CHAPTER II

TRANSITION-METAL IMPUTITIES

When a transition-metal impurity is dissolved in a metal, its possible magnetic state spans the range between magnetism and nonmagnetism. The magnetic behavior of these impurities may be characterized phenomenologically according to the assumption that the solute spins fluctuate in time with a frequency τ_{sf}^{-1}, τ_{sf} being the localized spin fluctuation lifetime. In the limit $\tau_{sf} \gg \tau_T$ where τ_T is the thermal fluctuation lifetime ($\sim h/k_B T$ at temperature T), the solutes behave magnetically; in the limit $\tau_{sf} \ll \tau_T$, they behave nonmagnetically.

The effect of magnetic impurities on superconductivity has received a great deal of attention since the discovery that they produce a precipitious drop in the superconducting transition temperature T_c (23). The conduction-electron-impurity-spin exchange interaction can account for this strong depression of T_c. Assuming that exchange scattering of conduction electrons by the impurity spins can be described within the first Born approximation (to second order in the exchange interaction parameter $\mathcal{J}$), Abrikosov and Gor'kov (24)(here after AG) developed in 1960 theory for superconductors with paramagnetic impurities. Their theory successfully explained the basic features of early experiments and predicted the striking phenomenon of gapless superconductivity.

In recent years, deviations from the AG theory were found. First, the assumption that the solute spins are well defined does not apply to weakly magnetic systems (such as <u>Al</u>Mn) in which the localized spins apparently fluctuate with a finite frequency τ_{sf}^{-1}. Secondly, even when the impurity spins are well defined, the effect of exchange scattering of conduction electrons to higher order than $\mathcal{J}^2$ (i.e., the Kondo effect) can be very significant. These important developments have stimulated the current interest in the effects of impurities on superconductivity which are outside the scope of the basic AG theory.

2.1 Long-Lived Local Moments in Superconductors

2.1.1 The Abrikosov-Gor'kov Theory

The classic theory of superconductivity in the presence of paramagnetic impurities is due to Abrikosov and Gor'kov (24). AG assumed that a paramagnetic impurity spin $\vec{S}$ interacts with the conduction electron spin density $\vec{s}$ at the impurity site via an exchange interaction

$$H_{int} = -2\mathcal{J}\vec{S}\cdot\vec{s} \qquad (2.1)$$

where $\mathcal{J}$ denotes the exchange interaction parameter. The impurity spins were assumed to be randomly distributed in space and uncorrelated with one another.

Within the first Born approximation, the inverse lifetime τ^{-1} (or pair breaking parameter α) which characterizes the superconducting-paramagnetic impurity system is given by

$$\alpha = \tau^{-1} = h^{-1}\, nN(0)\, \mathcal{J}^2\, S(S+1), \qquad (2.2)$$

where n is the paramagnetic impurity concentration and N(0) is the density of states at the Fermi level (for one spin direction). The theory predicts a second-order transition into the superconducting state and a rapid decrease of the transition temperature with α given by the relation

$$\ln\left(\frac{T_c}{T_{co}}\right) = \psi\left(\frac{1}{2}\right) - \psi\left(\frac{1}{2} + \frac{0.14\ \alpha\ T_{co}}{\alpha_{cr} T_c}\right) \quad (2.3)$$

T_{co} corresponds to $\alpha = 0$, $\alpha_{cr} = k_B T_{co} / 4 \hbar \gamma$ ($\ln \gamma$ is Euler's constant) corresponds to $T_c = 0$ (complete destruction of superconductivity), and ψ is the digamma function (25).

If α is varied by changing the solute concentration n, α / α_{cr} in Eq. (2.3) may be replaced by n/n_{cr}. The superconducting - normal phase boundary has been verified in the system (La,Gd)Al_2(26) (Fig. 2.1) and ThGd to concentration near n_{cr} (i.e., to $T_c/T_{co} \sim 0.1$). The value of the reduced Curie-Weiss temperature (θ_p/T_{co}) for a (La, Gd) Al_2 sample of reduced concentration $n/n_{cr} = 1.41$ (denoted by the solid triangle in Fig. 2.1) essentially satisfied in the temperature range studied.

