it. For a pump strength which just depletes ($\tau = 0$), we find $I_{3/2} \sim 8.5\%$, compared with $\sim 15\%$ in the numerical results.[9]

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Superconducting Properties of the Singlet–Ground-State System (LaPr)Sn_3

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The depressions of the superconducting transition temperature T_c as a function of Pr concentration and the specific-heat jump ΔC at T_c as a function of T_c have been measured for the singlet–ground-state system (LaPr)Sn_3. The results are well represented by numerical calculations based on the Pr energy-level scheme determined from separate measurement of the Schottky heat-capacity anomaly and the Van Vleck paramagnetic susceptibility contributed by the Pr ions.

In a recent series of papers, Fulde and co-workers have developed a theory for the effect on superconductivity of paramagnetic rare-earth impurities with crystal-field–split energy levels.[1-5] According to this theory, the superconducting properties of the matrix are modified by two competing mechanisms. The first, a *depairing* mechanism, involves the usual conduction-electron–impurity spin-exchange interaction which can be operative even when the relevant impurity energy

levels are nonmagnetic via off-diagonal matrix elements. The second, a *pairing* mechanism (in addition to the electron-phonon interaction), is associated with inelastic charge scattering of conduction electrons from the aspherical part of the $4f$ shell of the rare-earth solute. Given the structure (i.e., splittings and degeneracies) of the energy levels of the rare-earth impurity ion in the crystal field of the matrix, the theory admits the calculation of various superconducting properties, two of which concern us here: the variation of the superconducting transition temperature T_c with impurity concentration n,[2] and the dependence of specific-heat jump ΔC at T_c on T_c.[4] The numerical calculations of Refs. 2 and 4 have neglected the inelastic charge-scattering mechanism since there has been no experimental evidence that it plays a detectable role.

In this Letter we report detailed measurements of both T_c/T_{c_0} versus n (where n is the Pr concentration) and $\Delta C/\Delta C_0$ versus T_c/T_{c_0} (ΔC_0 and T_{c_0} refer to the matrix) for the singlet-ground-state system $(La\text{Pr})Sn_3$ and compare them with numerical calculations based on the theory of Keller and Fulde.[2,4] The Pr energy level scheme which served as input for the calculations was determined with the aid of the theory of Lea, Leask, and Wolf[6] (hereafter LLW) from separate measurements (also presented) of the Schottky heat-capacity anomaly and the Van Vleck paramagnetic susceptibility contributed by the Pr ions.

Samples of $(La\text{Pr})Sn_3$ having the characteristic Cu_3Au ($L1_2$) structure[7] were prepared from high purity elements by arc melting in high purity argon. At the University of California, San Diego (UCSD), specific-heat measurements were made between 0.6 and 10 K in a He^3 semiadiabatic calorimeter with a heat pulse technique. These were augmented with ac mutual-inductance measurements in a He^3-He^4 dilution refrigerator. At Bell Laboratories (BL), specific-heat measurements were performed from 1.5 to 9 K using a heat-pulse method and magnetic susceptibility measurements were made with a pendulum magnetometer.

The results of the measurements of the superconducting properties of the $(La\text{Pr})Sn_3$ system are presented in Fig. 1. In Fig. 1(a), the reduced transition temperature T_c/T_{c_0} is plotted versus Pr concentration, while in Fig. 1(b), the reduced specific-heat jump $\Delta C/\Delta C_0$ is plotted versus T_c/T_{c_0}. The values of T_{c_0} and ΔC_0 are 6.38 K and 126 ± 3 mJ/K mole $LaSn_3$, respectively. Both linear BCS dependence and the Abrikosov-Gor'kov

