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BRILLOUIN-WIGNER THEORY OF MIXED-VALENCE IMPURITIES IN BCS SUPERCONDUCTOR: T_c/T_{c0} AND $\Delta C/\Delta C_0$ *

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ABSTRACT

The (lowest order) Brillouin-Wigner perturbational expansion theory is adopted to describe the mixed-valence impurities in the BCS superconductor. Two substantial quantities characterizing the superconducting state, i.e. the reduced transition temperature T_c/T_{c0} and the reduced specific heat jump $\Delta C/\Delta C_0$ are calculated numerically as a function of the impurity concentration x and the energy level difference E_f between two $4f$ configurations. A comparison with the experimental data of the $Th_{1-x}Ce_x$ and $Th_{1-x}U_x$ alloys is also included with a more reasonable fitting than Kaiser's theory.

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I. INTRODUCTION

Measurements of superconducting alloys have proved to be a sensible probe for the properties of both the matrices and dissolved impurities [1]. Two excellent examples are worth mentioning here. 1) The magnetic-nonmagnetic transition of Ce (cerium) impurities under the external pressure found in (La, Th)Ce alloys and 2) demonstration of the nonmagnetic state of Ce and U (uranium) impurities in $Th_{1-x}Ce_x$ and $Th_{1-x}U_x$ alloys. These were among the earliest discoveries of the mixed-valence behaviour in the rare earth and the actinide elements and their alloys [2].

The concentration dependence of the reduced superconducting transition temperature T_c/T_{c0} of $Th_{1-x}Ce_x$ and $Th_{1-x}U_x$ alloys was explained as a modified exponential law with the nonmagnetic $4f$ resonance (Anderson - Friedel) model of Kaiser [3] in the language of pair-weakening in contrast with the language of pair-breaking in the famous Abrikosov-Gor'kov theory [4] of magnetic impurities dissolved in the BCS superconductor. It is surprising that such a simple theory initially devised for transitional metal alloys ($Al_{1-x}Mn_x$ for example) can be fitted to the data of the rare earth alloys so well even if the physical interpretations in terms of pair-weakening force due to the intermediate Coulomb repulsion between two electrons on the same impurity site are characteristic of the 3d electrons.

It is well-known nowadays that the exclusion of double electron occupation on the mixed-valence impurity in a metal host means a nearly infinite Coulomb correlation energy within the same $4f$ configuration. All the physical properties of these alloys are accounted for by including both spin and charge fluctuations between two proximate configurations, namely $4f^n$ (with energy E_0) plus a conduction electron and $4f^{n+1}$(with energy E_1, $N = 2J + 1$- fold degenerate) with the energy level difference $E_f = E_1 - E_0 - E_f$ comparable to the effective resonance width $\Gamma = \pi N(E_F)V^2$, where E_F and $N(E_F)$ stand for the Fermi level and the density of states at the Fermi level of the host metal [5].

In this short communication, we review the problem of nonmagnetic impurities in the BCS superconductor in the context of mixed-valence theory bearing the $Th_{1-x}Ce_x$ and $Th_{1-x}U_x$ alloys in mind. The Brillouin-Wigner expansion for the free energy of an infinite Coulomb repulsion, i.e. U = infinite, Anderson model in the large N limit [6] (or lowest order approximation), for the rare earth alloys in the superconducting state is adopted directly leaving the mathematical generalization of the Keiter-Kimball theory [7] to superconducting matrix to be published elsewhere. Suppression of the reduced superconducting transition temperature T_c/T_{c0} with respect to the mixed-valence impurity concentration x and the T_c/T_{c0} dependence of the reduced specific heat jump $\Delta C/\Delta C_0$ are calculated numerically. A comparison of these two quantities with the experimental data of $Th_{1-x}Ce_x$ and $Th_{1-x}U_x$ is provided with a re-examination of the Kaiser theory fitted to these alloys. We conclude that parameters used in the present paper are more reasonable than those used in the Kaiser theory.