One of the most striking predictions of the AG theory is the phenomenon of the gapless superconductivity. This results from the fact that the finite lifetime corresponds to an energy-broadening $\sim h/\tau$ which introduces states into the gap and spreads out the BCS peak in the density of states. The energy gap $\Delta_G(\alpha)$ no longer corresponds to the order parameter $\Delta_B(\alpha)$ and with increasing (or n), $\Delta_G(\alpha)$ goes to zero faster than $T_c(\alpha)$. For all concentrations the superconductor is gapless at the temperatures sufficiently near T_c; while for $n > 0.91\ n_{cr}$, the superconductor is gapless at all temperatures. For example, the theory predicts an attenuated specific heat jump at the transition (compared to the BCS law of corresponding states; see Fig. 2.3), and a linearly temperature-dependent term in the specific heat below T_c in the gapless region $n > 0.91\ n_{cr}$.

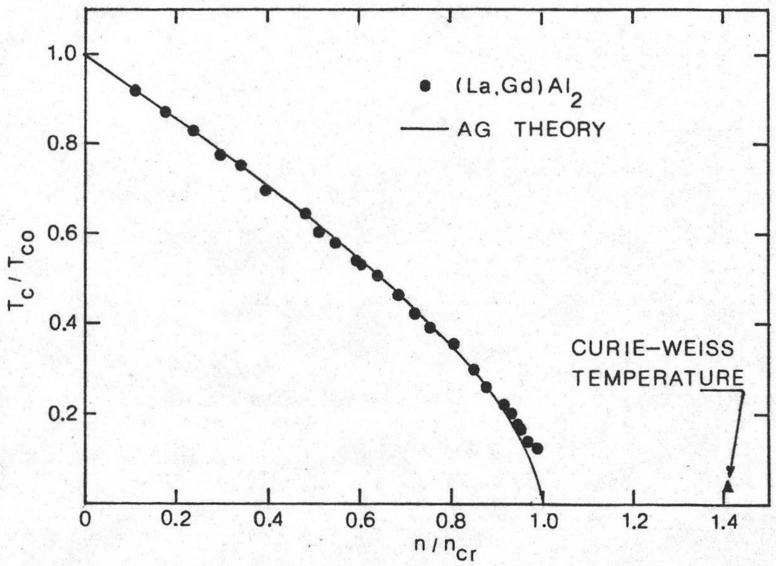

Fig. 2.1. Reduced transition temperature T_c/T_{c_0} vs. reduced concentration n/n_{cr} for ($\underline{La}$,Gd)Al_2 compared to the AG theory [solid curve; Eq. (2.3)]. T_{c_0} = 3.24°K and n_{cr} = 0.590 at.% Gd substitution in La. The reduced Curie-Weiss temperature θ_P/T_{c_0} measured at n/n_{cr} = 1.41 is denoted by solid triangle [After Maple (26)].

The phenomenon of gapless superconductivity has been verified by tunneling experiments on PbGd quenched films by Woolf and Reif (27) and by specific heat measurements on bulk LaGd alloys by Finnemore et al.(28)

2.1.2 The Kondo Effect in Superconductor

As discussed previously, in the AG theory the scattering of conduction electron is caused by impurity spins only to order $\mathcal{J}^2$. The Kondo effect arises when higher order terms in $\mathcal{J}$ are considered. It is expected to affect superconducting properties as profoundly as it does normal state properties. The Kondo effect in superconductors has recently received considerable attention from theorists, and some rather unusual properties have been predicted such as the appearance of a bound state in the energy gap.

Before discussing the manifestations of the Kondo effect observed in the superconducting state, we briefly describe some of the normal state properties of these systems from which an estimated characteristic temperature T_K has been established, and consider the physical origin of the effect.

By considering conduction-electron-impurity-spin exchange coupling scattering to third order in $\mathcal{J}$, Kondo (29) explained the normal state resistivity minimum phenomenon in metals containing magnetic impurities. The resultant perturbation theory expression for the magnetic contribution to the resistibity (ρ_m) varied as (-ln T) in agreement with experiement. The expression diverged for negative $\mathcal{J}$ at a characteristic temperature T_K given by

$$T_K \sim T_F \exp(-1 / N(0)|\mathcal{J}|) \qquad (2.4)$$

where T_F is the Fermi temperature. Since Kondo's original work, much theoretical effort has been devoted to removing the divergence at the Kondo temperature T_K and to understanding the various normal state properties for all temperature $T \gtrless T_K$. A physical interpretation which has emerged from these theories is that T_K is a characteristic temperature below which the impurity spins tend to be compensated by the conduction-electron spin, and the degree of compensation increases smoothly with decreasing temperature.

