RELATIONSHIP BETWEEN THE CRITICAL TEMPERATURE AND NORMAL-STATE MAGNETIC PROPERTIES OF A SUPERCONDUCTOR CONTAINING MAGNETIC IMPURITIES

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Measurements of the superconducting critical temperature and normal-state magnetization have been carried out on a series of samples of $LaSn_3$ with up to 12.3 at.% of the lanthanum replaced by gadolinium. The observed variation of critical temperature with Gd concentration follows the Abrikosov-Gorkov[1] (AG) relation for the more dilute samples, but at higher Gd concentration deviations are observed which are qualitatively similar to those observed for La-Gd alloys.[2] Because the normal-state magnetization measurements strongly suggest that spin correlations between Gd atoms should be important, a theoretical model is derived which relates the superconducting critical temperature to the normal-state magnetic properties. Although this model is oversimplified, the predicted deviations from AG are very similar to those experimentally observed. These results, experimental and theoretical, strongly suggest that spin-spin correlations, even in the absence of magnetic ordering,[3] are important in determining the properties of superconductors containing magnetic impurities.

The end member of the solid solution series, $LaSn_3$, is a superconductor with a critical temperature $T_S \simeq 6.4$°K and the ordered Cu_3Au crystal structure.[4] Because of the chemical similarity between La and Gd, it is possible to substitute Gd for La without modifying the crystal structure. However, each Gd atom carries with it a half-filled f-shell ($J = S = \frac{7}{2}$) and hence a localized moment of $7\mu_B$. Thus we can produce a superconductor with a known (or at least measurable) magnetic impurity concentration. The experimental techniques for measuring T_S and preparing the samples have been described elsewhere.[5]

The critical temperature of a superconductor containing localized moments was first calculated by AG on the basis of a model which assumes the impurities to be noninteracting and hence uncorrelated. In Fig. 1 is shown the measured values of T_S as a function of Gd concentration, as well as the best fitting AG curve. The bars on the data indicate the 10 and 90% points of the transition to show the width. At the lower Gd concentrations, the data follow the AG curve quite well. For $x > 0.10$, however, the value of T_S remains approximately constant up to $x \simeq 0.115$, where there is an abrupt drop below 1°K, our present lower limit of measurement. This "plateau" is qualitatively similar to, but not as pronounced as, that observed by Matthias and co-workers[2] in the La-Gd system. Deviations from AG of this sort were derived by Bennemann[3] on the basis of a model which postulates ferromagnetic ordering of the impurity spins. However, extensive measurements of the normal-state magnetization of the samples indicate the absence of long-range order down to 1°K even at Gd concentrations large enough to suppress superconductivity below 1°K. Hence, Bennemann's explanation of the deviations from AG is inapplicable to this system.

An explanation for the deviations from AG is suggested by a detailed examination of the normal-state susceptibility data. Over a wide temperature range the reciprocal susceptibilities of the samples vary linearly with temperature, i.e., obey a Curie-Weiss relation. The values of the Curie-Weiss θ are plotted as a function of Gd concentration in Fig. 1. As one can see from Fig. 1, the values of θ are negative and proportional to Gd concentration. These results imply that the impurity spins are correlated, and since θ is negative, it is likely that the spin correla-

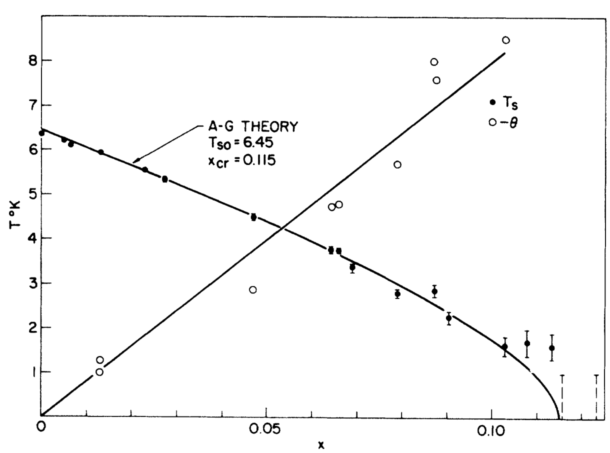

FIG. 1. Dependence of the superconducting transition temperature T_S and Curie-Weiss θ upon composition for the system $La_{1-x}Gd_xSn_3$. The bars on the T_S data indicate the 10 and 90% points of the transition to indicate the transition widths.

tion is antiferromagnetic in nature. The fact that the magnitude of θ becomes larger than T_S for $x \gtrsim 0.06$ suggests that the spin correlation may have an appreciable influence on the superconducting properties.