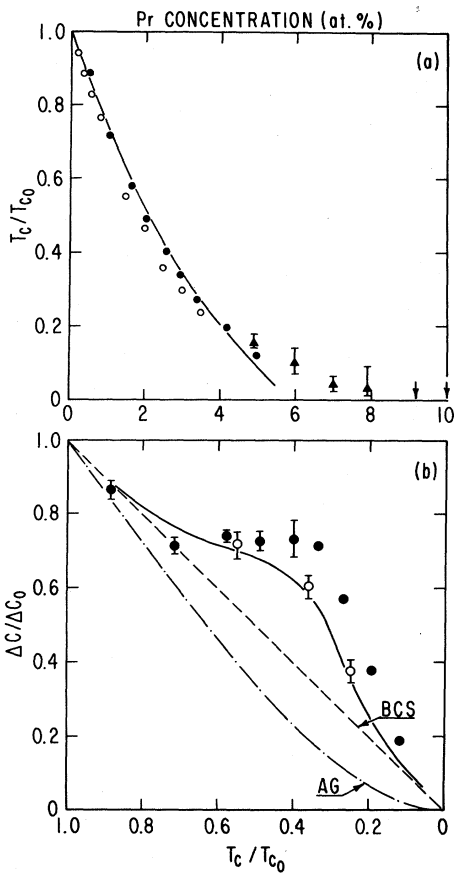

FIG. 1. (a) Reduced transition temperature T_c/T_{c_0} versus Pr concentration for the $(La\text{Pr})Sn_3$ system. Open circles, BL data; solid circles, UCSD heat capacity data; solid triangles, UCSD ac mutual inductance data. The solid line is derived from numerical calculations based on the theory of Keller and Fulde with $(dT_c/dn)_{n=0}$ as the only adjustable parameter. (b) Reduced specific heat jump $\Delta C/\Delta C_0$ versus reduced transition temperature T_c/T_{c_0} for the $(La\text{Pr})Sn_3$ system. Open circles, BL data; solid circles, UCSD data. The solid line is derived from numerical calculations based on the theory of Keller and Fulde with no adjustable parameters. The BCS curve (dashed line) and AG curve (dot-dashed line) are shown for comparison.

(hereafter AG) curve[8,9] for $\Delta C/\Delta C_0$ versus T_c/T_{c_0} are included in Fig. 1(b) for reference. While the curve of T_c/T_{c_0} versus Pr concentration exhibits the pronounced positive curvature characteristic of many matrix–rare-earth impurity systems with singlet impurity ground states,[3,10] the curve of $\Delta C/\Delta C_0$ versus T_c/T_{c_0} departs markedly from the linear BCS behavior in a manner not heretofore observed. Generally, the curves of $\Delta C/\Delta C_0$ versus T_c/T_{c_0} lie on or below the BCS

curve, depending on the magnetic state of the impurity,[10] but not above it as occurs here for the $(La\text{Pr})Sn_3$ system.

In order to compare the results presented in Fig. 1 with the theory, the sequence and splittings of the Pr^{3+} Γ_1, Γ_3, Γ_4, and Γ_5 energy levels in the cubic crystal field of the $LaSn_3$ matrix, needed for the numerical calculations of T_c/T_{c_0} versus n and $\Delta C/\Delta C_0$ versus T_c/T_{c_0}, were determined from normal-state measurements of the Van Vleck paramagnetic susceptibility and Schottky heat-capacity anomaly for various Pr concentrations. A plot of the zero-temperature magnetic susceptibility $\chi(0)$ versus Pr concentration is presented in Fig. 2(a), while typical data for the excess heat capacity C_m/R versus temperature are shown in Fig. 2(b) for Pr concentrations of 2.57 and 4.98 at.%.

