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Authors
Bader, S.D.
Fogle, W.E.
Phillips, Norman E.
et al.

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S. D. Bader, W. E. Fogle, Norman E. Phillips, M. B. Maple, and C. A. Luengo

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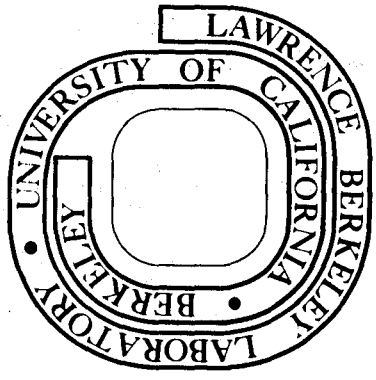

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HEAT CAPACITY OF THE SUPERCONDUCTING KONDO SYSTEM (LaCe)Al_2*

S. D. Bader,+ W. E. Fogle, and Norman E. Phillips

Inorganic Materials Research Division of the
Lawrence Berkeley Laboratory and Department of Chemistry
University of California, Berkeley, California 94720 U.S.A.

and

M. B. Maple and C. A. Luengo

Institute for Pure and Applied Physical Sciences,
University of California, San Diego, La Jolla, California 92037

The addition of magnetic impurities to a superconducting host introduces a "pair-breaking mechanism", i.e. the impurities interfere with the formation of Cooper pairs. In general, magnetic impurities tend to suppress the transition to the superconducting state, but the detailed behavior depends on the impurity concentration, on the relative strengths of the conduction electron-impurity exchange interaction and the net attractive interaction between electrons in the pure host, and on the sign of J, the conduction electron-impurity exchange parameter (1). When $J < 0$, 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 (2) 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}. Solutions of $CeAl_2$ (in which localized magnetic moments are associated with the Ce ions) in the superconductor $LaAl_2$ have been identified as showing this type of behavior; several properties indicate (3-9) that $J < 0$, and a return to the normal state with decreasing temperature has been observed (10,11) at T_{c2} [although no evidence has been found for a transition back to the superconducting state at T_{c3} to temperatures as low as

6 mK (11)]. To obtain more information on this system, we have made 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}.

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 20 K, and in magnetic fields from 0 to 38 kOe. The 0.640 at. % Ce sample showed reentrant superconductive behavior with T_{c1} = 1.1 K and T_{c2} = 0.25 K, as determined by ac mutual inductance measurements [see Figure 1(a)]. The 0.906 at. % Ce sample showed no transition to the superconducting state at temperatures above 0.3 K, 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 4.2 K, the results are similar to those obtained in earlier heat capacity measurements (5) that covered only that interval.

A complete analysis of the data on all samples 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 (Figure 2) appeared as an apparent enhancement of γ in the earlier measurements (5)]. 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 Figure 2, 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 unambiguously that the Ce ground state has an effective spin of 1/2, in accord with magnetic susceptibility measurements which suggest 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 100 K (7,8). Curve d represents the heat capacity associated with the formation of the Kondo spin-compensated state in zero-magnetic field. It was originally drawn to represent data (12) on CuCr, a typical and well-established Kondo system, in the single-impurity limit. It is also consistent with the calculations of Bloomfield and Hamann (13). As redrawn in Figure 2, 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

FIGURE 1

(a) Magnetically determined transitions in the 0.640 at. % Ce sample
(b) Zero field and 0.5 kOe heat capacity data for the 0.640 at. % Ce sample, relative to the zero-field normal-state heat capacity. The error bars represent the effect of a 1 % error in the total measured heat capacity.

