_{\mathbf{k}\sigma}^{\dagger}C_{\mathbf{k}\sigma}+\sum_{li\sigma}E_{li\sigma}C_{li\sigma}^{\dagger}C_{li\sigma}, \tag{2.2}$$

$$H_{\rm int}=N^{-1}\sum_{\substack{\mathbf{k}\mathbf{k}'\\ li\lambda_i\\ \sigma\sigma'}}[\{\langle\lambda_i k'|V_{12}|l_i k\rangle C_{\lambda_i\sigma'}^{\dagger}C_{li\sigma'}C_{\mathbf{k}'\sigma}^{\dagger}C_{k\sigma}+\text{c.c.}\}-\{\langle\lambda_i k'|V_{12}|kl_i\rangle C_{\lambda_i\sigma}^{\dagger}C_{li\sigma'}C_{\mathbf{k}'\sigma'}^{\dagger}C_{\mathbf{k}\sigma}+\text{c.c.}\}], \tag{2.3}$$

and

$$V_{12}\equiv\sum_{\mathbf{m},\mathbf{n}}(e^2/r_{\mathbf{mn}}), \tag{2.4}$$

where $r_{\mathbf{mn}}=(|\mathbf{r}_{\mathbf{m}}-\mathbf{r}_{\mathbf{n}}|)$ with $\mathbf{r}_{\mathbf{m}}$, $\mathbf{r}_{\mathbf{n}}$ standing for the positions of the impurity and conduction electrons, respectively. In Eq. (2.1), H_0 describes the Hamiltonian of the unperturbed system containing the noninteraction Bloch electrons in the conduction band with energy $\epsilon_{\mathbf{k}\sigma}$ in the state $|\mathbf{k}\sigma\rangle$ and the impurity electrons at the site i with energy E_{li} in the state $|l_{i\sigma}\rangle$. $C_{\alpha}^{\dagger}$, C_{α} are the creation and annihilation operators for the electrons in the state $|\alpha\rangle$. The first and second terms in Eq. (2.3), respectively, represent the Coulomb and exchange type interactions. In the Coulomb interaction the Bloch electron gets scattered from the state $|\mathbf{k}\sigma\rangle$ to $|\mathbf{k}'\sigma\rangle$. On the other hand in the exchange process it is scattered to $|\mathbf{k}'\sigma'\rangle$ because of the two-body interaction V_{12}. Simultaneously, for the Coulomb or exchange processes the impurity electron makes a transition from the ground state $|l_i\sigma\rangle$ to excited state $|\lambda_i\sigma\rangle$ or $|\lambda_i\sigma'\rangle$, respectively. Summing over the spin states σ, σ'; $H_{\rm int}$ can be written as

$$\begin{aligned}H_{\rm int}=N^{-1}\sum_{\mathbf{k},\mathbf{k}',\lambda_i,l_i}[\{&U_{li\mathbf{k}}{}^{\lambda_i\mathbf{k}'}(C_{\lambda i\uparrow}^{\dagger}C_{li\uparrow}C_{\mathbf{k}'\uparrow}^{\dagger}C_{\mathbf{k}\uparrow}+C_{\lambda i\downarrow}^{\dagger}C_{li\downarrow}C_{\mathbf{k}'\downarrow}^{\dagger}C_{\mathbf{k}\downarrow}+C_{\lambda i\downarrow}^{\dagger}C_{li\downarrow}C_{\mathbf{k}'\uparrow}^{\dagger}C_{\mathbf{k}\uparrow}+C_{\lambda i\uparrow}^{\dagger}C_{li\uparrow}C_{\mathbf{k}'\downarrow}^{\dagger}C_{\mathbf{k}\downarrow})\\ &-\mathrm{V}_{kli}{}^{\lambda_i\mathbf{k}'}(C_{\lambda i\uparrow}^{\dagger}C_{li\uparrow}C_{\mathbf{k}'\uparrow}^{\dagger}C_{\mathbf{k}\uparrow}+C_{\lambda i\downarrow}^{\dagger}C_{li\downarrow}C_{\mathbf{k}'\downarrow}^{\dagger}C_{\mathbf{k}\downarrow}+C_{\lambda i\uparrow}^{\dagger}C_{li\downarrow}C_{\mathbf{k}'\downarrow}^{\dagger}C_{\mathbf{k}\uparrow}+C_{\lambda i\downarrow}^{\dagger}C_{li\uparrow}C_{\mathbf{k}'\uparrow}^{\dagger}C_{\mathbf{k}\downarrow})\}+\text{c.c.}],\end{aligned} \tag{2.5}$$