In a superconductor, the binding energy k_BT_K of this so-called "quasibound" state competes with the superconducting pairing energy k_BT_{co}, and recent theories imply that the superconducting properties are most strongly affected when $T_K \sim T_{co}$. Calculations by Zuckermann (30) by Muller-Hartmann and Zittartz (31) show that the initial depression of T_c as a function of T_K/T_{co} exhibits a maximum when $T_K/T_{co} \sim 10$

The Kondo effect is also reflected in the detailed dependence of T_c on impurity concentration. Calculations by Muller-Hartmann and Zittartz (32) give description of the T_c vs. n curve of the ($\underline{La}$,Ce)$_3$In system (33) if T_K/T_{co} is assumed equal to 0.125 (T_K has not been estimated from the normal state properties for this system, but the value $T_K \sim$ 1.2 °K does not seen unreasonable). A striking prediction of the theory of Muller-Hartmann and Zittartz is that when $T_K \ll T_{co}$, alloys within a particular range of impurity concentration (which depends upon the ratio T_K/T_{co}) will have three transition temperatures. Thus, when an alloy of the appropriate composition is cooled to sufficiently low temperatures, it should successively become superconducting, then normal, and again superconducting. This "reentrant" T_c behavior has been observed for Ce impurities in several La-based alloys.

2.2 The Effect of Nonmagnetic Resonant States

Impurities which form nonmagnetic resonant d or f states depress the transition temperature of a superconductor at a rate intermediate between the strong depression due to magnetic impurities and the rather weak depression due to simple nonmagnetic (i.e., non-transition metal) impurities. This was first pointed out by Boato et al. (34) with regard to their measurements of the depression of T_c of Al by small additions of first-row transition element (Fe group) solutes. Since the work of Friedel (35) and Anderson (36), the apparent nonmagnetic nature of 3d transition element impurities in certain simple metals has been regarded as due to the fact that d-electron states, degenerate in energy with states in the conduction band, become broadened resonances. For Fe group additions to Al, the resonant state widths are great (~ 1 eV) that intra-atomic exchange and Coulomb correlations cannot support a local moment. Systematic study of the superconducting as well as normal state properties of Fe group solutes dissolved in Al was carried out by Aoki and Ohtsuka (37). Their results for the reduced initial depression of T_c, $T_{co}^{-1}(\Delta T_c/n)$, after correcting for the effect of gap anisotropy, are shown in Fig. 2.2. The effect of nonmagnetic resonant states on superconductivity was first treated theoretically by Zuckermann (38) According to Zuckermann's theory the scattering of conduction electrons into the large local density of states at each impurity site gives rise to an initially linear depression of T_c which is inversely proportional to the width Γ_d of the resonant state. In order to explain the observed depression of T_c in the Al-based Fe group alloys (Fig. 2.2a), Γ_d had to vary rapidly with transition element solute with a minimum value of about 0.1 eV for Mn.

