PHYSICAL REVIEW B VOLUME 9, NUMBER 1 1 JANUARY 1974

Experimental evidence for the formation of a singlet ground state at low temperatures in the dense Kondo system CeAl$_3$[†]

J. V. Mahoney, V. U. S. Rao, W. E. Wallace, and R. S. Craig
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

N. G. Nereson[*]
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544

(Received 30 March 1973)

Heat-capacity measurements have been performed on CeAl$_3$ and LaAl$_3$ between 1.8 and 300 K. The difference in the heat capacities of these two compounds (ΔC_p) has been regarded as the additional contribution due to the local moments on Ce^{3+} ($J = 5/2$) in CeAl$_3$. The ΔC_p-vs-T curve displays two pronounced anomalies peaking near 5 and 25 K. The total entropy under this curve is nearly R ln6 which is in excess of the maximum possible crystal-field entropy by R ln2. Of the two anomalies, the one at 25 K has been interpreted as being caused by crystal-field effects alone since it accounts for nearly R ln3 of the measured entropy. Neutron-diffraction measurements, performed at 3.5, 4.6, and 300 K, show that the lower-temperature heat-capacity anomaly is not caused by magnetic ordering in CeAl$_3$. The results have therefore been interpreted on the basis of the combined effects of crystal-field splitting and the Kondo effect on the Ce^{3+} ions. Analysis of the measured entropy leads to the conclusion that the low-temperature ground state in this Kondo system is a spin- and orbit-compensated singlet, in accord with recent theoretical predictions.

I. INTRODUCTION

The nature of the ground state at low temperatures in Kondo systems is a fundamental question on which calorimetric studies can provide valuable information.[1] Previous heat-capacity measurements[2] have been confined to dilute transition-metal impurities, such as Cr and Fe, in a Cu matrix. In the case of *Cu*Cr, an entropy reduction of $R\ln(2S+1)$ with $S=\frac{3}{2}$ points to the formation of a singlet ground state at low temperatures. However, no such evidence exists for the ground state of rare-earth Kondo systems which exhibit a number of interesting features resulting from strong L-S coupling and perturbations from crystal-field interactions. We have therefore conducted specific-heat measurements on the concentrated Kondo system CeAl$_3$. These results, which are reported in this paper, provide additional insights on the Kondo ground state in this system.

Electrical resistivity (ρ) measurements[3] on CeAl$_3$ not only indicate the usual minimum in the ρ-vs-T curve characteristic of the Kondo phenomenon, but also show a low-temperature maximum at 35 K. This behavior has been interpreted by Maranzana,[4] as being caused by the lifting of the sixfold degeneracy of the Ce^{3+} ($J=\frac{5}{2}$) ground multiplet by the hexagonal crystal field ($\mathcal{H}=B_2^0O_2^0+B_4^0O_4^0$) into three doublets characterized by $M_J=\pm\frac{5}{2}$, $\pm\frac{3}{2}$, and $\pm\frac{1}{2}$. In this situation, the inelastic scattering of conduction electrons by the local moments, when evaluated in the second Born approximation, leads to divergences in the inverse relaxation time τ_k^{-1} at energies removed from the Fermi level by $\pm\Delta E$ (sidebands), where ΔE is the crystal-field splitting. Furthermore, the absence of an additional upturn in ρ at very low T (i.e., absence of singularity in τ_k^{-1} at E_F) was explained by postulating that the crystal-field ground state was other than $|\pm\frac{1}{2}\rangle$.

Coqblin and Schrieffer,[5] in a more rigorous treatment of the Kondo effect in cerium alloys have used an Anderson-type model for the $4f^1$ configuration of Ce to describe the mixing of the conduction-electron and local-moment wave functions. A conclusion that emerges from their analysis is that a compensation of both spin and orbital momenta occurs below T_K. Furthermore, the change in the magnetic quantum numbers, $\Delta M=M'-M$, is not restricted to ±1 or 0, but can equal $\pm2J$, $\pm(2J-1)\cdots\pm1,0$. In an extension of this model, Cornut and Coqblin[6] have considered the additional influence of the crystalline field and have arrived at several new conclusions. First, provided that the effective-exchange-interaction constant between the conduction-electron and local-moment spins is negative, there is always a Kondo effect, irrespective of the nature of the ground state. Contrary to the Maranzana treatment, it is not a requisite that the ground state be $|\pm\frac{1}{2}\rangle$ for a Kondo effect to exist at the lowest temperatures. Second, the ρ-vs-T curve can be characterized by N regions of ln$T$ behavior, where N is the number of crystal-field levels. Of these various Kondo temperatures the lowest is termed T_K^L and the highest T_K^H. The evaluation of the resistivity in the second Born approximation breaks down near T_K^L. Kondo compensation of both spin and orbital momentum is achieved only below T_K^L which can therefore be considered the true Kondo temperature. Estimates for T_K^L range from a few millidegrees to 10 K for various cerium alloys, while T_K^H may be of the order of 100 K.