where

$$U_{li\mathbf{k}}{}^{\lambda_i\mathbf{k}'}\equiv\langle\lambda_i\mathbf{k}'|V_{12}|l_i\mathbf{k}\rangle, \tag{2.6}$$

and

$$V_{kli}{}^{\lambda_i\mathbf{k}'}\equiv\langle\lambda_i\mathbf{k}'|V_{12}|\mathbf{k}l_i\rangle. \tag{2.7}$$

Let us consider the following unitary transformation which eliminates the $\mathrm{H}_{\rm int}$ term in Eq. (2.1) in the first order and yields in the second order the effective electron-electron coupling for conduction electrons because of the virtual excitation and de-excitation of the impurity electrons:

$$\begin{aligned}H_T&=e^{-iS}He^{iS}\\ &=H+i[H,S]+\tfrac{1}{2}i^2[[H,S],S]+\cdots.\end{aligned} \tag{2.8}$$

The matrix S in the above expression is to be determined from the following condition:

$$H_{\rm int}+i[H_0,S]=0. \tag{2.9}$$

[11] S. V. Vonsovskii and Yu. A. Izyumov, Usp. Fiz. Nauk. **78**, 3 (1962) [English transl.: Soviet Phys.—Uspekhi **5**, 723 (1963)].

The Eq. (2.9) then gives us the expression for S as

$$S=\sum_{\mathbf{k}\mathbf{k}'li\lambda_i}\Bigg[\Bigg\{\frac{i(U_{li\mathbf{k}}{}^{\lambda_i\mathbf{k}'}-V_{\mathbf{k}li}{}^{\lambda_i\mathbf{k}'})}{\epsilon_{\mathbf{k}'}-\epsilon_{\mathbf{k}}+\Delta_{\lambda_i li}{}^{\mathrm{Cou}}}(C_{\lambda_i\uparrow}{}^{\dagger}C_{li\uparrow}C_{\mathbf{k}'\uparrow}{}^{\dagger}C_{\mathbf{k}\uparrow}+C_{\lambda_i\downarrow}{}^{\dagger}C_{li\downarrow}C_{\mathbf{k}'\downarrow}{}^{\dagger}C_{\mathbf{k}\downarrow})$$
$$+\frac{iU_{li\mathbf{k}}{}^{\lambda_i\mathbf{k}'}}{\epsilon_{\mathbf{k}'}-\epsilon_{\mathbf{k}}+\Delta_{\lambda_i li}{}^{\mathrm{Cou}}}(C_{\lambda_i\downarrow}{}^{\dagger}C_{li\downarrow}C_{\mathbf{k}'\uparrow}{}^{\dagger}C_{\mathbf{k}\uparrow}+C_{\lambda_i\uparrow}{}^{\dagger}C_{li\uparrow}C_{\mathbf{k}'\downarrow}{}^{\dagger}C_{\mathbf{k}\downarrow})$$
$$-\frac{iV_{\mathbf{k}li}{}^{\lambda_i\mathbf{k}'}}{\epsilon_{\mathbf{k}'}-\epsilon_{\mathbf{k}}+\Delta_{\lambda_i li}{}^{\mathrm{ex}}}(C_{\lambda_i\uparrow}{}^{\dagger}C_{li\downarrow}C_{\mathbf{k}'\downarrow}{}^{\dagger}C_{\mathbf{k}\uparrow}+C_{\lambda_i\downarrow}{}^{\dagger}C_{li\uparrow}C_{\mathbf{k}'\uparrow}{}^{\dagger}C_{\mathbf{k}\downarrow})\Bigg\}+\mathrm{c.c.}\Bigg]. \quad (2.10)$$