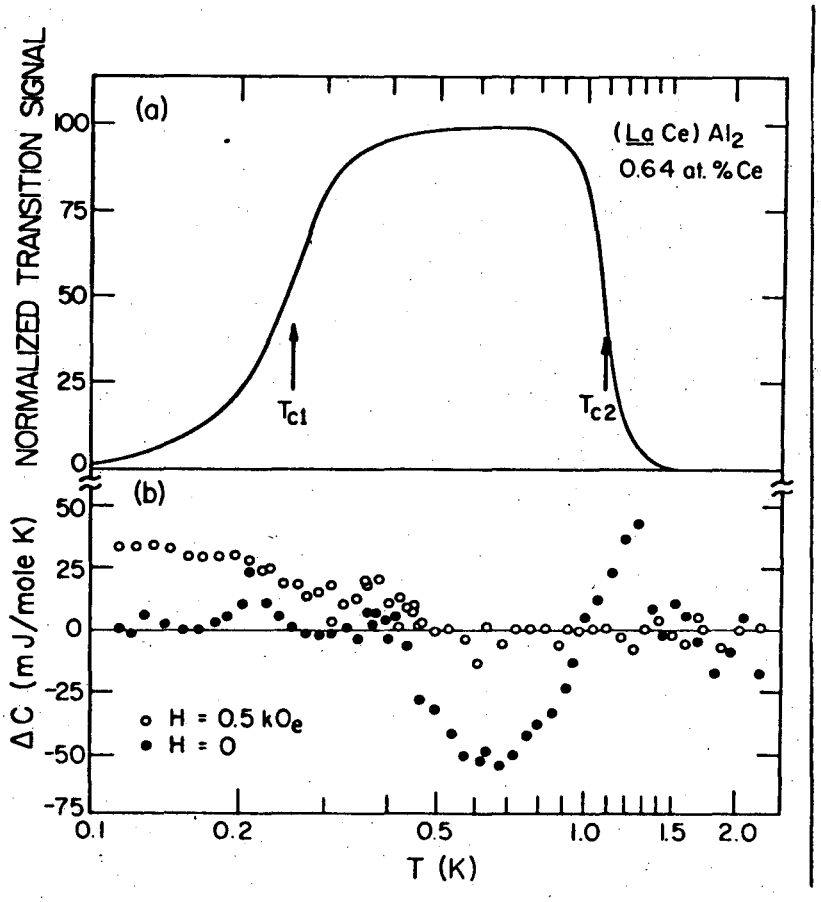
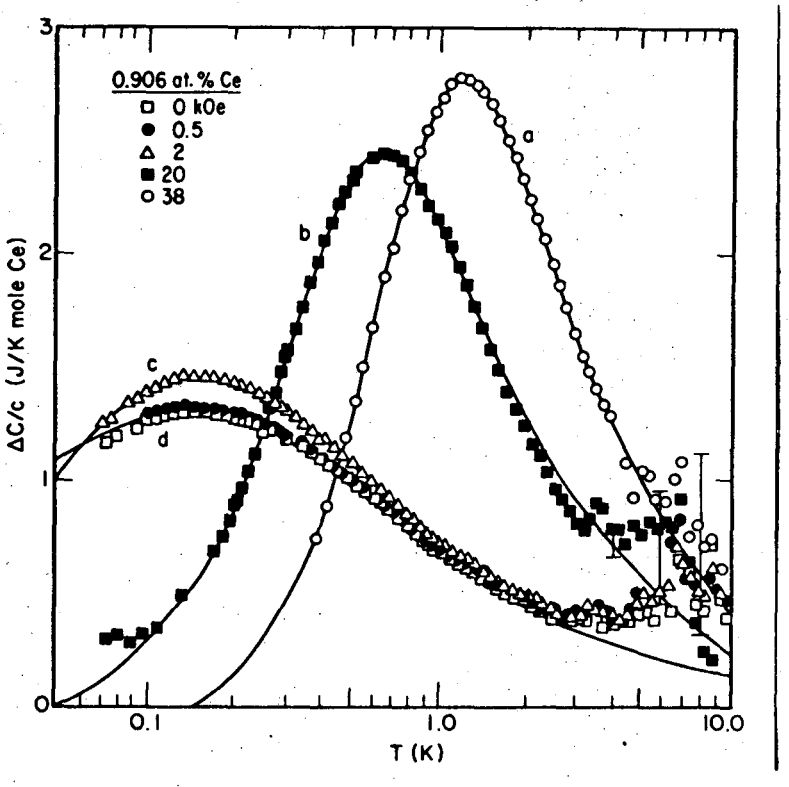


FIGURE 2

Heat capacity of the 0.64 at. % Ce sample.
(See text for complete explanation).