II. THEORY

The density of the free energy for the model stated above, described in terms of the statistical quasiparticles $\tilde{E}_0$ and $\tilde{E}_1$ (effectively, the energy shifts of E_0 and E_1 levels) and in independent impurity approximation, can be written as

$$g(\beta, \Delta^2) = g_0(\beta, \Delta^2) - \frac{x}{\beta} \ln\left\{ e^{-\beta(E_0+\tilde{E}_0)} + N e^{-\beta(E_1+\tilde{E}_1)} \right\} \tag{1}$$

where $g_0(\beta,\Delta^2)$ is the density of the free energy for pure BCS superconductor, $\tilde{E}_0$ and $\tilde{E}_1$ are given by the Brillouin-Wigner equations $\tilde{E}_i = \Gamma_i(\tilde{E}_i)$ in the lowest order (or in the large N limit) as

$$\tilde{E}_0 = NV^2N(E_F)\left\{ \int_0^{\omega_D} d\xi \left[\frac{f(E)}{\gamma_0+E} + \frac{f(-E)}{\gamma_0-E} \right] + \int_{\omega_D}^{D} d\xi \left[\frac{f(\xi)}{\gamma_0+\xi} + \frac{f(-\xi)}{\gamma_0-\xi} \right] \right\}_{\gamma_0=\tilde{E}_0-E_f} \tag{2}$$

and

$$\tilde{E}_1 = V^2N(E_F)\left\{ \int_0^{\omega_D} d\xi \left[\frac{f(E)}{\gamma_1+E} + \frac{f(-E)}{\gamma_1-E} \right] + \int_{\omega_D}^{D} d\xi \left[\frac{f(\xi)}{\gamma_1+\xi} + \frac{f(-\xi)}{\gamma_1-\xi} \right] \right\}_{\gamma_1=\tilde{E}_1+E_f} \tag{3}$$

with $E = (\xi^2 + \Delta^2)^{1/2}$, ω_D and D being the Debye frequency and the half width of the flat conduction electron band, i.e. $N(E_F) = 1/2D$.

All the thermodynamic properties near the superconducting transition temperature T_c are determined by the following variational condition for a minimal free energy

$$\frac{\partial}{\partial\Delta^2} g(\beta, \Delta^2) = \ln(T/T_{c0}) + A(x,T) + B(x,T)\Delta^2(T) = 0 \tag{4}$$

where T_{c0} is the transition temperature of the pure BCS superconductor.

Thus, setting $\Delta(T_c) = 0$, the self-consistent equation of T_c reads as

$$\ln(T_{c0}/T_c) = A(x, T_c) \tag{5}$$

with

$$\frac{A(x,T_c)}{x} = \frac{1}{2}NV^2\left\{ \tilde{P}_0 \frac{\mathrm{Re}\,\psi(\frac{1}{2}+z_0) - \psi(\frac{1}{2})}{\gamma_0\left[\gamma_0 + NV^2N(E_F)u_0\,\mathrm{Im}\,\psi'(\frac{1}{2}+z_0)\right]}\Bigg|_{\gamma_0=\tilde{E}_0-E_f} + \tilde{P}_1 \frac{\mathrm{Re}\,\psi(\frac{1}{2}+z_1) - \psi(\frac{1}{2})}{\gamma_1\left[\gamma_1 + V^2N(E_F)u_1\,\mathrm{Im}\,\psi'(\frac{1}{2}+z_1)\right]}\Bigg|_{\gamma_1=\tilde{E}_1+E_f} \right\}_{z=iu,\ u=|\gamma|/2\pi T}$$

and the renormalized occupation probabilities of $\tilde{E}_0$ and $\tilde{E}_1$ levels

$$\tilde{P}_0 = e^{-\beta\tilde{E}_0} / \left[e^{-\beta\tilde{E}_0} + N e^{-\beta(E_f+\tilde{E}_1)} \right] \tag{6}$$

$$\tilde{P}_1 = e^{-\beta(E_f+\tilde{E}_1)} / \left[e^{-\beta\tilde{E}_0} + N e^{-\beta(E_f+\tilde{E}_1)} \right] \tag{7}$$

The expression of the reduced specific heat jump $\Delta C/\Delta C_0$ is given as

$$\frac{\Delta C}{\Delta C_0} = \frac{T_c}{T_{c0}} \frac{1 + T_c\,\partial A(x,T_c)/\partial T_c}{1 + \tilde{B}(x,T_c)} \qquad (8)$$

where $1 + \tilde{B}(x,T_c) = B(x,T_c)\Big/\frac{7\zeta(3)}{8(\pi T_c)^2}$, $\psi(\frac{1}{2} + Z)$ and $\zeta(3)$ are the di gamma function and the Riemann ζ-function, respectively. The expression of $\tilde{B}(x,T_c)$ is too lengthy to be written here.