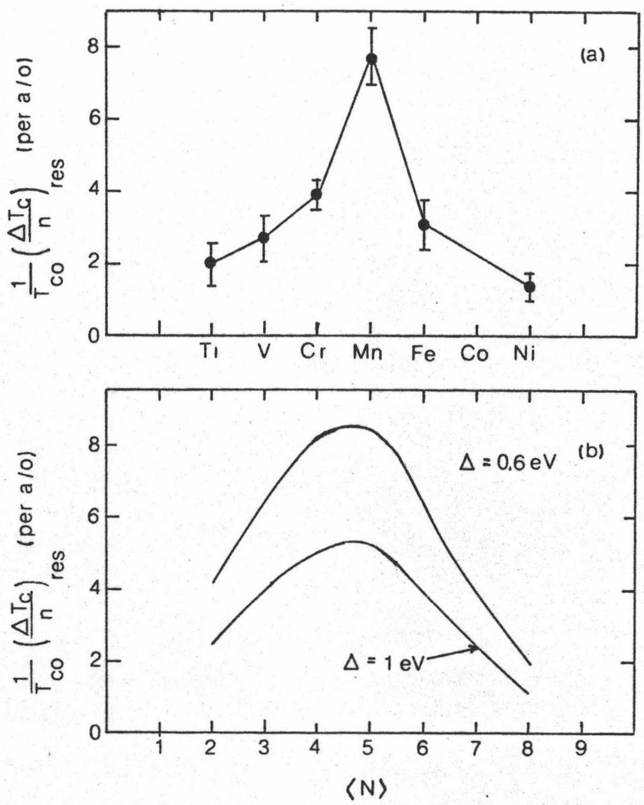

Fig. 2.2. (a) Initial depression of transition temperature due to localized d states for 3d transition metal impurities in Al. (b) Calculated depression of the transition temperature of Al-based alloys due to localized d states vs. d-state occupation number $\langle N \rangle$ for U = 10 eV [after Ratto and Blandin (39)].

This discrepancy was resolved, by including the intra-atomic Coulomb repulsion between d electrons with opposite spin at an impurity site (39, 40) Physically when a Cooper pair scatters into a local impurity state the two paired electrons with opposite spin are strongly repelled by the intra-atomic Coulomb interaction which leads to a weakened net attraction and a depressed transition temperature. With this modification, Ratto and Blandin (39) showed that $T_{co}^{-1}(\Delta T_c/n)$ varies as indicated in Fig. 2.2b with Γ_d constant across the first-row transition series. The theory provides a good qualitative description of the data in Fig. 2.2a for $\Gamma_d \sim 1$ eV and U = 10 eV (the nonmagnetic limit still holds since $\Gamma_d > U_{eff}$ where U_{eff} is defined below).

Kaiser (41), in 1970, derived from the Ratto-Blandin Hamiltonian the concentration dependence of T_c. According to Kaiser's theory $T_c(n)$ is given by a modified exponential of the form

$$\frac{T_c}{T_{co}} = \exp\left[\frac{-(A+B)\,n}{\lambda(1-Bn)}\right] \tag{2.5}$$

where

$$A = \frac{N_d(O)}{N(O)} \tag{2.6}$$

and

$$B = \frac{N_d(O)}{N(O)}\left[\frac{N_d(O)U_{eff}}{(2\ell+1)\lambda}\right] \tag{2.7}$$

$N_d(O)$ is the local density of states at an impurity site (for one spin direction), λ is the BCS coupling constant [N(O)V], and U_{eff} is the intra-atomic Coulomb repulsion reduced by correlations. In terms of the Friedel-Anderson (35,36) parameters-- Γ_d, E_d, and U,

$$N_d(O) = \frac{2\ell + 1}{\pi} \quad \frac{\Gamma_d}{\Gamma_d^{\,2} + E_d^{\,2}} \quad \text{(for one spin direction)} \qquad (2.8)$$

where

$$E_d = \Gamma_d \cot\left[\frac{\pi \langle N \rangle}{2(2\ell + 1)}\right] \qquad (2.9)$$

and $\langle N \rangle$ is the d-state occupation number, while

$$U_{eff} = \frac{U}{1 + (U/\pi E_d) \tan^{-1}(E_d/\Gamma_d)} \qquad (2.10)$$

The coefficient A represents the one-body dilution effect first studied by Zuckermann, whereas B represents the pair weakening term due to the Coulomb repulsion considered by Ratto and Blandin (39). The theory also predicts a critical concentration given by

$$n_{cr} = \frac{N(O)\ (2\ell + 1)}{N_d^2(O)\ U_{eff}} \qquad (2.11)$$

and it should be noted, a law of corresponding states as in BCS theory.

The modified exponential proposed by Kaiser (41) describes the T_c vs. n curves of a number of systems including the Al-transition element alloys first studied by Boato et al (34).