To support the hypothesis that the deviations from AG are the result of spin correlations, we have generalized AG to include spin correlations. Making quite reasonable assumptions, one can obtain theoretical curves of T_S vs Gd concentration quite similar to the experimental data of Fig. 1.

Consider the ratio T_S/T_{S0}, where T_S and T_{S0} are the critical temperatures with and without magnetic impurities, respectively. Following AG, this ratio is assumed to be a universal function of the spin-flip scattering time τ_S, i.e.,

$$\frac{T_s}{T_{s0}} = F\left(\frac{1}{\tau_s}\right) = \exp\left\{2\sum_{m=0}^{\infty}\left[\frac{1}{2m+1} - \frac{1}{2m+1+(\pi\tau_s T_{s0})^{-1}}\right]\right\}. \tag{1}$$

In the absence of spin correlations, τ_S in the Born approximation is given by

$$(1/\tau_s)_{\text{random}} \propto nJ^2 S(S+1), \tag{2}$$

where n is the impurity concentration, J is the s-f exchange constant, and S is the spin quantum number. When spin correlations are taken into account, the expression for τ_S replacing (2) is found to be[6]

$$\frac{1}{\tau_s} \propto \frac{J^2}{2q_F^2}\int_0^{2q_F} q\,dq \langle|\vec{S}_q|^2\rangle, \tag{3}$$

where q_F is the Fermi wave vector, and the quantity in brackets is the spin correlation function, which is defined as the thermal average

$$\langle|\vec{S}_q|^2\rangle \equiv \langle\sum_{ij}\exp[i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)]\vec{S}_i\cdot\vec{S}_j\rangle. \tag{4}$$

For random spins, (4) gives the result $nS(S+1)$, and (3) reduces to (2). From (2) and (3), one can obtain the important relationship

$$\frac{1}{\tau_s} = \left(\frac{1}{\tau_s}\right)_{\text{random}} \frac{1}{2q_F^2}\int_0^{2q_F} q\,dq\frac{\langle|\vec{S}_q|^2\rangle}{nS(S+1)}. \tag{5}$$

The spin correlation function is, in fact, closely related to the wave-vector-dependent susceptibility χ_q:

$$\chi_q = \langle|\vec{S}_q|^2\rangle/3kT, \tag{6}$$

where k is the Boltzmann's constant and T is the absolute temperature. It will be convenient to express $\langle|\vec{S}_q|^2\rangle$ in the general form

$$\langle|\vec{S}_q|^2\rangle = nS(S+1)kT/[kT+K(n,q)], \tag{7}$$

where K is a function to be specified. It is clear that for noninteracting spins, $K=0$. If one knew $K(n,q)$ and $(1/\tau_S)_{\text{random}}$, one could calculate T_S vs n exactly from (5) and (1).

Neither of these quantities is known for $La_{1-x}Gd_xSn_3$. However, one can, by making some reasonable assumptions and simplifications, obtain some interesting and provocative results. What properties must $K(n,q)$ have? First, it must yield a static susceptibility (i.e., $\chi_{q=0}$) which obeys a Curie-Weiss law with negative θ whose magnitude is proportional to magnetic impurity concentration. Second, one would expect these samples to order antiferromagnetically at low enough temperature. This is implied by the negative θ values. In addition, the end member $GdSn_3$ has been found to be antiferromagnetic[7] with $T_N = 31°K$. For simplicity, it will be assumed that θ and T_N both vary linearly with paramagnetic impurity concentration. A simple $K(n,q)$ which satisfies these requirements is given by

$$K = nk(\theta_c+\theta_0)(1-q/q_0)^2 - nk\theta_c, \tag{8}$$

where θ_0, θ_c, and q_0 are constants which will be defined below. From (8)

$$\langle|\vec{S}_q|^2\rangle = nS(S+1)kT/[(kT-nk\theta_c) + nk(\theta_c+\theta_0)(1-q/q_0)^2]. \tag{9}$$

