Indian J. Phys. **66A** (6), 731-739 (1992)

Superconductivity of alloys containing dilute ferromagnetic impurities

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Received 5 September 1991, accepted 19 December 1991

Abstract : The theory superconductivity of alloys with magnetic impurities is reinvestigated with the roles of non-magnetic potential scattering and spin-exchange interactions between conduction electrons and impurities with special attention paid to the role of potential scattering term in the electron-impurity interaction. The impurity spins are treated as classical vectors in a mean-field approximation and the pair-breaking mechanism in the Abrikosov-Gorkov approximation for small but finite concentration of impurities. The theoretical results are applied to the experimental findings on spin-fluctuation effects in some Zr-based ferromagnetic alloys. All results are found to be in good agreement with experiments.

Keywords : Superconductivity, alloys, ferromagnetic impurities, spin-fluctuation effects.

PACS Nos. : 74.20.Hi, 75.50.Cc

1. Introduction

The classical question of the behaviour of magnetic impurities in superconductors has been the subject of many experimental and theoretical studies for quite sometime. The theories of ferromagnetic superconductors have been formulated by many workers [1-3] by considering the interaction between the conduction electrons and magnetic impurities. The results of the AG theory are known to be valid for the rare-earth impurities in superconductors with weak electron-impurity interactions. Shiba [4] and Rusinov [5] proposed a theory of low concentration of uncorrelated magnetic impurities in superconductors. In this model the scattering of electrons by impurities is calculated exactly by treating the impurity-spins classically. The interaction of conduction electrons of spin σ with a magnetic impurity atom of spin S is given by

$$U(kk') = V(kk')\,\delta_{\alpha\beta} - 1/2\, I\,(S, \sigma_{\alpha\beta}) \tag{1}$$

where σ denotes Pauli matrices, V and I are the strengths of the potential and spin-exchange interactions respectively.

In the AG theory, a weak scattering of the conduction electrons in the presence of

magnetic impurities has been shown to destroy the Cooper-pairing and suppress superconductivity, and the thermodynamic properties have been found to be independent of the potential interaction V. The purpose of this work is mainly to discuss the effect of the potential scattering in addition to the electron-impurity spin-interaction on the superconducting properties of alloys containing ferromagnetic impurities. This is specially important in the discussion of anisotropy problems where the potential scattering plays an important role.

The present work is an analytical extension of our recent work [6] on spin-fluctuation effects on the superconducting properties of metallic glasses. The presence of potential interaction has been found to affect the superconducting gap parameter although the contribution is very small for dilute impurity cases. A critical concentration has also been obtained to define the transition of the alloys from one cooperative state to another viz. from superconducting to ferromagnetic state and their coexistence.

In general, the ordinary scattering of electrons by impurities does not have any effect on the critical temperature of the superconductor. The situation is somewhat different in the case of magnetic impurities. Under AG theory, the gap parameter Δ is assumed to be constant in space. This conclusion is valid at absolute zero near an impurity. At temperatures close to the superconducting transition temperature, the spatial part leads to the appearence of an additional term in the gap parameter. This can be seen from Green's function of a superconductor averaged over the coordinates of spin-directions of the impurities and their positions. We shall assume in the present work that the impurities are randomly distributed in the crystal and the concentration of magnetic impurities is finite but small in the sense that one can neglect the spin interaction between neighbouring impurities.