The system which appears to satisfy best the conditions of the Kaiser's theory is ThCe. (42,45). The reduced specific heat jump at T_c, $\Delta C/\Delta C_o$ (where ΔC_o is the specific heat jump of the matrix), vs. reduced transition temperature T_c/T_{co} is shown in Fig. 2.3 for ThCe and ThGd (43) system. The ThCe data follow the BCS law of corresponding states

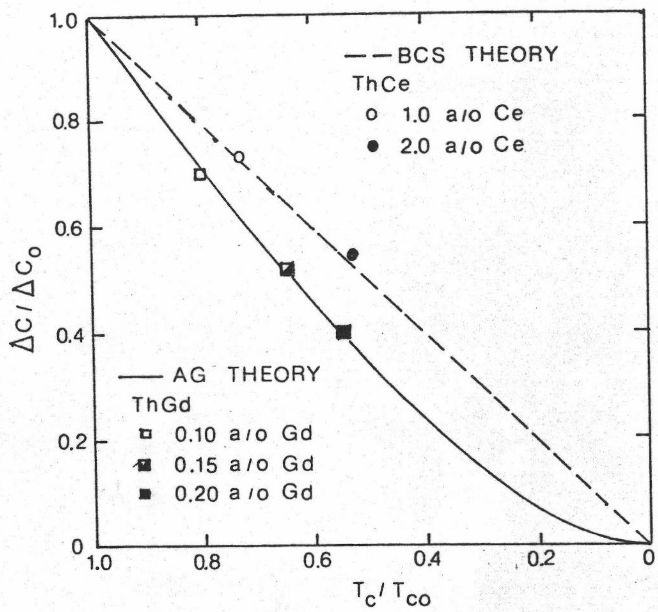

Fig. 2.3. Reduced specific heat jump ($\Delta C/\Delta C_0$) at T_c vs. reduced transition temperature for ThCe and ThGd alloys. The dashed line represents the BCS law of corresponding states, whereas the solid line is the result of the AG theory as calculated by Skalski et al (44) [after Huber and Maple (45)].

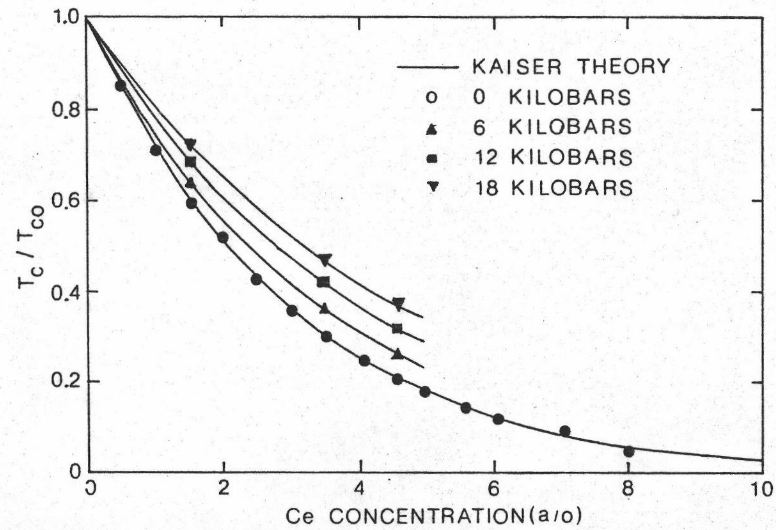

Fig. 2.4. Reduced transition temperature of ThCe alloys vs. Ce concentration at various pressure. The curves represent the result of Kaiser's theory [Eq. (2.5)] fitted to the data by the method of least squares [after Huber and Maple (45)].

(i.e., $\Delta C/\Delta C_o = T_c/T_{co}$) demonstrating the nonmagnetic nature of Ce impurities in Th, whereas the ThGd data follow the dependence calculated by Skalski et al (44) from the AG pair breaking theory. Accordingly, an excellent fit of Kaiser's modified exponential [Eq. (2.5)] to the experimental T_c vs. n curve for ThCe is obtained for various pressure between 0 and 18 kbar as shown in Fig. 2.4

2.3 The Effect of Localized Spin Fluctuations

As indicated in the last section, the depression of T_c for AlMn alloys is greater than expected from the Ratto-Blandin theory (39) (the Ratto-Blandin theory preceded the Kaiser theory and is essentially its low concentration limit). This discrepancy has been attributed to the importance of localized spin fluctuations for which a sizeable amount of evidence has been accumulated through studies of the normal state properties of the AlMn system. Gallieani d'Agliano and Ratto (46) proposed that this may be accounted for by a renormalization of the effective Coulomb repulsion due to spin fluctuations; i.e., in the Ratto-Blandin theory, U_{eff} should be replaced by a parameter U^* to be deduced by comparison with experiment.

