Low Temperature Properties of (La, Nd)Sn$_3$ Alloys

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Dilute (La$_{1-x}$Nd$_x$)Sn$_3$ alloys with $0.01 < x < 0.15$ are characterized by determination of the superconducting transition temperature $T_c$ as well as low temperature measurements of the specific heat and inelastic neutron scattering. As an important result of these experiments we found that the Nd impurities in LaSn$_3$ exist as stable trivalent ions, in contrast to all other light rare earths. In addition, specific heat and neutron scattering results revealed the scheme of crystal field (CF) levels of Nd$^{3+}$. Using this level scheme, the concentration dependence of the superconducting transition temperature, $T_c(x)$, could be quantitatively fitted up to $x \approx 9$ at % by the theory of Keller and Fulde [J. Low. Temp. Phys. 4, 289 (1971)]. From the relatively high initial slope of $T_c(x)$ we inferred that - besides isotropic spin exchange - other pair-breaking processes are important.

In contrast to $T_c(x)$, the reduced specific heat jumps $\Delta C/\Delta C_0$ as a function of $T/T_c$ were found to lie considerably below the theoretical curve for isolated Nd$^{3+}$ ions. This is explained by Nd–Nd interactions resulting in a mean Zeeman splitting ($< k_B T_d$) of the CF ground state, which could be directly observed in the form of broadened Schottky humps in the normal state specific heats.

I. Introduction

In dilute magnetic alloys containing rare earth (RE) impurities certain quantities, e.g. the initial depression of the superconducting transition temperature $T_c$, scale with the de Gennes factor $(g - 1)^2 J(J + 1)$, where $g$ is the Landé factor and $J$ is the quantum number of the total angular momentum of the RE impurities. This behavior has been proved experimentally for the alloys LaRE and (La$_{1-x}$RE)Al$_2$ [1]. There, only Ce impurities cause a deviation from this scaling law as a consequence of hybridization between 4f- and conduction electrons.

Two of the authors have found previously that in (La, RE)Sn$_3$ the initial depression of $T_c$ is not at all correlated with the de Gennes factor [2]. Especially all the light RE impurities depress $T_c$ essentially stronger. One could think of two reasons for this striking behavior, namely hybridization effects and/or additional scattering processes of the conduction electrons at the RE impurities, not only the isotropic spin exchange scattering.

Several experiments, performed recently on LaSn$_3$ with Ce, Pr and Sm support the relevance of hybridization effects for these alloys. The dependence of $T_c$ on the Ce concentration has been discussed in the
framework of Kaiser's theory for nonmagnetic states [3].

In the investigations on (La, Sm)Sn₃, both, Kondo effect and valence fluctuations are discussed in order to explain various experiments [4, 5]. Very recent experiments show, however, that valence fluctuations can be ruled out [6].

(La, Pr)Sn₃ shows an anomaly in the resistivity which indicates a Kondo effect [7]. But from the crystal-field (CF) splitting, Pr³⁺ in LaSn₃ has a singlet ground state [8], thus the unusual situation arises that the Kondo anomaly results from an interaction of the conduction electrons with excited CF levels. Furthermore it is surprising, that the Kondo effect does not appear in other quantities, e.g. the jump of the specific heat at \( T_c \) [8].

With respect to the value of the initial depression of \( T_c \), the Kondo effect should be of importance, but we want to emphasize that no theory exists for systems where the Kondo effect is correlated with the CF splitting except for systems containing the 4f¹ and 4f¹³ ions, Ce³⁺ and Yb³⁺ [9]. Therefore, it is not possible to decide to what extent the enhanced \( T_c \) depression in (La, Pr)Sn₃ results from a Kondo effect. Finally it should be noted that in (La, Pr)Sn₃ a pair enhancement effect due to the aspherical Coulomb scattering has been found [8]. This scattering process is of the type \( (\Sigma, \Lambda) = (0, 2) \) in the notation of Hirst [10]. Thus, it is not unreasonable to expect that also other (pair breaking) scattering processes discussed in Ref. 10 are relevant in (La, Pr)Sn₃ and other (La, RE)Sn₃ alloys.

We have investigated LaSn₃ with Nd, which – from its position in the middle of the light RE series – is expected to be a stable trivalent ion. In a previous paper [11] we have shown that actually no Kondo anomaly appears in the electrical resistivity. We have also reported preliminary results of the specific heat and the \( T_c \)-depression [12]. A detailed discussion of the resistivity will be given in a following paper [13]. In this paper we report on measurements of the specific heat and neutron scattering, which reveal the CF splitting of the Nd³⁺ ions. Measurements of the superconducting transition temperature as a function of the Nd concentration and the reduced jump of the specific heat as a function of the reduced transition temperature are then compared with calculations taking into account this CF splitting. In order to draw out the open problems we start the presentation of the results with a discussion of both, the initial depression of \( T_c \) for the alloy systems (La, RE)Sn₃ and the magnetic ordering temperatures of the binary compounds RESn₃.

II. Sample Preparation

The alloys (La, Nd)Sn₃ were prepared by high frequency melting on a water-cooled copper crucible in an atmosphere of highly purified argon. The elemental purity was La – 99.99 %, Nd – 99.99 % and Sn – 99.999 %. First, the (La, Nd) composition was prepared by melting the corresponding quantities of the constituent elements or by diluting a master alloy. The procedure depended on the final Nd concentration required. In any case, the (La, Nd) alloys were melted several times, turning around the sample after each melting process. Ensuing, the alloy (La, Nd)Sn₃ was melted several times in the same way and then the melt was quenched to room temperature. Alternatively, LaSn₃ and RESn₃ were produced first, and then the desired alloys were prepared in a similar way from these constituents. No difference could be found in the quality of the samples.

For the determination of \( T_c \) by the ac susceptibility, small amounts (\( \approx \) 10 mg) were used, taken from the big samples or from additional alloys with a weight of about 0.3 grams. For the neutron scattering experiments we used a total amount of 24 grams consisting of 15 samples.

X-ray measurements, performed with a goniometer, showed that the samples were of pure phase within a resolution of better than one percent. Samples which were not quenched from the melt revealed tin precipitations with a typical amount of some percent increasing with the mass of the sample. Furthermore it should be noticed that different heat treatments have been carried out. In a vacuum of \( 10^{-6} \) Torr various temperatures from 190°C up to 850°C have been applied for 3 days. However, no essential improvement of the samples was achieved with respect to the sharpness of the superconducting transition or the X-ray spectrum.

Furthermore, we have carefully measured the lattice constants of the alloys (La₁₋ₓNdₓ)Sn₃ in the full concentration range \( 0 \leq x \leq 1 \) and found strictly linear dependence of the lattice constant on the Nd concentration \( x \). The mean scatter of the data, caused by instrumental sources, corresponds to an uncertainty in \( x \) of \( \pm 0.01 \). From this, Nd precipitations do not play an important role, not even in the higher concentrated alloys.

III. Superconducting Transition Temperature

The measurement of \( T_c \) with the ac susceptibility was done by putting a small amount of a powdered sample into the inductance of a resonance circuit and