2. Formulation of the problem

We assume in the present model, that the impurities are randomly distributed and their concentration is finite but low enough so that the impurity interactions are negligible,

$$H = H_{BCS} + H_{e-s} + H_p \tag{2}$$

where
$$H_{BCS} = \sum_{k\sigma} \varepsilon_k C^{\dagger}_{k\sigma} C_{k\sigma} - \Delta \sum_{k} (C^{\dagger}_{k\uparrow} C^{\dagger}_{-k\downarrow} + C_{-k\downarrow} C_{k\uparrow}) + \frac{\Delta^2}{V} \tag{3}$$

and
$$\Delta = q \sum_{k} < C_{-k\downarrow} C_{k\uparrow} >.$$

Here Δ is the superconducting order parameter, g the electron-phonon coupling constant, $C^{\dagger}_{k\sigma}$ ($C_{k\sigma}$) is the creation (destruction) operator for an electron with momentum k and spin σ and $< >$ indicates thermodynamic averages. In eq. (2), the expression for H_{e-s} and H_p are, respectively

$$H_{e-s} = -\frac{1}{2N} \sum_{i,\sigma,\beta} C^{+}_{k\alpha} C_{k'\beta} (S_i, \sigma_{\alpha\beta}) \exp [i (k - k') R_i] \tag{4}$$

and $$H_p - \frac{1}{N} \sum_{i,k,k'} V(k-k') \exp\,[i(k-k').R_i]\, C^{\dagger}_{k\alpha} C_{k'\alpha}\,. \tag{5}$$

In eq. (4) S_i is the localised spin at the i-th site located at R_i and V is the potential scattering of the electron by the impurity.

Fulde in 1965 [7] showed that both the potential scattering and the spin-exchange scattering terms [eqs. (4) and (5)] reduce the superconducting transition temperature and also the gap parameters. Actually, the exchange scattering terms has the pair-breaking effect whereas the potential scattering term acts to smoothen the gap anisotropy [8].

We proceed in the manner similar to Balseiro and Falicov [9] and treat the spins S_i to be classical vectors. It is well-known at present [4] that at finite concentration of impurity, localised excited states, appearing due to the interaction of conduction electrons with localised spins, form impurity-band and the energy of localised excited states are affected by the potential scattering. One of the important consequences of the interaction between localised spins and conduction electrons is that it causes an indirect interaction between the spins [10] which tends to form a magnetically ordered state. This changes the structure of the BCS energy gap equation. We discuss the effect of potential scattering in the process of growth of impurity band and hence on the observable quantities like the variations of superconducting gap parameters, the critical temperatures etc. and apply the theory to the experimental results on Ni, Co and Fe-doped Zr amporphous superconducting compounds.

The Green's function of our impurity problem is a 4×4 matrix Green's function given by

$$\underset{\sim}{G}_{k,p}(E) = \underset{\sim}{G}^{\circ}_{k}(E) + \underset{\sim}{G}^{\circ}_{k}(E)\, \underset{\sim}{x}(k,p)\, \underset{\sim}{G}_{p}(E) \tag{6}$$

where $$\underset{\sim}{G}^{\circ}_{k}(E) = -\frac{1}{(E^2 - \varepsilon^2_p - \Delta^2)} \begin{bmatrix} E-\varepsilon_p & \Delta \\ \Delta & E+\varepsilon_p \end{bmatrix} \tag{7}$$

$$\underset{\sim}{x}(k,p) = \begin{bmatrix} 0 & -U(k,p) \\ U(k,p) & 0 \end{bmatrix}, \tag{8}$$

and $$\underset{\sim}{G}_{p}(E) = \begin{bmatrix} G^{(1)}_{k,p} & G^{(4)}_{k,p} \\ G^{(2)}_{k,p} & G^{(3)}_{k,p} \end{bmatrix} \tag{9}$$

In eq. (8), the interaction term $U(k,p)$ is given by

$$U(k,p) = -\frac{1}{2N} \sum (S \,.\, \sigma) \exp\,[i(k-p)\,.\,R_i] + \frac{1}{N} \sum V(k,p) x \times \exp\,[i(k-p)\,.\,R_1] \tag{10}$$

and in eq. (9) $G_{k,p}(E)$ are the Fourier transforms of

$$G^{(1)}_{p,p}(t) = \langle\langle C^{\dagger}_{-p\downarrow} \mid C^{\dagger}_{p\uparrow} \rangle\rangle \tag{11a}$$

$$G^{(2)}_{p,p}(t) = \langle\langle C_{p\uparrow} \mid C_{p\uparrow} \rangle\rangle \tag{11b}$$

$$G^{(3)}_{p,p}(t) = \ll C_{p\uparrow} \mid C_{p\uparrow} \gg \tag{11c}$$

$$G^{(4)}_{p,p}(t) = \ll C^{\dagger}_{-p\downarrow} \mid C_{p\uparrow} \gg . \tag{11d}$$