The symbols $\Delta_{\lambda_i li}{}^{\mathrm{Cou}}$ and $\Delta_{\lambda_i li}{}^{\mathrm{ex}}$ in Eq. (2.10) denote the excitation energies of the impurity electrons where the superscripts "ex" and "Cou" designate the excitation in which there is spin-flip or no spin-flip, respectively of the impurity electrons. Substituting Eq. (2.10) in (2.8), one obtains the transformed Hamiltonian as,

$$H_T=H_0+H_{\mathrm{int}}{}^{T}$$
$$=H_0+2\xi\sum_{kk'l\lambda}[\{|U_l{}^{\lambda}(|\mathbf{k}-\mathbf{k}'|)-V_l{}^{\lambda}(|\mathbf{k}-\mathbf{k}'|)|^2+|U_l{}^{\lambda}(|\mathbf{k}-\mathbf{k}'|)|^2-|V_l{}^{\lambda}(|k-k'|)|^2\}$$
$$\times\Delta_{\lambda l}{}^{\mathrm{Cou}}/((\epsilon_{\mathbf{k}'}-\epsilon_{\mathbf{k}})^2-(\Delta_{\lambda l}{}^{\mathrm{Cou}})^2)-|V_l{}^{\lambda}(|\mathbf{k}-\mathbf{k}'|)|^2\cdot\Delta_{\lambda l}{}^{\mathrm{ex}}/((\epsilon_{\mathbf{k}'}-\epsilon_{\mathbf{k}})^2-(\Delta_{\lambda l}{}^{\mathrm{ex}})^2)]C_{k'\uparrow}{}^{\dagger}C_{-k'\downarrow}{}^{\dagger}C_{-k\downarrow}C_{k\uparrow}, \quad (2.11)$$

where $\xi=N_I/N$, the impurity concentration. In writing Eq. (2.11) we have considered only those scattering processes which affect the correlation between the BCS pairs without taking cognizance of the renormalization of $\epsilon_{\mathbf{k}}$ and E_l owing to these and other scattering processes. Further, as we are interested in very low-impurity-concentration regions, the impurities can be assumed to be randomly distributed and therefore only the average effect of impurities is considered. Abrikosov and Gorkov[6] have already shown that such averaging amounts to taking into account only those processes in which the conduction electrons are excited and de-excited by the localized electrons at the same impurity site. Thus, we have assumed that all the impurity-dependent parameters, namely, $\Delta_{\lambda_i li}{}^{\mathrm{Cou,\ ex}}$, $U_{li\mathbf{k}}{}^{\lambda_i\mathbf{k}'}$ and $V_{\mathbf{k}l_i}{}^{\lambda_i\mathbf{k}'}$ can be taken as the same for all the impurity sites and accordingly the site index i is dropped in Eq. (2.11). Furthermore, we have also made use of the following approximations[8]:

$$U_{l\mathbf{k}}{}^{\lambda\mathbf{k}'}\approx U_l{}^{\lambda}(|\mathbf{k}-\mathbf{k}'|), \quad (2.12)$$
$$V_{\mathbf{k}l}{}^{\lambda\mathbf{k}'}\approx V_l{}^{\lambda}(|\mathbf{k}-\mathbf{k}'|). \quad (2.13)$$