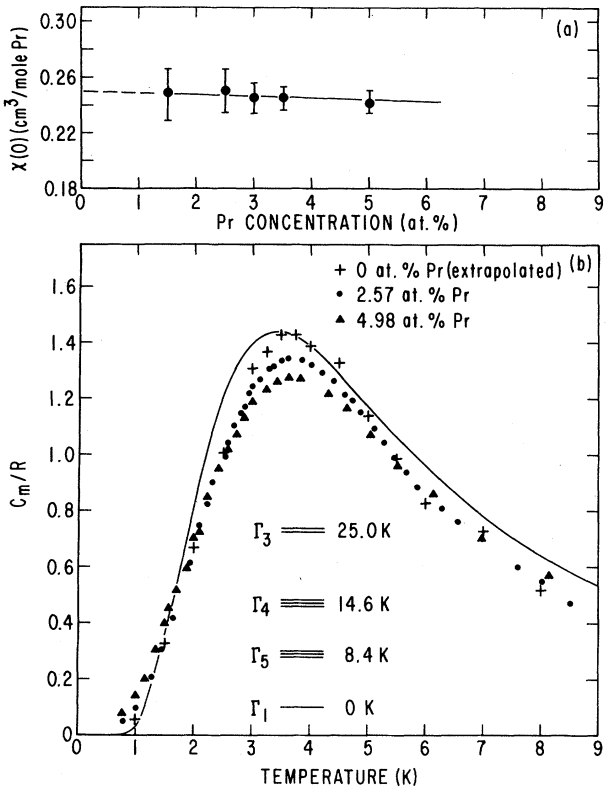

FIG. 2. (a) Zero-temperature magnetic susceptibility $\chi(0)$ versus Pr concentration for the $(La\text{Pr})Sn_3$ system (BL data). (b) Excess specific heat C_m/R versus temperature for the $(La\text{Pr})Sn_3$ system (UCSD data) for impurity concentrations of 0 (extrapolated), 2.57, and 4.98 at.% Pr. The solid line represents the best fit of the theoretical Schottky function to the extrapolated zero Pr concentration data corresponding to the Pr energy level scheme indicated in the figure.

Evident in Figs. 2(a) and 2(b) are weak dependences of $\chi(0)$ and C_m/R versus T on Pr concentration which most likely arise from interimpurity exchange effects. Therefore, the measurements were extrapolated to zero Pr concentration to attain an estimate of the value of $\chi(0)$ and the behavior of C_m/R versus T in the single-Pr impurity limit. The extrapolated single-Pr impurity data, indicated in Figs. 2(a) and 2(b), were then analyzed in the following manner.

First, the splitting between the Pr^{3+} Γ_1 and Γ_4 levels, Δ_{14}, was estimated from the formula for the zero-temperature Van Vleck paramagnetic susceptibility in second order,

$$\chi(0) = 2g_J^2\mu_B^2\alpha^2/\Delta_{14}, \tag{1}$$

where $\alpha = \langle\Gamma_1|J_z|\Gamma_4\rangle = (20/3)^{1/2}$, g_J is the Landé g factor for the Pr^{3+} $J=4$ Hund's-rule multiplet, and the experimental value of $\chi(0)$ is 0.25 cm^3/mole Pr. The value $\Delta_{14} = 12.8$ K deduced from this calculation was then used as a first approximation for the energy scale in the LLW energy-level diagram for Pr^{3+} in a cubic crystal field. This diagram gives the sequence and relative splittings of the Pr^{3+} energy levels in terms of a parameter x which represents the ratio of the fourth- and sixth-degree angular momentum operators in the expansion of the electrostatic potential of the crystal. Computer-generated Schottky functions were then compared to the extrapolated zero-Pr-concentration C_m/R versus T data. The best fit corresponds to a value of the LLW parameter x of 0.2 and the following Pr^{3+} energy-level scheme: Γ_1(singlet), 0 K; Γ_5(triplet), 8.4 K; Γ_4(triplet), 14.6 K; and Γ_3(doublet), 25.0 K. Finally, the temperature dependence of the magnetic susceptibility contributed by the Pr ions was calculated within second-order perturbation theory. In Fig. 3, the computed $\chi(T)$ curve is compared with data for two $(La\text{Pr})Sn_3$ samples with Pr concentrations of 3.5 and 5.0 at.%. Apart from the maximum in the theoretical curve at 3.2 K which does not appear in either of the experimental curves, the theoretical and experimental $\chi(T)$ curves are in reasonable agreement. The maximum in each of the experimental curves may be obscured by a low-temperature tail which arises from small amounts of other magnetic impurities which are present in the starting materials.