The Fourier transforms of the above Green's functions are

$$G^{(1)}_{p,p}(E) = \frac{\Delta}{E-\varepsilon_p} G^{(2)}_{p,p}(E) - \frac{U(p,p)}{E-\varepsilon_p} G^{(1)}_{k,p} \tag{12a}$$

$$G^{(2)}_{p,p}(E) = -\frac{1}{E-\varepsilon_p} + \frac{\Delta}{E+\varepsilon_p} G^{(1)}_{p,p}(E) + \frac{U(p,p)}{E+\varepsilon_p} G^{(2)}_{k,p} \tag{12b}$$

$$G^{(3)}_{p,p}(E) = \frac{\Delta}{E+\varepsilon_p} G^{(4)}_{p,p}(E) + \frac{U(p,p)}{E+\varepsilon_p} G^{(3)}_{k,p}(E) \tag{12c}$$

$$G^{(4)}_{p,p}(E) = -\frac{1}{E-\varepsilon_p} + \frac{\Delta}{E-\varepsilon_p} G^{(3)}_{p,p}(E) - \frac{U(p,p)}{E-\varepsilon_p} G^{(4)}_{k,p}(E) . \tag{12d}$$

The above eqs. (12a-12d) are the coupled Green's function equations which may be solved to obtain the Green's function required for the superconducting gap parameter and transition temperature.

3. The gap parameter and transition temperature

The response of the localised excited states and the states due to potential scattering to the energy of the bound state within the BCS gap may be studied from the poles of the impure Green's function which is obtained by solving eqs. (12a) and (12b) for $G^{(1)}_{p,p}(E)$ as

$$G^{(1)}_{p,p}(E) = -\frac{\Delta}{[E^2-\varepsilon^2_p-\Delta^2]} - \frac{\Delta U^2(0)}{[E^2-\varepsilon^2_p-\Delta^2]^2} + \frac{2\varepsilon_p U(0)\Delta}{[E^2-\varepsilon^2_p-\Delta^2]^2} \tag{13}$$

where $$U(0) = -\frac{IC}{2} S_z + CV(0), \tag{14}$$

C is the concentration of the impurity given by $C = \frac{N_i}{N}$; N_i is the number of impurity atoms distributed randomly at the lattice sites and N is the total number of atoms. For random distribution of spins and the position of impurities, the growth of the impurity band and the critical temperature are studied and the necessary informations are obtained from the Green's function (13) averaged over the random spatial distribution and orientation of spins. For averaging over the position of impurity and over the impurity spins, we follow the techniques of Abrikosov *et al* [11] and Balseiro and Falicov [9].

The averaged Green's function is therefore

$$G^{(1)}_{p,p}(E) = -\frac{\Delta}{[E^2-\varepsilon^2_p-\Delta^2]} - \frac{\Delta \langle U^2(0)\rangle}{[E^2-\varepsilon^2_p-\Delta^2]^2} + \frac{2\varepsilon_p \langle U(0)\rangle \Delta}{[E^2-\varepsilon^2_p-\Delta^2]^2} . \tag{15}$$