Of particular interest is the detailed dependence of T_c on n. Shown in Fig. 2.5a is the measured T_c vs. n curve of AlMn system (47) which exhibits the same general positive curvature as the ThCe system. It should be noted that this curve is described well by the Kaiser theory after applying an energy gap anisotropy correction. Kaiser (48) suggested that his theory may be applicable to the AlMn system when U_{eff} is replaced by U^* since $T_O \gg T_{co}$ ($T_{co} = 1.2\ ^oK$ for Al). A good fit of Eq. (2.5) with the experimental T_c vs. n curve of AlMn is

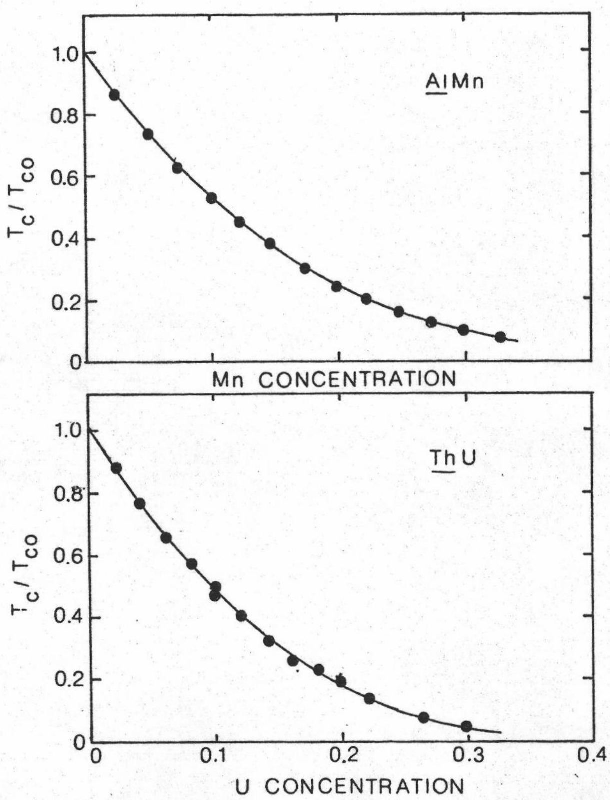

Fig. 2.5. (a) Reduced transition temperature of AlMn alloys vs. Mn concentration; T_{c_0} (1.17°K for Al) has been corrected for gap anisotropy as a function of concentration. (b) Reduced transition temperature of ThU alloys vs. U concentration; T_{c_0} = 1.36°K for Th. The curves are from Kaiser's theory [Eq. (2.5)] fitted to the data by the method of least squares.

obtained for $\Gamma_d = 1.2$ eV and $U^* = 7.3$ eV.

Another system which resembles AlMn is ThU where T_c vs. n curve is shown in Fig. 2.5b.(49). On the basis of the similarity between the T_c vs. n curves for the three systems ThCe, ThU, and AlMn, Huber and Maple (47) proposed that this may be a general result for the superconducting-normal phase boundary when $T_0 \gg T_{co}$. The T_c vs. n curve of ThU is also described well by the Kaiser theory with U_{eff} presumably replaced by U^*. However, the Kaiser theory yields a value for $N_f(0)$ which is negligibly small compared to the very large 103 states /eV-atom determined from the low-temperature normal state specific heat. Thus even though the form of the Kaiser expression for T_c vs.n is correct when localized spin fluctuations are present and $T_0 \gg T_{co}$, the parameter $N_f(0)$ and U_{eff} both apparently require renormalization. It would be highly desirable to have a theory that begins with the Kaiser model and allows U to increase continuously until a local moment can be said to exist, tracing the behavior of $T_c(n)$.

A model based on an instantaneous exchange interaction between conduction-electron spins and fluctuating impurity spins was developed by Rivier and MacLaughlin (50). A single phenomenological parameter, the spin fluctuation lifetime τ_{sf} (or temperature $T_0 = h/k_B\tau_{sf}$), characterizes the dependence of T_c on n. The AG result for $T_c(n)$ is obtained for temperatures $T \gtrsim T_0$ in the limit $T_0/T_{co} \ll 1$, where as an exponential dependence of T_c on n, similar to the Kaiser result, is found for $T_0/T_{co} \gg 1$. Thus the superconducting behavior is implicitly related to the parameters of the Friedel-Anderson model (35,36) via τ_{sf}.