The present study was undertaken with the expectation that Kondo spin and orbit compensation near T_K^L should be revealed by an additional contribution to heat capacity at low temperatures. Accordingly, heat-capacity measurements were performed on $CeAl_3$ and $LaAl_3$, the latter to provide estimates of the lattice and electronic contributions to the heat capacity. In addition, neutron-diffraction studies were performed to eliminate the possibility of a contribution to the heat capacity from magnetic ordering.

II. EXPERIMENTAL DETAILS

The purity of the rare-earth constituents used for preparing these compounds was rated at 99.9% while that of aluminum was 99.999%. The elements were melted together under high-purity argon in a water-cooled copper boat placed at the center of an rf induction coil. The samples were annealed at 850 °C for about three weeks. X-ray diffraction of the compounds showed them to be single phase with lattice constants in good agreement with those reported in literature.[7]

The heat-capacity measurements on $CeAl_3$ and $LaAl_3$ were performed in the temperature range 1.8–300 K, using two calorimeters with fully automated data-acquisition systems. One of these, using a calibrated germanium thermometer, operated between 1.5 and 10 K and required a 5-g sample. The control of the measurements made by this calorimeter was delegated to a Hewlett-Packard 2416B on-line computer. An accuracy of better than 1% in heat capacity could be expected. Details of this apparatus will be forthcoming.[8] The other calorimeter which used a Leeds and Northrup platinum resistance thermometer, operated between 5 and 300 K and needed about an 80-g sample. An accuracy in the measured heat capacity of 0.2% above 30 K and better than 1% below that temperature was obtained. Details of this apparatus can be found elsewhere.[9,10]

The neutron-diffraction data were taken using a 42-g powdered sample (80 mesh) of $CeAl_3$ contained in a TiZr null-matrix disk holder; measurements were made with the holder mounted inside a variable temperature cryostat at a neutron wavelength of 1.142 Å. The room-temperature measurements confirmed the sample purity since the experimental reflection intensities agreed reasonably well with nuclear intensities calculated from the hexagonal cell (Ni_3Sn type with $a_0 = 6.55$ Å and $c_0 = 4.61$ Å) and neutron-scattering amplitudes of 0.48 and 0.35×10^{-12} cm for Ce and Al, respectively. Measurements were also made at 4.6 and 3.5 K.

III. RESULTS AND DISCUSSION

The experimentally determined heat capacity curves of $CeAl_3$ and $LaAl_3$ are shown in Fig. 1 for the range 5–300 K. Since the two curves approach each other very closely above 200 K, the data points for $LaAl_3$ have not been indicated. The curves shown, however, are drawn on the basis of a large number of experimental points, half of which are shown in the case of $CeAl_3$. It is important to note that in addition to the close approach to each other above 200 K, the two curves actually coincide within experimental error near 300 K. Similar behavior has been found[11] in the case of the isostructural compound $PrAl_3$, in which the heat capacity above 180 K is identical to that of $LaAl_3$. It is reasonable to assume that the electronic and phonon contributions to the total heat capacity of $CeAl_3$ can be well approximated by the C_p of $LaAl_3$. Figure 2 indicates the difference (ΔC_p) between the measured heat capacities of $CeAl_3$ and $LaAl_3$ as a function of T. The ΔC_p-vs-T curve is characterized by pronounced anomalies near 5 and 25 K. While the nature of the maximum at 25 K was typical of a Schottky anomaly, the results of accurate pulse calorimetric measurements between 1.8 and 10 K demonstrated the lower anomaly to consist of two distinct maxima, as shown in Fig. 3. It is evident that these lowest temperature maxima are reminiscent of neither the usual λ-type heat-capacity anomaly resulting from magnetic ordering nor a pure crystal-field Schottky anomaly.

