Depression of the superconducting transition temperature caused by 3d magnetic impurities*

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The observed depressions of the superconducting transition temperature caused by 3d magnetic impurities are compared with the maximum possible value given by theory. Several discrepancies are found, but they might be completely removed by including in the theory the effect of orbital degeneracy.

It has been known since the early 1950's that magnetic impurities almost always drastically depress the transition temperature T_c of superconductors.[1,2] (Exceptions are known; there are some cases in which the host metal is a transition element and the density of states is increased drastically by small concentrations of impurities because of the narrowness of the electron d band.[3,4]) Almost all of the experimental work so far has gone into studying rare-earth impurities because of the good solubility of the rare earths in some of the superconductors (especially lanthanum and some of its compounds).[5,6] The magnetic electrons in the rare-earth atoms are in the 4f shell, rather deep inside the atom, where they react only weakly with the conduction electrons of the host metal. The weakness of the interaction enables a successful theory to be developed entirely in terms of the first Born approximation. This theory was initiated by Abrikosov and Gor'kov[7] and was developed further by Skalski *et al.*[8] and by others. It has been very successful in interpreting the influence of the rare-earth impurities except for cerium. (Cerium is an exception. Its electronic structure puts the 4f electronic energy level very close to the Fermi energy, and this results in an antiferromagnetic coupling between the 4f electrons and the conduction electrons. The antiferromagnetic coupling brings in special features which are the superconducting analog of the Kondo effect in the normal state. The theory of these special features is in good agreement with the data for Ce impurity atoms.[9])

Experiments have also been performed on superconductors containing magnetic impurities which have electronic structures with an incomplete 3d shell. For these 3d magnetic impurities the interaction between the magnetic impurity and the conduction electrons is sufficiently strong to demand a theory which goes beyond the first Born approximation. This has been demonstrated by measurements of tunneling into In-Fe and Pb-Mn alloys,[10] far-infrared absorption in Pb-Mn alloys,[11] and thermal conductivity of In-Mn alloys.[12,13] In those measurements, the samples were made by simultaneously quench-condensing the alloy constituents from the vapor phase onto a cold substrate. If the sample is kept cold throughout the experiment, precipitation of the constituents is prevented and the impurity atoms provide localized magnetic moments. This has been shown by transition-temperature data obtained by the Göttingen group.[14,15] Only in the cases of Zn-Mn and Zn-Cr alloys is it possible to dissolve considerable amounts of 3d magnetic impurities in bulk superconducting samples and have the impurity atoms retain their localized moments.[15,16]

Theoretical treatments of localized-moment impurities are available which go beyond the first Born approximation, and which therefore might apply to the 3d magnetic impurities. These theories all indicate that the magnetic impurity atoms introduce electron states into the BCS energy gap. Rusinov[17] and Shiba[18] have treated the impurity spin classically (i.e., ignoring noncommutation of the different components of the spin), and their theory has been used by Nagi and collaborators to calculate the transition temperature,[19] critical field,[19] specific-heat jump,[19] electron tunneling,[20] and thermal conductivity.[21] The theoretical tunneling curves fit the experimental data[10] well for Pb-Mn alloys, but probably not for In-Fe alloys. The theoretical thermal-conductivity values for In-Mn alloys do not agree with the experimental data.[12,13] Furthermore, Shiba shows that his presumably more reliable Hartree-Fock calculation[22] of the specific-heat jump at T_c does not fit the data for Zn-Mn and Zn-Cr alloys.

According to the calculation of Chaba and Nagi,[19] the maximum depression δT_c of T_c occurs when their parameter $\epsilon_0 = 0$. In that case, they find that

$$(\delta T_c)_{\max}/C_i = 1/8N(0)k , \quad (1)$$

where C_i is the impurity concentration, $N(0)$ is the normal-state electron density of states for one spin direction, and k is Boltzmann's constant.

Müller-Hartmann and Zittartz have constructed a theory[23] which takes into account the correct

TABLE I. $\delta T_c/C_i$, the ratio of the depression of the superconducting transition temperature to the impurity concentration in K/at.%.

Host metal	Impurity Cr	Mn	Fe	Co	$(\delta T_c)_{max}/C_i$ according to Eq. (1)
In	65[a]	53[a] 49[b]	2.5[a] 2.0[c]	0.07[a]	43
Pb		21[d]	4.7[e]	0.8[e]	23
Sn	16[f]	69[f]	1.1[f]	0.15[f]	38
Zn		285[g] 305[h]			106

[a]Reference 26.
[b]Reference 12.
[c]Reference 10.
[d]Reference 27.
[e]Reference 28.
[f]Reference 29.
[g]Ref. 16, film samples.
[h]Reference 16, bulk samples.

commutation relations for different components of the spin, which is necessary for treating the Kondo effect. They find that δT_c depends on the impurity spin and the Kondo temperature T_k of the alloy. When T_k is about 12 times the transition temperature of the pure host metal, δT_c has its maximum value, which is again given by Eq. (1), independent of the impurity spin.

Smith[24] noted that his experimental value of $\delta T_c/C_i$ for bulk Zn-Mn alloys, 260 K/at.%, was greater than the maximum value indicated by the calculation of Müller-Hartmann and Zittartz, (see Table I). We have called attention here to the fact that the theory of Chaba and Nagi yields the same maximum value. Falke *et al.*[16] assembled the published data for $\delta T_c/C_i$ for bulk samples of Zn-Mn alloys, and calculated an average of (305 ± 10) K/at.%. They also measured $\delta T_c/C_i$ for quench-condensed Zn-Mn alloy films and obtained (285 ± 30) K/at.%, in good agreement with the value for bulk samples, and again larger than the value given by Eq. (1).

The main purpose of this paper is to point out that there are many other published experimental values of $\delta T_c/C_i$ for $3d$ magnetic impurities. These values were obtained by using quench-condensed films; they are listed here in Table I, along with the previously mentioned results for Zn-Mn alloys. Also indicated in Table I is the value which is given by Eq. (1) for the four host metals. We have assumed that the quench-condensed films have the same value of $N(0)$ as the corresponding bulk metals, since the superconducting transition temperature of a pure film is nearly the same as for a bulk sample of indium, lead, or tin, although this is not true for zinc. To determine $N(0)$ we used experimental values[25] of the Sommerfeld specific-heat coefficient γ and the relation

$$N(0) = 3\gamma/2\pi^2 k^2 \ . \qquad (2)$$

The numbers in Table I indicate that, in addition to Zn-Mn alloys, three other alloy systems have transition temperatures for which $\delta T_c/C_i$ exceeds the value given by Eq. (1). These are the In-Cr, In-Mn, and Sn-Mn alloys. (In the case of Pb-Mn alloys, the discrepancy between theory and experiment is within the experimental uncertainty.) If the impurity spin and Kondo temperature of the alloys were known, one could determine whether there are other discrepancies of this type.

Shiba[22] has discussed the effect of the orbital degeneracy $2l+1$. He showed that, within the Hartree-Fock approximation, and treating the impurity spins classically, the effect of the impurity atoms is increased by a factor of $2l+1$. Therefore[30] the value for $(\delta T_c/C_i)_{max}$ given in Eq. (1) must also be multiplied by $2l+1$, removing the disagreement with the result of Chaba and Nagi[19] who assumed $l=0$. He believes that the value of δT_c yielded by the theory of Müller-Hartmann and Zittartz[23] would be modified in the same way if orbital degeneracy were taken into account.[30] This would make the values listed in Table I compatible with their theory, assuming the orbital angular momentum is not quenched.

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