It should be noted that $\tilde{E}_0$ and $\tilde{E}_1$ in the final expressions (5) - (8) are the same as those in the normal state with $T = T_c$, i.e.

$$\tilde{E}_0 = NV^2N(E_F)\left\{-\ln\left(\frac{D}{2\pi T_c}\right) + \mathrm{Re}\,\psi\left(\frac{1}{2} + i\,\frac{\tilde{E}_0 - E_f}{2\pi T_c}\right)\right\} \qquad (9)$$

and

$$\tilde{E}_1 = V^2N(E_F)\left\{-\ln\left(\frac{D}{2\pi T_c}\right) + \mathrm{Re}\,\psi\left(\frac{1}{2} + i\,\frac{\tilde{E}_1 + E_f}{2\pi T_c}\right)\right\} \qquad (10)$$

III. NUMERICAL RESULTS OF T_c/T_{c0} AND $\Delta C/\Delta C_0$

A clean interpretation of superconductor containing rare earth impurities can be obtained in terms of fluctuations between the two valence states E_0 and E_1 from the appearance of renormalized occupation probabilities $\tilde{P}_0$ and $\tilde{P}_1$ in Eq.(5). In the mixed-valence regime, one has $-\tilde{E}_0 > -(\tilde{E}_1 + E_f)$ so that $\tilde{P}_0 \gg \tilde{P}_1$, i.e. the rare earth impurities stay mainly in the singlet configuration rather than in the magnetic multiplet configuration. Thus, the influence of mixed-valence impurities on the BCS superconductor will be nonmagnetic similar to 3d transitional metal impurities although a very different physical background exists in these two systems. Following the numerical results of T_c/T_{c0} and $\Delta C/\Delta C_0$ serve as quantitative evidence.

Figs.1a) and b) represent the concentration x dependence of T_c/T_{c0} at several energy level difference E_f and the T_c/T_{c0} variation with respect to E_f at different concentrations x calculated from Eq.(5). E_f and the half

bandwidth D are in units of Γ/π. The T_c/T_{c0} vs. x curve is of the exponential form as derived for a nonmagnetic behaviour and the T_c/T_{c0} vs. E_f curve stimulates the pressure dependence of T_c/T_{c0} found in $Th_{1-x}Ce_x$ alloys experimentally. The suppression of T_c/T_{c0} by impurity concentration increases quickly with the decreasing energy difference $E_f = E_1 - E_0 - E_F$ and a transition to the AG form is expected when E_f is negative enough to put the rare earth impurity into magnetic regime with long-lived local moments, but this is beyond the present theory.

Fig.2 gives the T_c/T_{c0} vs. x curve calculated from the present theory fitted to the data of $Th_{1-x}Ce_x$ alloys by setting

$$\Gamma/\pi = 0.01\ \mathrm{eV}, \quad E_f = -5.25\,(\Gamma/\pi), \quad D = 75\,(\Gamma/\pi) \qquad (11)$$

and U =infinite originally in the model. These parameters coincide with the estimate from a Bethe ansatz solution fitting the normal state spin susceptibility of these alloys [8].