Let us examine Eq. (2.11) in some detail. First, only those conduction-electron transitions are important for superconductivity which fulfil the condition[10] $|\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}|<\hbar\omega_D\ll\Delta_{\lambda l}{}^{\mathrm{Cou}}$, $\Delta_{\lambda l}{}^{\mathrm{ex}}$ where ω_D is the Debye frequency. Second, it is assumed that the parameters $U_l{}^{\lambda}(|\mathbf{k}-\mathbf{k}'|)$ and $V_l{}^{\lambda}(|\mathbf{k}-\mathbf{k}'|)$ can be replaced by constant-average matrix elements:

$$V\equiv\langle V_l{}^{\lambda}(|\mathbf{k}-\mathbf{k}'|)\rangle_{\mathrm{av}}, \quad (2.14)$$
$$U\equiv\langle U_l{}^{\lambda}(|\mathbf{k}-\mathbf{k}'|)\rangle_{\mathrm{av}}. \quad (2.15)$$

Third, it is obvious from Eqs. (2.6) and (2.7) that $U_{l\mathbf{k}}{}^{\lambda\mathbf{k}'}\gg V_{\mathbf{k}l}{}^{\lambda\mathbf{k}'}$ as the former depends on the overlap of two localized orbitals $|\lambda\rangle$ and $|l\rangle$ at the same impurity site and the overlap of two Bloch states $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle$, whereas the latter depends on the overlap of states $|\lambda\rangle$ and $|\mathbf{k}\rangle$, and $|\mathbf{k}'\rangle$ and $|l\rangle$. Finally, as $\Delta_{\lambda l}{}^{\mathrm{ex}}$ and $\Delta_{\lambda l}{}^{\mathrm{Cou}}$ differ only by the intra-atomic exchange integral between the localized orbitals $|\lambda\rangle$ and $|l\rangle$ which is small compared to the difference in the orbital energy $(E_\lambda-E_l)$, we can take $\Delta_{\lambda l}{}^{\mathrm{Cou}}\sim\Delta_{\lambda l}{}^{\mathrm{ex}}\approx\Delta_{\lambda l}$. Under these approximations Eq. (2.11) reduces to the following simple form,

$$H_{\mathrm{int}}{}^{T}=-\xi W\sum_{\mathbf{k}\mathbf{k}'}C_{k'\uparrow}{}^{\dagger}C_{-k'\downarrow}{}^{\dagger}C_{-k\downarrow}C_{k\uparrow}, \quad (2.16)$$

where

$$W=(2/\Delta_{\lambda l})(|U-V|^2+|U|^2-2|V|^2)$$
$$\equiv 2|J|^2/\Delta_{\lambda l},\ \text{a positive-definite quantity}. \quad (2.17)$$

In writing Eq. (2.16), for simplicity, we have considered only the lowest non-degenerate excited localized orbital, as its contribution will be the most important compared to the other higher states. It is evident from Eq. (2.17) that the indirect interaction involving localized impurity states envisaged here gives an additional attractive interaction between the BCS pairs. In the following section, an expression for the resulting change in T_c due to the types of interactions discussed in Sec. I is obtained and the results are compared with the experimental data for some specific systems.

III. CALCULATION OF T_c AND COMPARISON WITH EXPERIMENT

In what follows, we derive the expression for the change in T_c in solid solutions under consideration owing to the additional attractive interaction between BCS pairs. This is over and above the usual phonon-induced pair interaction considered by BCS. The method of derivation is parallel to theirs. Thus we take the