It may be noted that for classical spins along the z-direction the $\langle S_z \rangle$ appearing in eq. (15) through $U(0)$ may be equated to the magnetisation M. The quantity $(1/2)IS_z$ gives the maximum relative displacement of up spin band with respect to the down spin band which

is a measure of the ferromagnetic driving force. It gives a very important quantity under AG theory represented by

$$(1/\tau_{AG}) = (1/2)\pi\rho_o (IS_z)^2. \tag{16}$$

The eq. (16) is the strength of the spin-flip scattering in terms of the density of conduction states per spin ρ_o and is responsible for pair-breaking [12]. Although the effect of the electron scattering by impurity spin on the order parameter will be more pronounced near the absolute zero, it is expected to be significant near the transition temperature T_c because of the interaction of electrons with localised phonons. The superconducting gap parameter in terms of the Green's function may be written as [13].

$$\Delta = \sum_p <C^\dagger_{-p\downarrow} C^\dagger_{p\uparrow} > = \frac{1}{\beta} \sum_p g\, G^{(1)}_{p,p}(E). \tag{17}$$

Using eq. (15) the above equation may be solved and written as,

$$1 = -\frac{1}{\beta} \sum_{n,k} \frac{g}{[E^2 - \varepsilon^2_p - \Delta^2]} - \frac{1}{\beta} \sum_{n,k} \frac{gU^2(O)}{[E^2 - \varepsilon^2_p - \Delta^2]^2} + \frac{1}{\beta} \sum_{n,k} \frac{gU(0)}{[E^2 - \varepsilon^2_p - \Delta^2]^2}. \tag{18}$$

For $\Delta \to 0$ and $T \to T_c$ the eq. (18) becomes [14]

$$1 = \frac{2g\rho_o}{\beta} \left[\int_0^{\omega_D} \sum_{n=0}^{\alpha} \frac{d\varepsilon_p}{(\omega^2_n + \varepsilon^2_p)} - \int_0^{\omega_D} \sum_{n=o}^{\alpha} \frac{U^2(0)\, d\varepsilon_p}{(\omega^2_n + \varepsilon^2_p)^2} + \int_0^{\omega_D} \sum_{n=o}^{\alpha} \frac{2\varepsilon_p U(0)\, d\varepsilon_p}{(\omega^2_n + \varepsilon^2_p)^2} \right], \tag{19}$$

where $E = i\omega_n = \dfrac{(2n+1)i\pi}{\beta}$.

The second and third integrals in eq. (19) may be solved by using the Riemann-Zeta function $\zeta(z)$ [1] and the transition temperature may thus be written as

$$T_c = \left(\frac{\gamma\omega_D}{\pi}\right) \exp\left(-\frac{2}{\lambda_{e-p}} - \delta\right), \tag{20}$$

where $\delta = \dfrac{7}{2}\zeta(3)\left(\dfrac{U(0)}{\pi T_c}\right)^2$, $\lambda_{e-p} = \rho_o g$.

In order to determine the behaviour of the gap parameter with increasing concentration of ferromagnetic impurity, we evaluate eq. (18) for temperature T near the transition temperature T_c by expanding in powers of $(\Delta/T_c)^2$ to obtain

$$(\Delta/T_c) = 1.53\left[(1 - \frac{T}{T_c}) - \frac{4.2U^2(0)}{(\pi T_c)^2} \right]^{1/2} \tag{21}$$

Eq. (21) when compared with the gap parameter $\Delta(0)$ at $T = 0$ leads to

$$\frac{\Delta}{\Delta(0)} = \left[\frac{\eta - T/T_c}{\eta} \right]^{1/2}. \tag{22}$$

Also when $T \rightarrow 0$, the above eq. (22) in terms of the gap parameter Δ_∞ of the pure material may be written as

$$\Delta_\infty/\Delta(0) = \left[\frac{1 - T/T_c}{\eta} \right]^{1/2}, \tag{23}$$

where $$\eta = 1 - (7/2)\,\zeta(3)\left(\frac{U(0)}{\pi T_c}\right)^2.$$

The critical concentration at which the transition from superconducting to ferromagnetic phase takes place is obtained from the critical value $U_{cr}(0)$ by putting $\Delta \rightarrow 0$ in the limit $T \rightarrow T_c$ for ordinary material in eq. (21) which in turn yeilds

