PRESSURE-INDUCED MAGNETIC-NONMAGNETIC TRANSITION OF Ce IMPURITIES IN La†

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A transition of Ce impurities from a magnetic to a nonmagnetic state has been observed in superconducting La:Ce alloys at high pressure. The critical pressure for maximum pair breaking in La:Ce alloys is lower for the fcc than for the dhcp phase. The highest transition temperature of an elemental superconductor (12°K) is reported for pure La at 140 kbar.

In a recent Letter, a minimum was reported in the variation of the superconducting transition temperature (T_c) of $(La:Ce)_3In$ alloys with pressure (P).[1] From this it was inferred that the pair-breaking parameter (which characterizes the reduction of T_c by the Ce impurities) initially increases with pressure and then goes through a maximum associated with a transition of the Ce impurity from a magnetic to a nonmagnetic state.[2] However, the maximum pressure of 23 kbar attained in this experiment was not sufficient to achieve an appreciable reduction in pair breaking above the critical pressure. In order to observe the complete pressure-induced magnetic-nonmagnetic transition of the Ce impurity, and yet avoid the experimental difficulties associated with the $(La:Ce)_3In$ system,[3] we have studied the pressure dependence of T_c of La:Ce alloys to pressures as high as 140 kbar.

Pair breaking in La:Ce alloys has previously been observed to increase with pressure up to 10 kbar.[4] Our measurements confirm this observation, but in addition show that fcc La:Ce alloys, similar to $(La:Ce)_3In$ alloys, exhibit maximum pair breaking at a critical pressure near 15 kbar (Fig. 1). Moreover, by applying very high pressure we have achieved a substantial reduction in pair breaking above ~15 kbar which is apparently due to a complete transition of the Ce impurity from a magnetic to a nonmagnetic state (Fig. 2). A residual depression of T_c, approximately constant above ~100 kbar, is attributed to resonance scattering from the resultant nonmagnetic virtual impurity level near the Fermi level. The measurements also show that maximum pair breaking in dhcp La:Ce alloys would occur, were it not for the dhcp-fcc phase transition, at a higher pressure than in fcc La:Ce alloys (Fig. 1).

As-cast as well as dhcp La:Ce alloys were studied. The as-cast samples, prepared by melting the constituents under argon in a conventional arc-furnace, were undoubtedly mixtures of both fcc and dhcp phases of La, although the T_c of the as-cast La (5.9°K) suggests that these alloys were predominantly fcc (T_c = 6.0°K for fcc La). After measurement in the as-cast state, the alloys were converted to the dhcp phase by cold-rolling the ingots into foils ~0.1 mm in thickness which were subsequently annealed at 200°C for one day. The T_c of dhcp La prepared in this way was found to be 4.88°K, in good agreement with recently reported values of 4.87°K.[5]

A Be-Cu clamp was employed to generate pressures up to 23 kbar. Pressure was transmitted to the sample and superconducting manometer (Pb or Sn) nearly hydrostatically through a 1:1

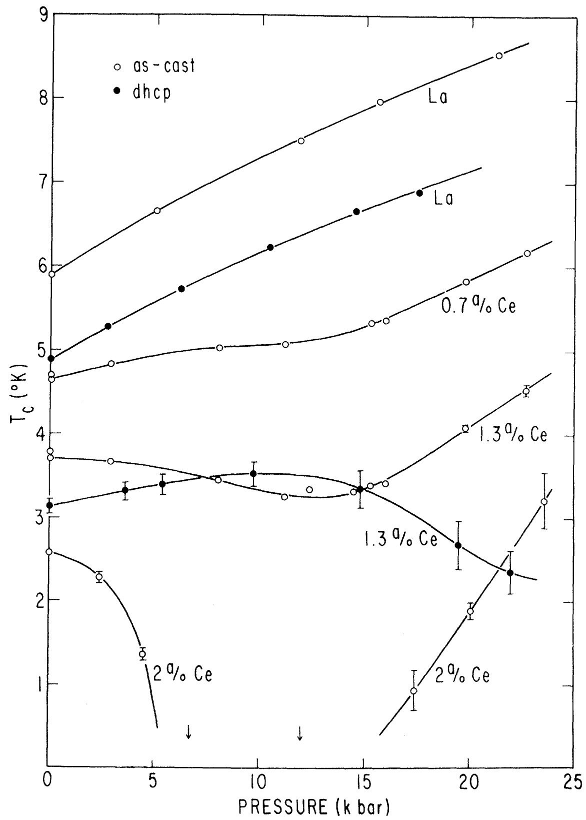

FIG. 1. The superconducting transition temperature (T_c) of a series of La:Ce alloys as a function of pressure. Nominal Ce compositions are indicated for each curve. Transition widths are denoted by vertical bars where greater than the diameter of the circles.