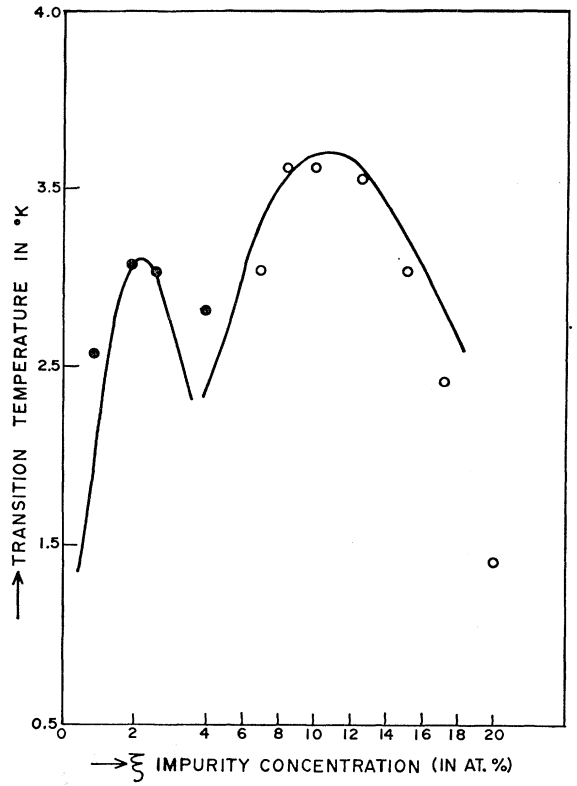

FIG. 1. Superconducting transition temperature of Fe solid solution in Ti. The solid curve is a plot of theoretical values. ●, ○ respectively represent experimental points for α and β phases of Ti-Fe solid solutions.

expression for T_c as

$$kT_c=1.14\hbar\omega\exp[-1/N(0)V_{\text{eff}}], \tag{3.1}$$

where V_{eff} in the present case is the sum of the strengths of the phonon-induced attractive interaction V_{Ph} and the impurity induced indirect interaction considered here, namely,

$$V_{\text{eff}}\equiv V_{\text{Ph}}+\xi W. \tag{3.2}$$

As we are interested in the solid solutions of magnetic element impurities in the low-concentration region only, Eq. (3.1) can be expanded in powers of ξ. Thus, keeping up to second-order term in ξ, Eq. (3.1) becomes

$$\Delta T_c^{(\text{I})}=a_{\text{I}}\xi+b_{\text{I}}\xi^2, \tag{3.3}$$

where

$$\Delta T_c^{(\text{I})}\equiv T_c-T_c^{(0)}, \tag{3.4}$$

T_c and $T_c^{(0)}$ being the transition temperature of the impure and pure systems, respectively. The parameters a_{I} and b_{I} in (3.3) are defined as follows:

$$a_{\text{I}}=-\left(\frac{W}{V_{\text{Ph}}}\right)\ln\left(\frac{kT_c^{(0)}}{1.14\langle\hbar\omega\rangle}\right), \tag{3.5}$$

$$b_{\text{I}}=\left(\frac{W}{V_{\text{Ph}}}\right)^2\ln\left(\frac{kT_c^{(0)}}{1.14\langle\hbar\omega\rangle}\right)\left[\frac{1}{2}+\ln\left(\frac{kT_c^{(0)}}{1.14\langle\hbar\omega\rangle}\right)\right]. \tag{3.6}$$

It can be easily seen that the parameters a_{I} and b_{I} are positive-definite quantities as $|\ln(kT_c^{(0)}/1.14\langle\hbar\omega\rangle)|>1$ for all superconductors. Similarly, the change in the transition temperature $\Delta T_c^{(\text{II})}$, owing to the scattering processes by impurity potential investigated by Suhl and Matthias as a function of nonmagnetic impurity concentration, can be obtained by considering the power-series expansion of Eq. (38) of their paper.[5] The resulting equation is given as

$$\Delta T_c^{(\text{II})}/T_c^{(0)}=-a_{\text{II}}\xi-b_{\text{II}}\xi^2, \tag{3.7}$$

where the parameters a_{II} and b_{II} in the present case are expressed as

$$a_{\text{II}}=-\frac{4w^2N(0)}{\langle\hbar\omega\rangle}\ln\left(\frac{\epsilon_0(\text{Pure})}{\langle\hbar\omega\rangle}\right), \tag{3.8}$$

$$b_{\text{II}}=-\frac{8w^4[N(0)]^2}{[\langle\hbar\omega\rangle]^2}\ln\left(\frac{\epsilon_0(\text{Pure})}{\langle\hbar\omega\rangle}\right)\left[1+\ln\left(\frac{\epsilon_0(\text{Pure})}{\langle\hbar\omega\rangle}\right)\right]. \tag{3.9}$$

In the above ϵ_0 (Pure) is the energy-gap parameter[10] for the pure system and w is the interaction parameter of Eq. (30) of Suhl and Matthias.