From (9) we see that

$$\chi_{q=0} = nS(S+1)/3(kT+nk\theta_0), \tag{10}$$

from which $-\theta \equiv n\theta_0$ and

$$\langle|\vec{S}_q|^2\rangle \to \infty \text{ for } q=q_0 \text{ and } T=n\theta_c, \tag{11}$$

which corresponds to antiferromagnetic ordering with $T_N \equiv n\theta_c$ and a periodicity of q_0. Therefore, (8) satisfies the requirements which were previously set down. To calculate T_s, one must also know $(1/\tau_s)_{\text{random}}$. In general this also is unknown.

However, in the dilute limit $\tau_s \to (\tau_s)_{\text{random}}$. This can be easily seen from (9) and (5). In this limit the AG model is applicable and $(1/\tau_s)_{\text{random}}$ is determined from the inital decrease of T_s with impurity concentration. Next, $1/\tau_s$ is calculated from (5) and (9). Finally, T_s is calculated from (1).

The starting T_s vs n_0 curve is indicated. The next three curves were calculated for $X_0 = 0.5$, $\theta_0 = 80°\text{K}$, and $\theta_c = 8$, 4, and 2°K, respectively, where $X_0 \equiv q_0/2q_F$. The top curve was obtained by making the very crude approximation that $\chi_q \simeq \chi_{q=0}$. This amounts to neglecting the large spin fluctuations which occur at $T \to T_N$. In this approximation T_s never decreases to zero but approaches asymptotically that value of T_s for which $T_s(n_0) = n_0\theta_0$. Consider next the curve for $\theta_c = 8°\text{K}$. Starting at $n = 0$, T_s initially decreases with increasing n as predicted by AG. With increasing n the slope becomes less negative, producing a "plateaulike" region. As n increases still more (and T_s decreases) T_s starts decreasing very rapidly, dT_s/dn becoming very large at $n \simeq 0.175$. For larger n, T_s drops discontinuously to zero. The reason for this is that $\langle|\vec{S}_q|^2\rangle$ is becoming very large for $q \simeq q_0$, corresponding to the large spin fluctuations which proceed by long-range ordering. In fact because $\langle|\vec{S}_q|^2\rangle$ increases so rapidly as T_s decreases near this critical concentration, the curve actually bends on itself as shown, giving rise to a lower branch. This lower branch, if it could be observed, would be a striking confirmation of the model. As Fig. 2 indicates, the $T_s(n)$ curve can be shifted by the variation of θ_c. It depends upon θ_0 and X_0 as well.

Thus the model predicts a "plateau" region and a discontinuity in $T_s(n)$ solely from a consideration of spin-fluctuations—without the need to postulate actual long-range order.

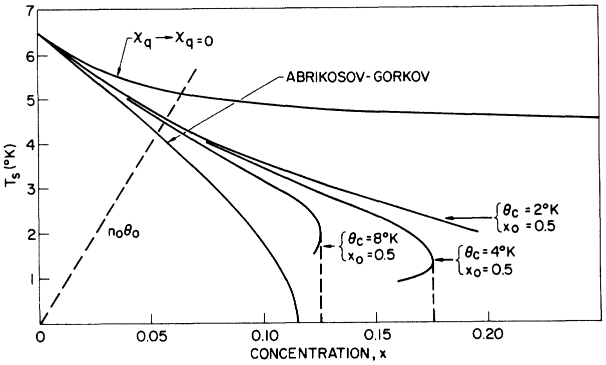

FIG. 2. Dependence of superconducting transition temperature T_s upon impurity concentration calculated from the theoretical model in the text which takes account of spin correlations.

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