Concerning the comparison between theory and available experimental data from superconducting mixed-valence alloys such as $Th_{1-x}Ce_x$ and $Th_{1-x}U_x$ alloys, one cannot ignore the 4f resonance model derived by Kaiser and applied to these alloys by Huber and Maple. A very good modified exponential law fitting was obtained for the T_c/T_{c0} vs. x curve as shown in Fig.2a) of Ref.3 if the following parameters were assumed in Kaiser's theory

$$\Gamma = 0.013\ \mathrm{eV}, \quad E_f = 0.076\ \mathrm{eV}, \quad U = 0.12\ \mathrm{eV} \qquad (12)$$

It should be noted that $E_f = 18(\Gamma/\pi)$, larger than half of U. For the cerium systems, E_f seems to be too larger than Γ/π while U unreasonably small in sharp contradiction to the currently received value of 5eV. So we conclude that calculation from the Friedel-Anderson resonance model is characteristic of the 3d transitional metal alloys. E_f seems to be over-estimated resulting from an underestimate of U for the mixed-valence rare earth alloys.

The $\Delta C/\Delta C_0$-curve vs. the T_c/T_{c0} one given in Fig. 3 shows qualitative agreement with the experimental data of $Th_{1-x}Ce_x$ and $Th_{1-x}U_x$ alloys. To our knowledge, this is the first time that these data are explained with a theory with upward deviation from the BCS law of corresponding states in contrast to the AG result with a downward deviation.

IV. CONCLUSION

We have carried out a lowest order Brillouin-Wigner theory calculation of the thermodynamic properties of BCS superconducting containing mixed-valence rare earth impurities. The numerical results of T_c/T_{c0} and $\Delta C/\Delta C_0$ show the influence of valence fluctuation on superconductivity in contrast with the case of magnetic rare earth impurities. A more deliberate consideration is needed when the $4f^{n+1}$ configuration is deep enough.

Details of the calculation and the interpretation will be published soon.

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FIGURE CAPTIONS

Figs.1 a) Reduced transition temperature T_c/T_{c0} vs. impurity concentration x with different 4f energy level separations E_f, where $\Gamma/\pi = \rho(\mu)V^2 = 0.02$eV, D = 150. Both D and E_f are in units of Γ/π. The orbital degeneracy factor $N = 6$.

b) Reduced transition temperature T_c/T_{c0} vs. E_f at different impurity concentrations x. All parameters are the same as in a).

Fig.2 Reduced transition temperature T_c/T_{c0} of $Th_{1-x}Ce_x$ alloys vs. Ce concentration [3] explained with present theory. Parameters are found to be $\Gamma/\pi = 0.01$ eV, D = 75, $E_f = -5.25$ and N = 6.

Fig.3 The reduced specific heat jump $\Delta C/\Delta C_0$ vs. T_c/T_{c0}. The straight line represents the BCS law of corresponding states, whereas the dashed line gives the result of the Abrikosov-Gor'kov theory [3]. Some experimental points of $Th_{1-x}Ce_x$ and $Th_{1-x}U_x$ alloys are also given.