The net change in the transition temperature (ΔT_c), after taking into account both types of scattering processes discussed above, can be obtained by combining Eqs. (3.3) and (3.7). Thus, one obtains for ΔT_c,

$$\begin{aligned}\Delta T_c/T_c^{(0)}&=(\Delta T_c^{(\text{I})}+\Delta T_c^{(\text{II})})/T_c^{(0)}\\&=(a_{\text{I}}-a_{\text{II}})\xi+(b_{\text{I}}-b_{\text{II}})\xi^2\\&\equiv A\xi+B\xi^2,\end{aligned} \tag{3.10}$$

Let us now consider the experimental results for the systems noted earlier in Sec. I. All the systems show essentially the same behavior,[12] i.e., up to 2 to 3 at. % addition of magnetic element impurities one finds a sharp increase in T_c. T_c however decreases with the further addition of impurities and increases again after passing through a minimum value. It has been clearly demonstrated by Matthias *et al.*[3] that the latter increase occurs in a different phase of the solid solution than the former one; specifically the host matrix undergoes a phase transition $\alpha(\text{hcp})\rightarrow\beta(\text{bcc})$. Thus, we assume in the following numerical estimate that impurity-dependent parameters A and B will have different values in the two phases. Following Eq. (3.10) a typical plot of T_c versus ξ is given in Fig. 1 for a solid solution of Fe in Ti for both α and β phases. For the numerical estimates, the following order-of-magnitude values were taken for the parameters $\langle\hbar\omega\rangle$, $N(0)$ and V_{Ph} from the literature[5,13,14]:

$$\langle\hbar\omega\rangle\sim 0.02\text{ eV}$$
$$N(0)\sim 0.2\text{ states eV}^{-1}\text{ atom}^{-1}$$
$$V_{\text{Ph}}\sim 0.4\text{ eV}$$

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The parameter w has been estimated with the help of Eq. (38) of Suhl and Matthias[5] and the experimental results[1] for these systems in which their mechanism seems to be the dominant one. It is found to be of the order of 0.2 eV. The parameter $\Delta_{\lambda l}$, V and U are very difficult to estimate from first principles. To the authors' knowledge all such theoretical studies have so far been, at best, qualitative. Experimental work also cannot unambiguously furnish us with a precise value of the parameters involved. We shall, therefore, attempt order-of-magnitude estimates. Physically, $\Delta_{\lambda l}$ is the difference in energy between nonmagnetic and magnetic states of the impurity electrons. The present theoretical situation has recently been reviewed by Mott[15] and one finds that $\Delta_{\lambda l}$ in transition metals can have any value between 1 to 10 eV as suggested by different authors. In our estimates, we have assumed $\Delta_{\lambda l}$ to be of the order of 1 eV. The parameter J is estimated from one point of the experimental graph for each phase which gives the best fit. This turns out to be of the order of 0.5 eV which is quite reasonable. This can be seen from the following arguments. The parameter J involves hybrid-Coulomb and exchange integrals. Ordinary intra-atomic Coulomb integrals are of the order of 10 eV or more. For hybrid Coulomb integrals of the type considered here, this is expected to be reduced by a factor of 10. If further, we take correction for screening by about 30% to 40%, we shall arrive at the figure of about 0.5 eV. for the parameter J. Calculations of such integrals in the context of magnetic interactions do show similar magnitudes.[16,17]