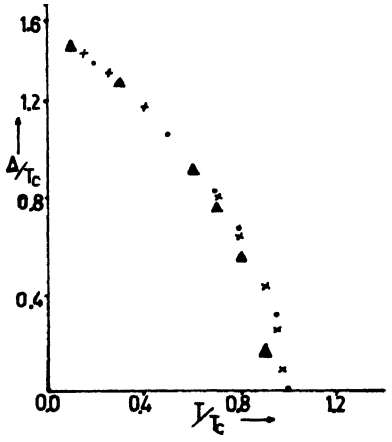
$$U_{cr}(0) = 0.51\, T_c \tag{24}$$

In the above equation $U_{cr}(0)$ contains two terms $A_{cr}(0) = -(1/2)\,CS_z$ and $B_{cr}(0) = CV(0)$, which determine the contributions due to spin-dependent and spin-independent scattering to the critical temperatures and gap parameters respectively.

4. Discussion

We have reinvestigated the theory of the influence of both the spin-spin scattering and the anisotropic potential scattering from impurities, in ferromagnetic superconducting alloys, in a generalised mean-field approximation with spin as a classical vector. The purpose of the present work is mainly to study the effect of potential scattering on the superconducting properties of ferromagnetic alloys. The pair-breaking mechanism due to spin-spin interaction has been treated in the AG fashion. The potential scattering of impurities resulting from the localised modes have been found to enhance the gap parameter through the variation of $\Delta(r)$ in space. As such, the local variation of the gap parameter may be neglected when we calculate the quantities which strongly reflect local properties about the paramagnetic impurity, but the neglect of such variation may not be allowed when we calculate thermodynamical properties with paramagentic impurities. It is well-known that around the classical spin in a superconductor, there exists a localised excited state which appears due to *s-d* interaction and breaks the time-reversal symmetry of electrons. At finite concentration, localised excited states around classical spins form impurity bands which grows with increase of impurity concentration and destroys the superconducting property. It is also interesting to consider the case for the spin-independent scattering (potential scattering) along with the spin-dependent scattering to examine the thermodynamic properties of superconducting alloys. We have explicitly derived the analytical expression of the superconducting properties of ferromagnetic alloys for classical spins. The nature of

variations of the gap parameters (Δ/T_c) for the pure and impure superconductors, have been shown in Figure 1 for different arbitrary values of spin-spin and potential scattering terms.



1. Variations of Δ/T_c with T/T_c for pure and impure superconductors.
   (●) (Δ/T_c) for A = 0, B = 0
   (▲) (Δ/T_c) for A = 2(K), B = 0
   (×) (Δ/T_c) for A = 2(K), B = 0.2(K)

It has been found that the potential scattering term enhances the gap parameter on one hand (although very little), the spin-dependent scattering term lowers it on the other. The presence of localised modes causes the softening of the frequency of the impurity modes,. thereby, favouring the superconducting phase, whereas for finite concentration of impurity, the spin-scattering term favours the ferromagnetic phase. A critical concentration may be obtained from eq. (24) which defines the transformation from superconducting to ferromagnetic phase and also their coexistence. Eq. (24) may be applied to the observed variation of T_c for an alloy system at different concentration and for the alloy which corresponds to the minimum value of T_c (at which Δ-variation has suddenly dropped) one may determine the critical concentration of impurity at which the ferromagnetic transition takes place.

The present theory was applied to make the numerical evaluation of the spin-fluctuation terms and electron-phonon parameters in case of some Zr-based amorphous glasses. Treating the micro-crystals of these glasses as ordered, which form the part of our earlier work [6] we discuss the idea of spin-fluctuation along with the contribution due to localised modes. Although the application of the present theory to the cases of amorphous alloys is a crude one, the results are surprisingly very close to the experimental values of Zr-based glasses. The reason for this is probably because of the fact that the theory may be applied to such systems when the impurity concentrations is not very high. To have a qualitative comparison of the theoretical results obtained with the experimental values we select some typical results of amorphous Zr [15-17].

i) Debye temperature θ_D = 110 K

ii) Transition temperature T_c = 3.88 K and

iii) the Pseudo-potential μ = 0.17.

