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Heat Capacity of the Superconducting-Kondo System $(LaCe)Al_2$*

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Abstract

Heat capacity measurements on $(LaCe)Al_2$ between 0.07 and 20K, show that the crystal-field ground state of the Ce ion is a doublet, and confirm the occurence of the Kondo effect in the normal state. In the superconducting state there is evidence for an impurity band at low energies within the gap and for a second order transition at the lower critical temperature, T_{c2}.

Recent theoretical[1-6] and experimental[7] work has shown that the properties of superconductors containing magnetic impurities depend strongly on the sign of the conduction electron-impurity spin exchange parameter $\mathcal{J}$. When $\mathcal{J} < 0$, the Kondo effect occurs in the normal state with a characteristic temperature T_K. For $T_K \ll T_{c0}$, where T_{c0} is the critical temperature for superconductivity in the pure host, "reentrant" behavior has been predicted[4] over a limited range of impurity concentration - as the temperature is reduced an alloy with an impurity concentration within this range should first become superconducting at T_{c1}, normal again at T_{c2} and finally superconducting at T_{c3}. The system $(LaCe)Al_2$ has been identified as showing this type of behavior: several properties suggest[8-14] that $\mathcal{J} < 0$, and a return to the normal state with decreasing temperature has been observed at T_{c2}[15,16] although no evidence has been found for a transition back to the superconducting state at T_{c3} to temperatures as low as 6 mK.[16] In this note we present the results of heat capacity measurements on several $(LaCe)Al_2$ alloys with Ce concentration varying from zero to above the turning point concentration of the reentrant T_c vs. Ce concentration curve. The measurements extend below the temperature of the maximum in C_n, the normal-state heat capacity, and, for the one sample that shows reentrant superconducting behavior, below T_{c2}. The results show that (1) the ground state of the Ce ion in the cubic $LaAl_2$ matrix is a doublet, (2) the Kondo effect occurs in the normal state with $T_K = 0.42K$, (3) for small Ce concentrations and low temperatures there is an upturn in C_s, the superconducting-state heat capacity, which is consistent with recent theoretical predictions of an impurity band at low energies within the gap, and (4) within the Ce concentration range in which alloys exhibit reentrant superconductive behavior, the transition at T_{c2} is second order.

Measurements were made on samples with 0, 0.193, 0.640 and 0.906 at.% Ce substituted for La, in the temperature range 0.07 to 20K, and in magnetic fields from 0 to 38 kOe. The 0.640 at.% Ce sample showed reentrant superconductive behavior with T_{c1}=1.1K and T_{c2}=0.25K, as determined by ac mutual inductance measurements. The 0.906 at.% Ce sample showed no transition to the superconducting state at temperatures above 0.3K, consistent with a turning point concentration of 0.67 at.% Ce. The samples were prepared as described in connection with other work except that the 0.906 at.% Ce sample was annealed at 800°C for one week (rather than 16 h). Between 0.5 and 4.2K, the results are similar to those obtained in earlier heat capacity measurements[10] that covered only that interval.