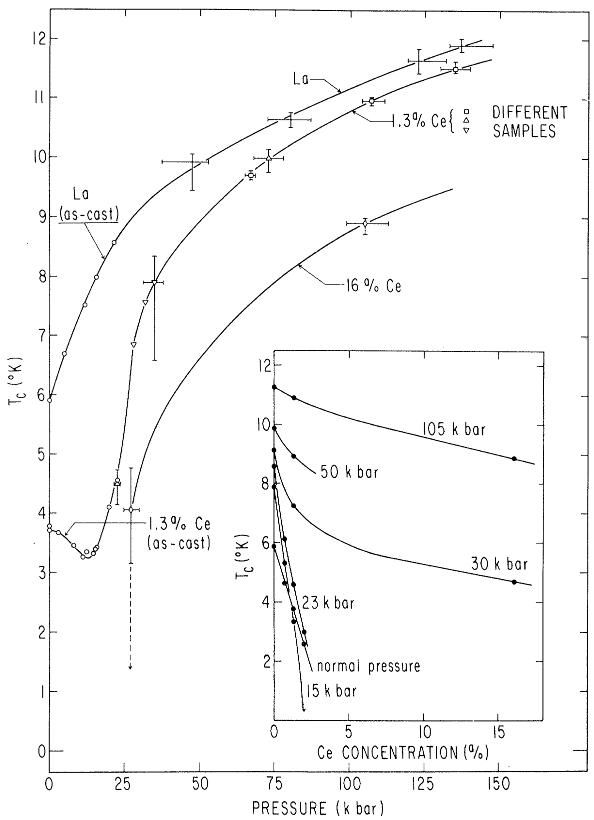

FIG. 2. Pressure dependence of the superconducting transition temperature (T_c) of pure La and two La:Ce alloys (1.3 and 16 at.% Ce) to very high pressures. The low-pressure data of Fig. 1 for pure La and one La:Ce alloy (1.3 at.% Ce) in the as-cast state are indicated by the open circles. The vertical bars represent the transition widths rather than uncertainty of the temperature measurement and the horizontal bars the pressure inhomogeneity in the cell. Isobars of T_c versus Ce concentration for as-cast alloys are shown in the inset.

mixture of isoamyl alcohol and n-pentane. An ac (140 cps) mutual-inductance technique was used to detect the transition to the superconducting state. Measurements between 20 and 140 kbar were performed with an opposed-anvil press designed for work at low temperatures.[6] The electrical resistance of the sample and a superconducting Pb manometer was measured by means of a six-lead dc technique. Superconducting transition curves are characterized by midpoint and transition width. Conversion of the manometer data into pressure values is based on the recently reinvestigated relation between T_c and P for Pb.[6] According to this work the corresponding horizontal bars of Fig. 2 represent the upper limit for the difference in pressure between sample and manometer (apart from an empirical factor of 1.3). Hence these horizontal bars are the error limits for the pressure determination. However, the small scatter of the data for three independent runs with the 1.3-at.% Ce samples (Fig. 2) shows that much higher accuracy is usually achieved.

Curves of T_c vs P between 0 and 23 kbar for as-cast La:Ce alloys of concentrations 0.7, 1.3, and 2 at.% Ce are shown in Fig. 1. The depression of T_c for the 0.7 and 1.3-at.% Ce samples shows that maximum pair breaking occurs near 15 kbar. As discussed previously,[1] within the first Born approximation of magnetic scattering of conduction electrons by magnetic-impurity spins, the magnitude of the pair-breaking parameter at any pressure is proportional to the concentration of paramagnetic impurities. This implies that pressure will have a greater effect on T_c for higher Ce concentrations, and a most striking demonstration of this is shown in Fig. 1. For the 2-at.% Ce sample, regions of superconductivity above ~0.35°K are separated by a "normal" gap on the pressure axis between 5 and 15 kbar.

For a dhcp sample (1.3 at.% Ce; Fig. 1), the pair-breaking parameter does not exhibit a maximum, but rather increases monotonically with pressure to ~23 kbar. It was not possible to establish the critical pressure for maximum pair breaking in the dhcp La:Ce alloy by the high-pressure opposed-anvil method, since the sample starts to transform into the fcc phase above 23 kbar as observed by monitoring the resistivity at room temperature. Therefore, for pressures exceeding ~23 kbar, T_c vs P is characteristic of the fcc phase regardless of the metallurgical history of the sample below 23 kbar. Actually, another rather sluggish phase transformation may occur above 70 kbar as indicated by the pressure dependence of the room-temperature resistivity. However, no discontinuities in $T_c(P)$ were observed at high pressure.