Using the Pr^{3+} energy-level scheme which was established from the normal-state measurements as input, we have calculated numerically the

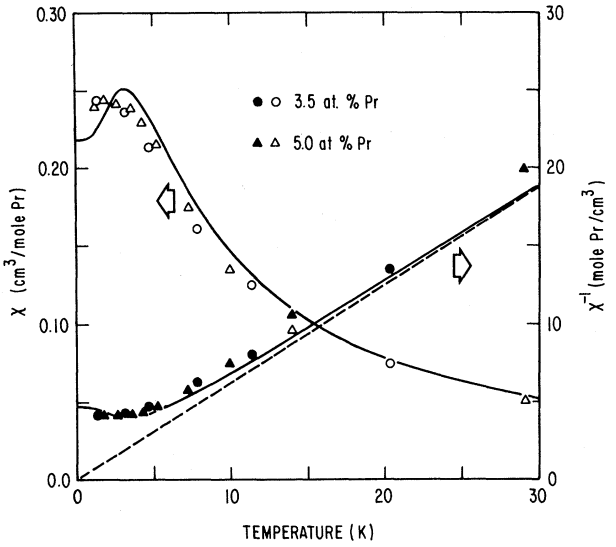

FIG. 3. Magnetic susceptibility χ (open symbols) and inverse magnetic susceptibility χ^{-1} (solid symbols) versus temperature for the $(La\mathrm{Pr})\mathrm{Sn}_3$ system (BL data) for impurity concentrations of 3.5 and 5.0 at.% Pr. The solid curves are derived from the Pr^{3+} energy-level scheme of Fig. 2(b) using second-order perturbation theory. The dashed line represents the high-temperature asymptotic "Curie law" dependence for a ninefold degenerate Pr^{3+} $J=4$ Hund's-rule multiplet.

curves of T_c/T_{c_0} versus n and $\Delta C/\Delta C_0$ versus T_c/T_{c_0} for the $(La\mathrm{Pr})\mathrm{Sn}_3$ system within the framework of the theory of Keller and Fulde.[2,4] The results are represented by the solid curves in Figs. 1(a) and 1(b). The initial slope of the theoretical T_c/T_{c_0} versus n curve, which depends upon the strength of the exchange interaction, has been fitted to the UCSD data at small Pr concentrations. The theoretical $\Delta C/\Delta C_0$ versus T_c/T_{c_0} curve does not depend on any adjustable parameters.

The positive curvature of T_c/T_{c_0} versus n in Fig. 1(a) is typical of systems in which the dominant pair-breaking contribution is from inelastic-exchange scattering processes involving transitions between a nonmagnetic ground state and the lowest excited states of the rare earth impurities. For Pr^{3+} ions in a cubic crystal field, Γ_4 is the only level which is connected to Γ_1 according to the selection rules for exchange scattering. However, elastic and inelastic scattering processes involving the thermally populated magnetic Γ_5 state also contribute considerably to the depairing when, as in the present case, the triplet Γ_5 level has a lower excitation energy than the triplet Γ_4 level. The numerical calculations, which take this into account, are in good agreement with the experimental results except for samples with high impurity concentrations. This disparity between the experimental and calculated T_c/T_{c_0} versus n curves for $n \gtrsim 4$ at.% Pr may be produced by the pairing mechanism that is associated with aspherical Coulomb scattering. Selection rules for aspherical Coulomb scattering allow transitions between the singlet Γ_1 ground state and the triplet Γ_5 and doublet Γ_3 excited states. A numerical analysis based on Ref. 1 reveals that Δ_{15} has to be $\gtrsim 6T_c$ in order to detect an enhancement of T_c after the initial slope of the T_c/T_{c_0} versus n curve has been adjusted. Thus we expect to observe this effect only for $T_c/T_{c_0} \lesssim 0.2$. This is in accord with experiment as illustrated in Fig. 1(a).

With respect to the behavior of $\Delta C/\Delta C_0$ versus T_c/T_{c_0}, Fig. 1(b) shows that the theory provides a rather good description of the data. It is the depairing effect of the low-lying Γ_5 energy level that is responsible for the large departure of the $\Delta C/\Delta C_0$ versus T_c/T_{c_0} curve from the BCS and AG curves.

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