A complete analysis of the data on all samples[17] shows that the lattice and normal state electronic heat capacities of the alloy samples are the same as those of pure $LaAl_2$. [The high-temperature tail of the Kondo anomaly (Fig. 1) appeared as an apparent enhancement of γ in the earlier measurements[10]]. In magnetic fields high enough to quench superconductivity, the magnetic impurity contribution to the heat capacity is approximately proportional to the Ce impurity concentration c and approaches the temperature dependence associated with the Kondo effect in the low field limit. This is illustrated in Fig. 1, where ΔC, the heat capacity in excess of that of the pure host, is plotted as $\Delta C/c$ vs. log T for the 0.640 at.% Ce sample. Curves a and b represent the 38 and 20 kOe data respectively for all the alloy samples to within experimental error, and correspond to an entropy of Rln2 per mole Ce. This shows that the Ce ground state has an effective spin of 1/2, in accord with magnetic susceptibility measurements which indicate that the cubic crystal field splits the Ce^{3+} J=5/2 multiplet into an excited-state quartet and a ground-state doublet with a splitting of ~100K[7,8]. Curve c was drawn to fit the 2 kOe data for the 0.906 at.% Ce sample, and it differs slightly in shape from fits to the data for the 0.640 and 0.193 at.% Ce samples. This difference may be associated with the difference in heat treatment of the samples. Curve d was originally drawn to fit data[18] on CuCr alloys and it is also consistent with the calculations of Bloomfield and Hamann[19]. As redrawn in Fig. 1, shifted in temperature and scaled by a factor of 1/2 to correspond to an entropy of Rln2 per mole Ce, it also fits the zero field data for the 0.906 at.% Ce sample. It is a good approximation to the 0.5 kOe normal state data for the 0.640 at.% Ce sample (and also to the zero field data for that sample for which it might be expected that the normal-state and superconducting-state electronic heat capacities do not differ much). The good agreement of curve d with the $(LaCe)Al_2$ data provides confirmation of the Kondo effect in this system. Comparison with the Bloomfield-Hamann theory also gives T_K=0.42K, in reasonable agreement with other estimates[8-14] of T_K, which range from 0.1 to 1K.

An anomaly in the zero-field data for the 0.640 at.% Ce sample is visible near T_{c1} in Fig. 1, and is shown more clearly as a plot of $\Delta C = C_s - C_n(H=0)$ in Fig. 2. [In Fig. 2, the zero-field experimental data were used for C_s, and $C_n(H=0)$ was taken as a smooth curve through the 0.5kOe data corrected to H=0 using the temperature dependence of $C_n(H=0.5\text{ kOe}) - C_n(H=0)$ for the 0.906 at.% Ce sample, but scaling the correction to make ΔC go to zero in the low-temperature limit.] The anomaly at T_{c1} has a shape consistent with a slightly broadened second-order transition. It is similar to that observed by Steglich and Armbrüster[20] who have shown that its size is consistent with a bulk superconducting transition. In Fig. 2 a similar anomaly appears just below T_{c2}, and the negative values of C_s-C_n(H=0) required by the equality of the free energies at T_{c1} occur at intermediate temperatures. [The shapes of the anomaly at T_{c2} and of C_s-C_n(H=0) at intermediate temperatures depend on the assumptions made in deriving C_n(H=0), but the existence of the anomaly is clear in any precise comparision of the zero-field and 0.5 kOe data.] The anomaly at T_{c2} appears to be smaller than that at T_{c1}, but that would be quite reasonable in view of the lower temperature, and we believe it is evidence for a bulk second-order transition.

The zero field normal-and superconducting-state heat capacities of the 0.193 at.% Ce sample are compared in Fig. 3. The points represent zero field data for $C - C_L$, where C_L is the lattice heat capacity; the horizontal line represents the normal state electronic heat capacity; the dashed and dash-dot curves represent, respectively, the sum of the normal state electronic and impurity heat capacities, and the normal state impurity heat capacity. Below 0.54K the total superconducting state heat capacity is less than the normal state impurity heat capacity alone. This shows clearly the modification of the Kondo effect by the formation of Cooper pairs. At temperatures from 0.3K to the lowest temperature reached, 0.08K, the superconducting state heat capacity increases with decreasing temperature. Unfortunately, the measurements do not extend to low enough temperatures to reveal the maximum in C_s

below 0.08K which is required by the equality of the normal and superconducting state entropies at 0K and T_c. Although the theory has not been developed to the point of permitting a quantitative comparison, this increase is qualitatively consistent with the predicted[6] impurity band at low energies in the gap.

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Figures

Fig. 1 - The heat capacity of the 0.64 at.% sample. (See text for complete explanation).

Fig. 2 - The superconducting-state heat capacity minus the zero-field normal-state heat capacity for the 0.64 at.% sample. (See text for complete explanation).