The results of the high-pressure measurements are shown in Fig. 2. For pure La, T_c increases monotonically with pressure to ~12°K at 140 kbar,[7] whereas T_c for the 1.3-at.% Ce alloy, above the minimum near 13 kbar, converges rapidly toward pure La with increasing pressure and is approximately parallel above ~100 kbar. From these data, the depression of T_c equals 0.4 ± 0.2°K above kbar, 4.5°K at maximum pair breaking (15 kbar), and 2.2°K at normal pressure. Hence the depression of T_c at high pressures ≳100 kbar is more than an order of magnitude smaller than at maximum pair breaking, and at least five times smaller than at normal pressure.[8] Further, a 16-at.% Ce sample, well above the normal-pressure critical concentration of ~3 at.% Ce, is superconducting above 27 kbar. The inset of Fig. 2 shows the isobaric concentration dependence of T_c for the as-cast La:Ce alloys.

For comparison, $T_c(P)$, measured to 125 kbar for a 0.7-at.% Gd sample, behaved qualitatively like pure La, showing that no substantial change in the magnetic character of the Gd impurities occurs in this pressure range.

The magnetic-nonmagnetic transition we infer from the variation of pair breaking in La:Ce and $(La{:}Ce)_3In$ alloys with pressure can be most simply understood in terms of the Anderson model of localized magnetic states in metals.[9] At normal pressure, the spin-up Ce 4*f* sublevel is assumed to lie slightly below the Fermi level and is occupied, while the spin-down sublevel, split by the Coulomb interaction from the spin-up sublevel, lies above the Fermi level and is unoccupied. As discussed previously,[10] the proximity of the Ce 4*f* level to the Fermi level gives rise to an admixing of Ce 4*f* with conduction-band states. This in turn generates a large antiferromagnetic coupling of conduction-electron and magnetic-impurity spins which increases in magnitude as the *f* level approaches the Fermi level with increasing pressure and accounts for the initial increase of pair breaking with pressure. However, the self-consistent conditions for the existence of a localized magnetic moment in the Anderson model cooperatively break down when the energy separation between the *f* level and the Fermi level becomes too small leading to a decrease in pair breaking as the spin-up and spin-down sublevels become degenerate and nonmagnetic. The residual pair breaking at very high pressures appears to be due to resonance scattering[11] by the resultant nonmagnetic Ce 4*f* level which remains in the proximity of the Fermi level. Alternatively, the *f* level may be well above the Fermi level, and the Ce 4*f* electron transferred into a nonmagnetic virtual 5*d* level near the Fermi level, leading to the residual depression of T_c by resonance scattering at high pressure.

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[1]M. B. Maple and K. S. Kim, Phys. Rev. Letters 23, 118 (1969).

[2]This would be the analog of the magnetic-nonmagnetic transition occurring in elemental Ce under pressure which was most decisively demonstrated by the observation of superconductivity in Ce at high pressure [J. Wittig, Phys. Rev. Letters 21, 1250 (1968)].

[3]T_c of La_3In was found to be very sensitive to the cold work introduced by the opposed-anvil method for generating high pressures, particularly during sample preparation. In spite of this, at high pressure $T_c(P)$ for cold-worked $(La{:}Ce)_3In$ alloys behaves qualitatively as reported here for fcc La:Ce alloys.

[4]T. F. Smith, Phys. Rev. Letters 17, 386 (1966).

[5]D. L. Johnson and D. K. Finnemore, Phys. Rev. 158, 376 (1967); T. Sugawara and H. Eguchi, J. Phys. Soc. Japan 23, 965 (1967).

[6]A. Eichler and J. Wittig, Z. Angew. Phys. 25, 319 (1968).

[7]This is the highest T_c yet reported for an elemental superconductor. Our measurements also show that T_c of dhcp La is ~1°K lower than that of fcc La up to the dhcp-fcc phase transformation at 23 kbar, in quantitative disagreement with the measurements on La reported by T. F. Smith and W. E. Gardner [Phys. Rev. 146, 291 (1966)]. This discrepancy probably arises because these authors studied a two-phase sample (judgfrom the normal pressure T_c of 5.5°K) subjected to pressures which were not sufficiently homogeneous. Our measurements do however qualitatively confirm their initial observation that both the dhcp and fcc phases of La exhibit a positive dependence of T_c on pressure.

[8]After submission of this Letter we were able to reduce considerably the quoted error limits for the residual depression of T_c at high pressure. We measured the quantity ΔT_c directly by comparing the T_c of pure La and the 1.3-at.% Ce alloy in the same pressure cell, thus avoiding the Pb manometer and consequently the higher combined error. This experiment yields $|\Delta T_c| = 0.31 \pm 0.08$°K at ~140 kbar ($T_{c,\mathrm{La}} = 11.93$°K).

[9]P. W. Anderson, Phys. Rev. 124, 41 (1961).

[10]Ref. 1 and references cited therein; also G. Toulouse and B. Coqblin, Solid State Commun. 7, 853 (1969).

[11]M. J. Zuckermann, Phys. Rev. 140, A899 (1965).