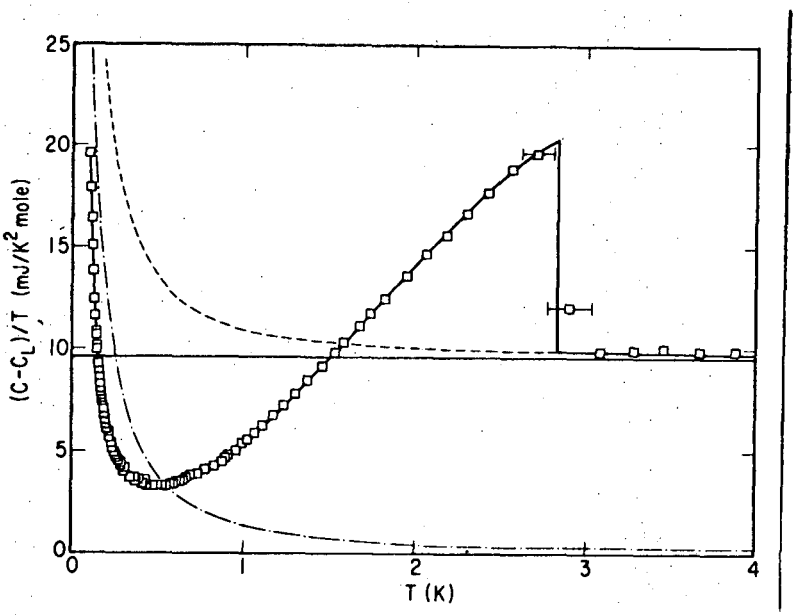


normal state data for the 0.640 at. % Ce sample (and also to the zero field data for that sample for which it might be expected that the normal-state and superconducting-state electronic heat capacities do not differ much). The good agreement of curve d with the (LaCe)Al_2 data provides confirmation of the Kondo effect in this system. Comparison with the Bloomfield-Hamann theory also gives T_K = 0.42 K, in reasonable agreement with other estimates (3-9) of T_K, which range from 0.1 to 1 K.

In order to display the heat capacity anomalies associated with the superconducting transitions, the zero-field and 0.5 kOe heat capacities for the 0.640 at. % Ce sample are shown on an expanded scale and compared with the magnetically determined transitions in Figure 1. In Figure 1(b), ΔC represents the heat capacity relative to a smooth reference curve that was chosen to approximate the zero-

FIGURE 3

Sum of the magnetic and electronic heat capacities of the 0.193 at. % Ce sample in zero-field. (See text for complete explanation).



field normal-state heat capacity. The 0.5 kOe points therefore represent the field dependence of the normal-state heat capacity and the zero-field points represent $C_s - C_n$ (H = 0). Since the zero-field normal-state heat capacity is not determined unambiguously by our measurements, this interpretation of either set of points in Figure 1(b) by itself is somewhat uncertain, but the difference between the zero-field and 0.5 kOe data is, of course, represented exactly. The precision of the data in the region 0.3 to 0.5 K is relatively poor because this is the region of overlap of two separate sets of measurements. Nevertheless, both the zero-field and 0.5 kOe data show a peak or shoulder in this region. The fact that it occurs in both fields shows that it reflects a systematic error (e.g., an error in the temperature scale or an irregularity in the reference curve) and that it has no significance for $C_s - C_n$ (H = 0). Relative to the 0.5 kOe data, however, there are two well-defined peaks in the zero-field data. They occur in the outer regions of the magnetically determined transitions [see Figure 1(a)],

but, given the breadth of the transitions and the different nature of the two measurements, the agreement in temperature is quite reasonable. 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 (14) who have shown that its size is consistent with a bulk superconducting transition. In Figure 1(b) 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 comparison 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 Figure 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 0.54 K 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 0.3 K to the lowest temperature reached, 0.08 K, 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 0.08 K which is required by the equality of the normal and superconducting state entropies at 0 K 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 (15) impurity band at low energies in the gap.

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+ Present address: Material Science Division, Argonne National Laboratory, Argonne, Illinois 60439.

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