Fig. 3 - The sum of the magnetic and electronic heat capacities of the 0.193 at.% sample in zero field. (See text for complete explanation).

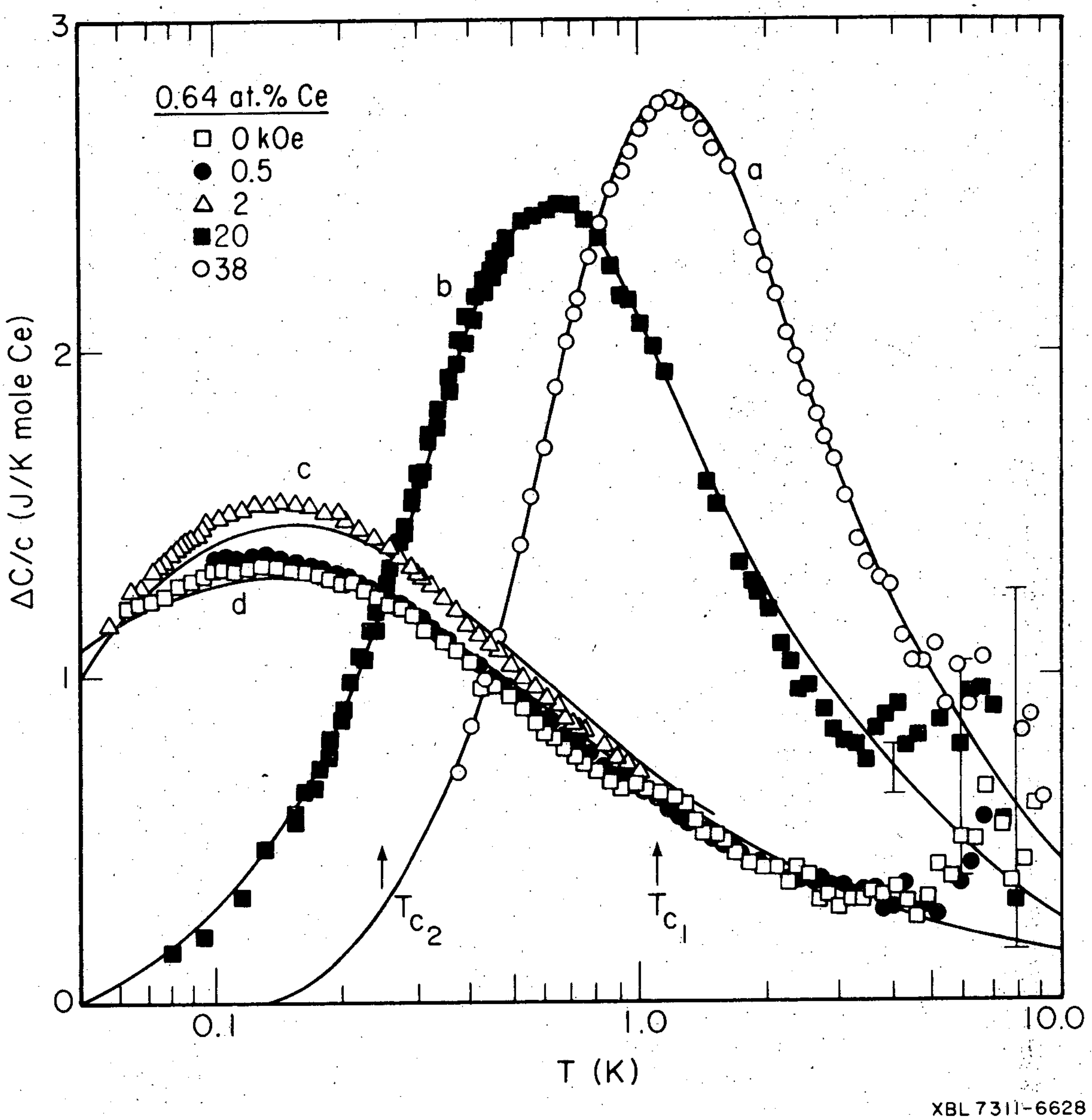
0.64 at.% Ce
0 kOe
0.5
2
20
38
a
b
c
d
T_{c_2}
T_{c_1}
ΔC/c (J/K mole Ce)
T (K)
0.1
1.0
10.0
0
1
2
3
XBL 7311-6628