If the total ΔC_p-vs-T curve is to be explained on the basis of a crystal-field (CF) model, it is important to note that the three doubly degenerate CF levels of Ce^{3+} in this compound would lead to an associated entropy at 300 K not exceeding $R\ln 6 - R\ln 2$, or 9.15 J/K mole. The total measured entropy connected with the ΔC_p curve, on the other hand, is in excess of this value and amounts to 12.8 J/K mole. This evidence clearly indicates that only a portion of the experimental ΔC_p is

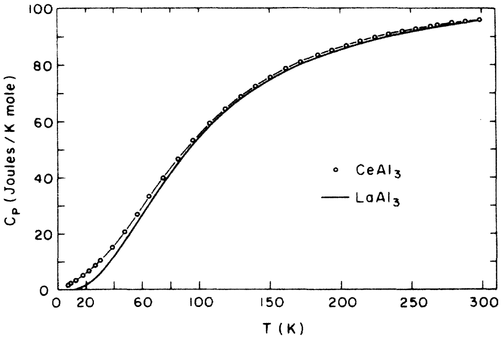

FIG. 1. Measured heat capacity of $CeAl_3$ compared to that of $LaAl_3$ between 5 and 300 K.

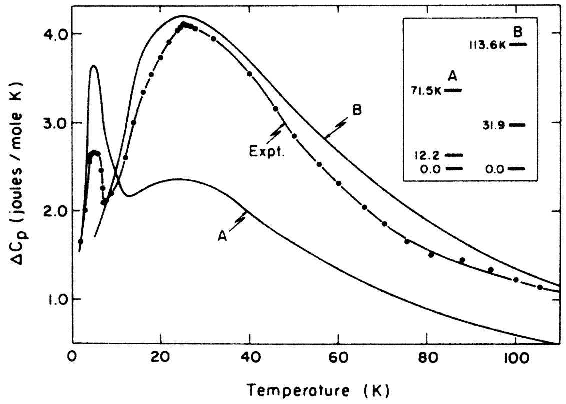

FIG. 2. Representation of the measured ΔC_p (difference in heat capacities between $CeAl_3$ and $LaAl_3$) vs T curve and the Schottky heat-capacity curves calculated according to crystal-field splitting schemes A and B shown in the inset.

associated with the thermal redistribution of Ce^{3+} ions among the three CF levels. Efforts to rationalize at least part of each anomaly (at 5 and 25 K) with the CF model, using reasonable values of the second- and fourth-order crystal-field parameters, B_2^0 and B_4^0 which predicted Schottky heat capacity curves with two maxima, one located near 5 K and the other near 25 K, were examined. In all cases, the calculated Schottky heat capacity was too high near the 5 K and too low near the 25 K anomaly, when compared to the measured values. The best attempt in this direction is shown as curve A in Fig. 2 along with the corresponding CF splitting scheme (see inset).

A more satisfactory explanation of the experimental results can be obtained by considering only the higher temperature anomaly, which indeed appears to be the Schottky type, to be representative of the redistribution of ions over the three CF levels. As will be presently demonstrated, this consideration provides a favorable comparison with the expected CF entropy of $R\ln\frac{6}{2}$. Thus focusing attention for the moment only on the high-temperature anomaly, one finds that the measured entropy from 20 to 300 K is 8.3 J/K mole, or approximately 91% of the maximum possible crystal-field entropy. The best attempt to fit only the experimental data above 10 K with a CF model is represented as curve B in Fig. 2, with the corresponding splitting scheme shown in the inset. This scheme assumes a CF over-all splitting of 114 K, which we believe is more accurate than the value of about 50 K obtained from an analysis of electrical resistivity.[12]

According to this assignment, an entropy of 4.5 J/K mole out of the total measured value remains unaccounted, and is associated with the lower anomaly down to a temperature of 1.8 K. An approximation of the additional unmeasured entropy between 0 and 1.8 K can be obtained by a linear extrapolation of the C_p-vs-T curve to 0 K, and amounts to about 0.7 J/K mole. This would bring the total entropy under the lower anomaly to 5.2 J/K mole which is approximately 90% of $R\ln 2$, where $R\ln 2$ is the entropy associated with the removal of the degeneracy of the ground doublet. One is thus left with one alternative, namely, that the ground state is indeed a singlet.

It is pertinent to note at this point that in studies of this nature, it is sometimes desirable to extend the heat-capacity measurements to extremely low temperatures (of the order of 10^3 K) in order to account for the total third-law entropy. Our measurements, on the other hand, have extracted nearly the maximum possible entropy for a $J=\frac{5}{2}$ system at 1.8 K. We therefore feel that measurements below this temperature are not likely to yield additional contributions to the entropy sizable enough to significantly alter the arguments being put forth in this work.