IV. CONCLUDING REMARKS

In the foregoing sections we have attempted to explain the observed increase in T_c in certain superconductors containing magnetic element impurities in low concentrations. The theory developed here, in essence, takes into account the Coulomb and exchange-type interactions between the conduction electrons and the impurity electrons in the singlet states; such type of interactions can be described as generalized Coulomb and exchange processes which involve localized impurity states. These have been shown elsewhere to be very important for explaining the electronic properties of dilute alloys and pure systems.[11] The other types of s-d interactions[18] which are not included in the present investigation are s-d mixing and $\langle \mathbf{k},\mathbf{k}'|V_{12}|\mathbf{k}'',l\rangle$, $\langle l,l|V_{12}|\lambda,\mathbf{k}\rangle$. Their contribution to the BCS-pair correlation will come only in the fourth order and therefore they are not expected to be important. Bailyn has already considered $\langle \mathbf{k},\mathbf{k}'|V_{12}|\mathbf{k}'',l\rangle$ and it seems that it is completely screened out.

Further, we have obtained in second order the impurity induced correlation between electrons of a BCS pair by making use of the conventional canonical transformation. Although the unitary transformation employed in Sec. II is adequate for all practical purposes particularly for obtaining the BCS-pair interaction, the Eliashberg transformation[19] is superior in that, it is not restricted to the weak-coupling limit of BCS and it takes into account the renormalization of energies and the damping of excitations.

Finally, the calculated variation of T_c with the impurity concentration owing to the interaction considered here for Fe in Ti is compared with the experimental data. The theory seems to give a good account of the general behavior of T_c with impurity concentration for the systems of present interest. The tentative estimates for the various impurity-dependent parameters are of the right order of magnitude. The relative position of the localized states with respect to the Fermi surface which is of central importance may be determined from crystal-field or other considerations.[20,21] Such impurity orbital states above the Fermi surface will give rise to another process involving virtual BCS-pair transition to these states. The two-body interaction will be of the form

$$H_{\rm int}{}^{(a)}=\sum_{\lambda_i,k,k'}(G_{\mathbf{k}\mathbf{k}'}{}^{\lambda\lambda}C_{\lambda\uparrow}{}^{\dagger}C_{\lambda\downarrow}{}^{\dagger}C_{\mathbf{k}\uparrow}C_{\mathbf{k}'\downarrow}+\text{c.c.}), \quad (4.1)$$

where

$$G_{\mathbf{k}\mathbf{k}'}{}^{\lambda\lambda}\equiv\langle\lambda\lambda|e^2/r_{12}|\mathbf{k}\mathbf{k}'\rangle. \quad (4.2)$$

Making use of a canonical transformation similar to that in Sec. II, we get the effective electron-electron interaction emanating from this process in the second order. We get,

$$H_{\rm int}{}^{(a)}(\text{transformed})=-\frac{1}{4}\sum_{\lambda_i,k,k'}\left[\frac{(G_{\mathbf{k},-\mathbf{k}'}{}^{\lambda,\lambda})^*G_{\mathbf{k},-\mathbf{k}}{}^{\lambda\lambda}}{\epsilon_\lambda-\epsilon_{\mathbf{k}}}+\frac{(G_{\mathbf{k}',-\mathbf{k}'}{}^{\lambda,\lambda})^*G_{\mathbf{k},-\mathbf{k}}{}^{\lambda,\lambda}}{\epsilon_\lambda-\epsilon_{k'}}\right]C_{\mathbf{k}'\uparrow}{}^{\dagger}C_{-\mathbf{k}'\downarrow}{}^{\dagger}C_{-\mathbf{k}\downarrow}C_{\mathbf{k}\uparrow}. \quad (4.3)$$

The integral $G_{\mathbf{k},-\mathbf{k}'}{}^{\lambda\lambda}$ is similar to the s-d exchange in metal and alloys; the only difference is that we are dealing with empty impurity states above the Fermi surface. Ignoring the $\mathbf{k}$ dependence of such integrals,[22] we can see that such interaction processes [cf. Eq. (4.3)] will be attractive for $\epsilon_\lambda > \epsilon_k$. A detailed consideration of such processes will be given in a later publication.

The mechanisms discussed above may have wider validity and can be extended to metals and their alloys which are nonmagnetic or contain antiferromagnetically coupled impurity atoms and provide localized states of the type visualized above.

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