Fig. 1

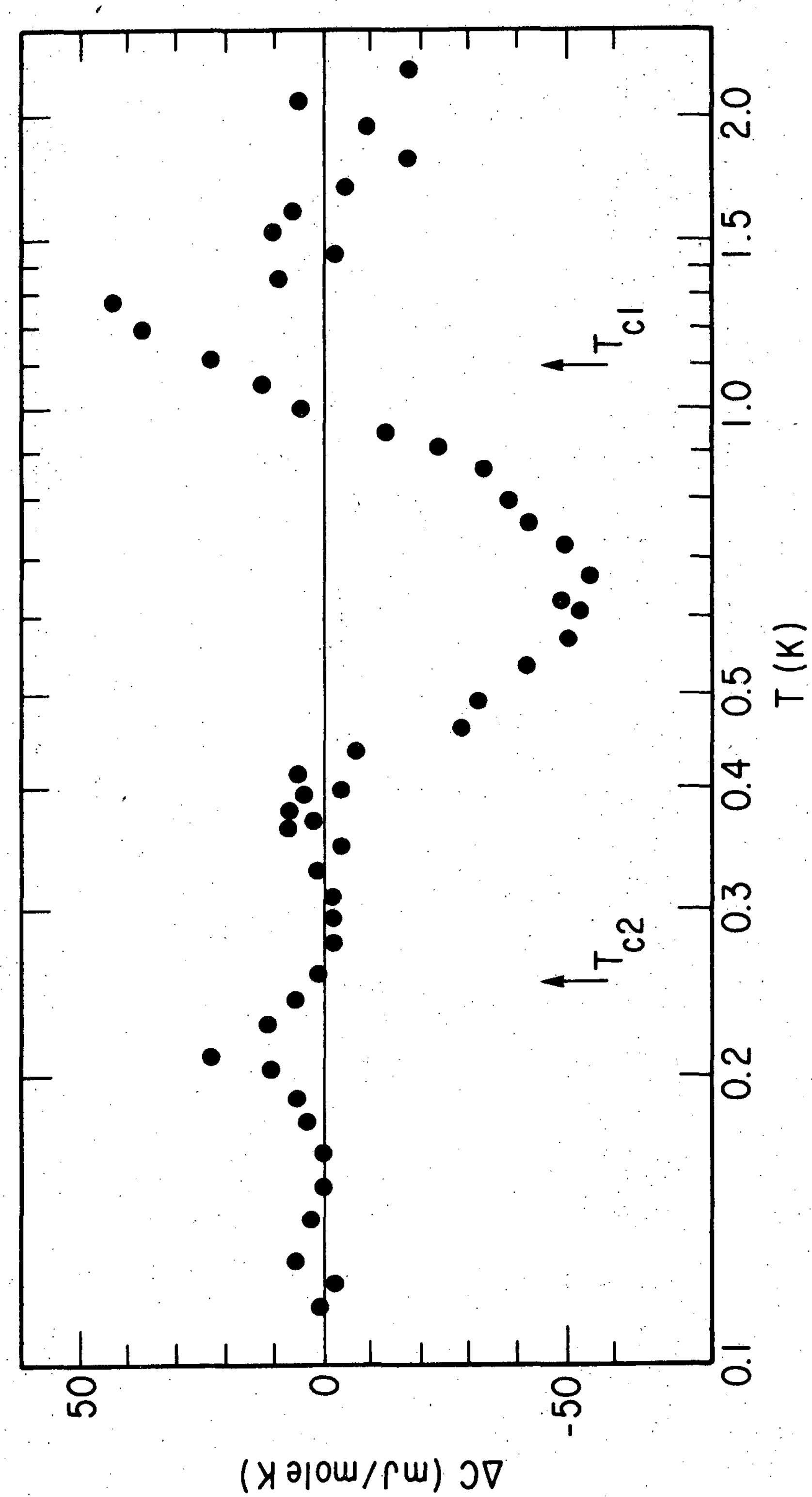

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