There seem to be only two mechanisms in this system which can lead to a nondegenerate ground state at low temperatures. The first possibility that is likely to come to one's mind is the splitting of the ground doublet by an exchange field resulting from the onset of magnetic ordering. The other possibility, based on the theoretical work of Cornut and Coqblin,[6] attributes the formation of a singlet to the total compensation of spin and orbital momenta of Ce^{3+} below T_K^L. Although not fully conclusive, previous magnetic[13] and resistivity[12] measurements have resulted in no indication of magnetic ordering down to 2 K, which is well below the region of occurrence of the low-temperature anomaly. Furthermore, the detailed heat-capacity[14] behavior of this anomaly, shown in Fig. 3, does not exhibit a λ anomaly, which is to be expected if mag-

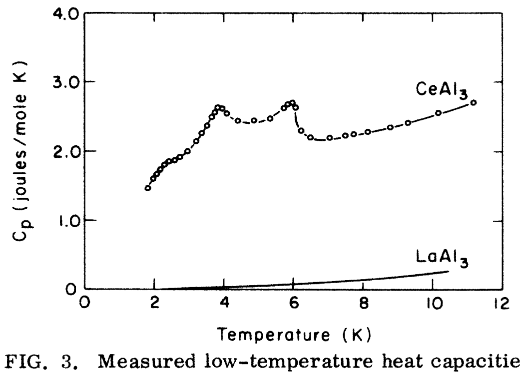

FIG. 3. Measured low-temperature heat capacities of $CeAl_3$ and $LaAl_3$. The curve for $CeAl_3$ demonstrates the exact nature of the low-temperature anomaly seen in Fig. 1.

netic ordering occurs.

It was thought that before one could completely discount the first possibility, it would be preferable to perform neutron-diffraction measurements on this system, especially in the vicinity of the low-temperature anomaly.

The neutron-diffraction data at temperatures of 4.6 and 3.5 K were identical to the data at 300 K over a scattering-angle range of 5° to 35°. No extra or superlattice reflections were observed and no extra intensity was noted on the nuclear peaks; the paramagnetic background intensity also remained the same at all three temperatures. Therefore, these powder data indicate that no ordered magnetic structure develops in CeAl$_3$ between room temperature and 3.5 K; however, an ordered moment less than about 0.3μ_B would not have been detected with the present powder sample. Thus, present low-temperature neutron-diffraction data support the negative results of previous bulk magnetic measurements[13]; cryostat limitations prevented any measurements below 3.5 K.

IV. CONCLUDING REMARKS

It is evident from heat-capacity measurements that an entropy of nearly $R\ln 6$ has been recovered between 300 and 1.8 K. Crystal-field effects alone can account for only $R\ln 3$. It is thus obvious that additional effects are present at low temperatures which lift the ground-state degeneracy and yield a singlet ground state. Neutron-diffraction measurements have shown that mangetic ordering cannot be responsible for the observed effect. We therefore conclude that our unambiguous observation of a ground singlet can only be associated with the Kondo phenomenon and substantiates the theoretical predictions by Cornut and Coqblin[6] of a spin- and orbit-compensated ground state below T_K^L. The detailed interpretation of the low-temperature heat-capacity anomaly must, however, await further theoretical developments in this area.

---

†This work was supported by a grant from the U. S. Army Research Office, Durham, N. C.

*The contribution of this researcher was supported by the U. S. Atomic Energy Commission.

[1] For a review of this problem see A. J. Heeger, Solid State Physics, edited by F. Seitz, D. Turnbull, and E. Ehrenreich (Academic, New York, 1969), Vol. 23, p. 284.

[2] B. B. Triplett and Norman E. Phillips, Phys. Rev. Lett. 27, 1001 (1971).

[3] K. H. J. Buschow and H. J. Van Daal, Solid State Commun. 8, 383 (1970).

[4] F. E. Maranzana, Phys. Rev. Lett. 25, 239 (1970).

[5] B. Coqblin and J. R. Schrieffer, Phys. Rev. 185, 847 (1967).

[6] B. Cornut and B. Coqblin, Phys. Rev. B 5, 4541 (1972).

[7] J. H. N. Van Vucht and K. H. J. Buschow, J. Less-Common Metals 10, 98 (1965).

[8] R. S. Craig and R. A. Butera (unpublished).

[9] J. V. Mahoney, Ph. D. thesis (University of Pittsburgh, 1972) (unpublished).

[10] A. W. Thompson, Ph. D. thesis (University of Pittsburgh, 1971) (unpublished).

[11] J. V. Mahoney, R. S. Craig, and W. E. Wallace, J. Appl. Phys. (to be published).

[12] K. H. J. Buschow, H. J. Van Daal, F. E. Maranzana, and P. B. van Aken, Phys. Rev. B 3, 1662 (1971).

[13] K. H. Mader and W. M. Swift, J. Phys. Chem. Solids 29, 1859 (1968).

[14] These data are in agreement with the recent low-temperature heat-capacity measurement of M. H. Van Maaren, K. H. J. Buschow, and H. J. Van Daal [Solid State Commun. 9, 1981 (1971)]. However, the present work shows better resolution of two maxima in this anomaly.