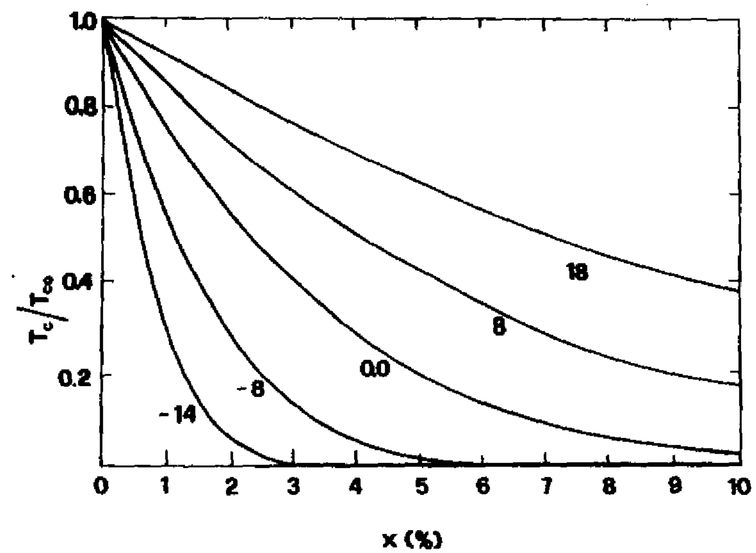


Fig.1a

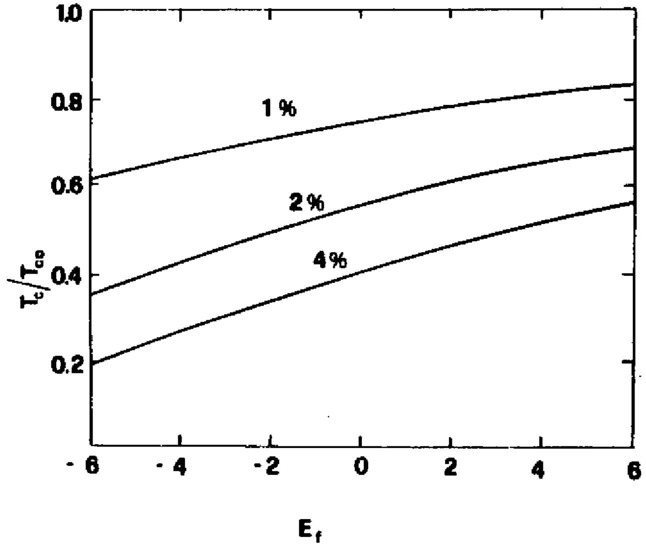

1.0
0.8
0.6
0.4
0.2
T_c/T_{co}
1%
2%
4%
- 6
- 4
- 2
0
2
4
6
E_f

Fig.1b

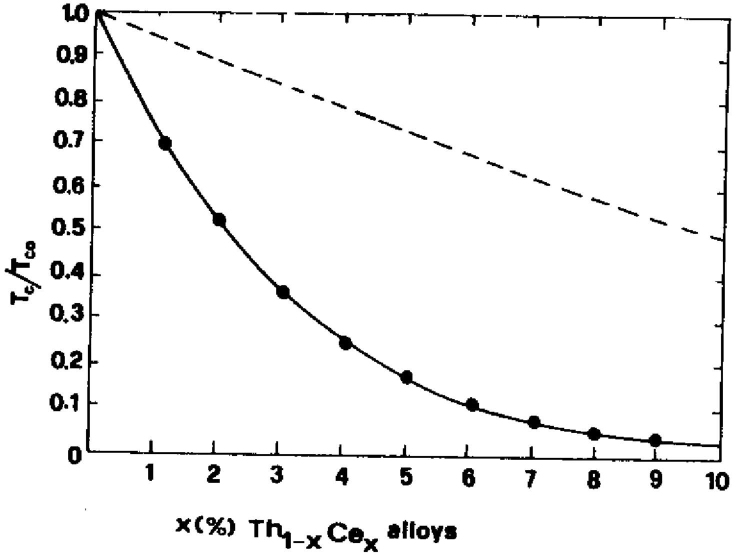
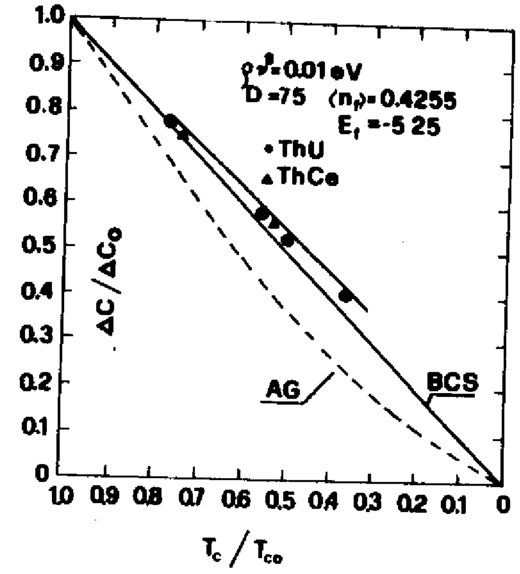

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
T_c/T_{co}
1
2
3
4
5
6
7
8
9
10
x(%) $Th_{1-x}Ce_x$ alloys

Fig.2



ρ J^2=0.01 eV
D =75 ⟨n_f⟩= 0.4255
E_f = -5 25
• ThU
▲ ThCe
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
ΔC / ΔC₀
AG
BCS
1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0
T_c / T_{co}

Fig.3