Fig. 2

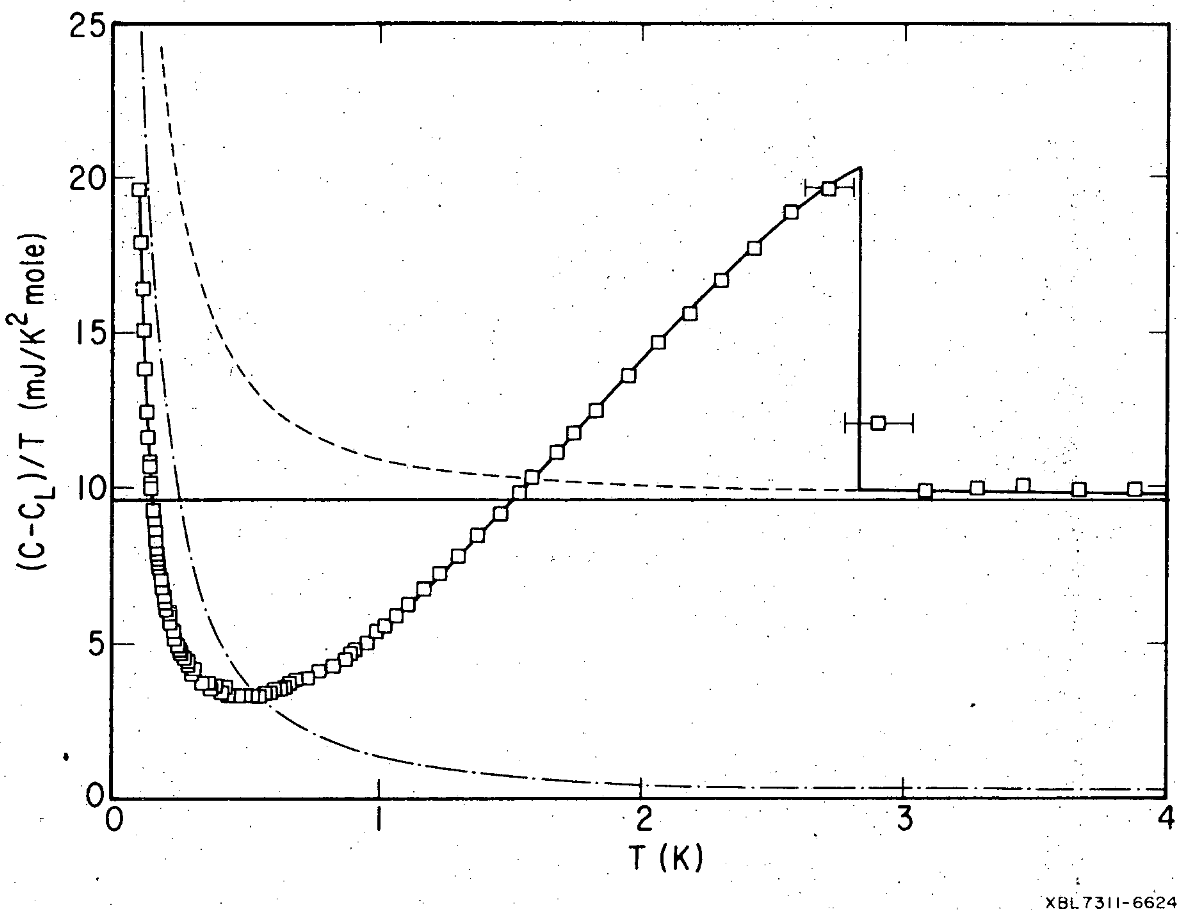

Fig. 3