Now, we use them to evaluate electron-phonon coupling constant which is $\lambda_{e-p} = 0.96$. We then compare eq. (20) with the renormalised equation for T_c [15, 18] to obtain

$$\lambda_{sf} = \lambda_{ep} - \mu - \frac{\lambda_{ep}\,[2\lambda_{ep} - \mu + 1]}{[\lambda_{ep} + \delta\lambda_{ep} + 2]} \,. \tag{25}$$

It may be noted that eq. (25) consists of the Pseudo potential $\mu \rightarrow (\lambda_{sf} + \mu)/(1 + \lambda_{sf})$ and electron-phonon parameter $\lambda_{ep} \rightarrow \lambda_{ep}/(1 + \lambda_{sf})$ normalised by considering the spin fluctuation part λ_{sf}, and indicates that λ_{sf} increases with increasing δ (drop in transition temperature eq. (20)) *i.e.* increase in the concentration of ferromagnetic impurity increases the spin fluctuation part of the electron-phonon parameter and lowers the transition temperature. Results obtained from our theoretical calculations for parameters δ and hence for λ_{sf} are given in Table 1 along with the values of λ_{ep}. From eq. (24) for $U_{cr}(0) = A_{cr}(0) - B_{cr}(0)$ and from the critical values of $A_{cr}(0)$ obtained by Balseiro and Falicov [9], one may

Table 1. Comparison of T_c, λ_{e-p} and λ_{s-f} with the experimental values reported by Altounian *et al* [15]

System	T_c (K)	θ_D (K)	δ	λ_{e-p} (theo)	λ_{e-p} (expt)	λ_{s-f} (theo)	λ_{s-f} (expt)
$Fe_{.27}Zr_{.73}$	1.3	177.5	2.46	1.071	0.950	0.293	0.317
$Fe_{.28}Zr_{.72}$	0.6	180.0	3.25	1.073	0.913	0.355	0.358
$Fe_{.20}Zr_{.80}$	3.3	160.0	1.42	1.068	0.981	0.181	0.221
$Co_{.33}Zr_{.67}$	3.0	192.5	1.71	1.089	0.942	0.216	0.235
$Co_{.35}Zr_{.65}$	2.76	197.5	1.81	1.069	0.952	0.228	0.255
$Co_{.40}Zr_{.60}$	2.05	210.0	2.17	1.070	0.982	0.267	0.311
$Ni_{.24}Zr_{.76}$	3.59	170.0	1.40	1.071	0.947	0.177	0.201
$Ni_{.33}Zr_{.67}$	2.89	192.5	1.75	1.070	0.893	0.221	0.214
$Ni_{.40}Zr_{.60}$	2.35	210.0	2.05	1.073	0.867	0.253	0.228

make an estimate of $B_{cr}(0)$ which gives the measure of potential scattering term. This is minimum at the critical value of $A_{cr}(0)$. The spin independent potential scattering term is therefore appearing as the additive term to the single particle energy thereby changing the single particle energy in the Hamiltonian of the system. It is interesting to note that the theoretical values of λ_{sf} are in good agreement with experimental results, particularly for low impurity concentration, which signify the validity of the model used. It may therefore, be concluded that the localised excited states appear even in the presence of potential scattering, however small it may be, with a consequent enhancement of gap parameter.

Acknowledgment

The authors are thankful to Dr M P Das, Australian National University, Australia and Dr I Bose, Bose Institute, Calcutta, India for their valuable suggestions during the work. The authors (SKR and NM) are also thankful to Prof Abdus Salam, International Centre for Theoretical Physics (ICTP), International Atomic Energy Agency and UNESCO for the facilities provided at ICTP where the work started.

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