Pressure Dependence of the Low-Temperature Specific Heat of the Heavy-Fermion Compound $CeAl_3$

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(Received 12 November 1985)

The specific heat (C) of $CeAl_3$ has been measured between 0.35 and 20 K at pressures to 8.2 kbar. A very strong and nonlinear dependence on pressure is observed. In particular, the maximum in C/T, a prominent feature at zero pressure which is apparently closely related to the other unusual properties characteristic of the low-temperature behavior, disappears at even very low pressures. There is no transition to a superconducting or magnetically ordered state under pressure. Measurements at zero pressure to 50 mK show a quadratic term in C in addition to the linear term.

PACS numbers: 71.20.+c, 65.40.−f

$CeAl_3$ is the prototypical example of a heavy-fermion compound that does not undergo a transition to either of the commonly observed ordered ground states—neither superconductivity nor magnetic order occur.[1] At temperatures of a few degrees Kelvin and above, its properties, including particularly the specific heat (C), are suggestive of Kondo behavior.[2] However, near 0.5 K, C/T passes through a maximum that is inconsistent with the single-impurity Kondo effect, and which has been associated with the development of coherence in an ordered Kondo lattice.[1,2] Recent specific-heat measurements on $CeCu_2Si_2$, which is similar to $CeAl_3$ in many respects, support this association: The maximum was suppressed by alloying with $LaCu_2Si_2$ or YCu_2Si_2.[3] The electrical resistivity[4,5] (ρ), magnetic susceptibility[1] (χ), and thermal expansion[1,6] (α) also show qualitative changes in behavior near 0.5 K which are apparently related to the maximum in C/T. Considered together, these properties point to a fundamental change in the nature of the dominant interactions that occur near 0.5 K, and below that temperature the properties are often discussed in terms of Fermi-liquid behavior. In this Letter we report measurements of C as a function of pressure (P). At $P=0$, the measurements extend from 0.06 to 20 K; and at four pressures between 0.4 and 8.2 kbar, from 0.35 to 20 K. The pressure dependence of C is highly nonlinear, and, at low pressures, enormously strong. The maximum in C/T, and presumably the transition to a region of qualitatively different behavior below 0.5 K more generally, is suppresed by even rather low pressures.

$CeAl_3$ melts incongruently, and samples are generally contaminated by $CeAl_2$ and/or Ce_3Al_{11} inclusions.[7] The sample for which data are reported here is the purest (G2) of four samples for which it was shown that, below 1 K, C could be consistently corrected to that for pure $CeAl_3$.[8] The experimental methods were similar to those used earlier,[9] except that the sample was surrounded by a thin layer of AgCl to reduce pressure gradients, and Pb manometers were placed at each end of the sample.[10]

The zero-pressure data below 0.8 K are compared with smoothed representations of other data[1-3] in Fig. 1. The discrepancies probably arise in part from differences in measuring techniques (e.g., in temperature measurements), but, given the extreme pressure sensitivity of C at low pressure (see below), they could also reflect sample-to-sample differences related to differences in the state of aggregation of the impurity phases or even to sample mounting techniques. As shown in Fig. 1, the present data are well represented by $C=1.20T+1.96T^2$ J/mole·K at $T<0.25$ K. This result is qualitatively consistent with two of the independent measurements, and we suggest that this is the correct form for C in the low-temperature, zero-pressure limit, and that it reflects the nature of the low-energy excitation spectrum for this particular heavy-fermion compound. The T^2 term deserves theoretical investigation—calculations based on a density-of-states model can give only a T^3 term.

The data for $P\neq 0$ are included in Fig. 2. The measurements at $P\neq 0$ were made in order of decreasing pressure, but measurements at $P=0$ were made on parts of the same sample both before and after the pressure cycle to establish the reversibility of the effect. Unlike results reported[7] for measurements of ρ, no significant[12] pressure hysteresis was observed. Qualitatively, the effect of pressure is in agreement with that found in earlier measurements at 0 and 7 kbar and $T>1.5$ K.[13] However, the extension of the data to lower temperatures and to intermediate pres-

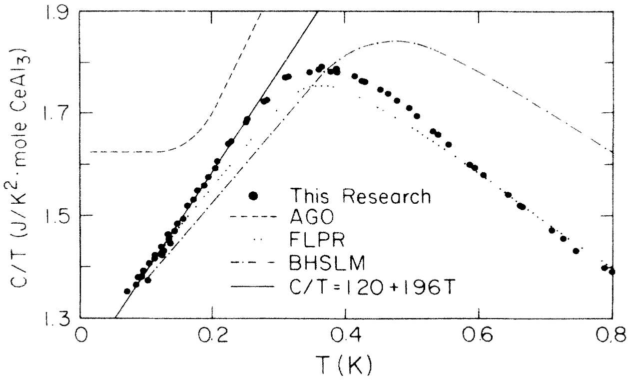

FIG. 1. Specific heat of $CeAl_3$ for $T \leq 0.8$ K and $P = 0$. Curves representing data from three other laboratories are also shown: AGO (Ref. 1), FLPR (Ref. 2), and BHSLM [Ref. 3; but as shown here, the data have been corrected to a revised temperature scale (Ref. 11)].

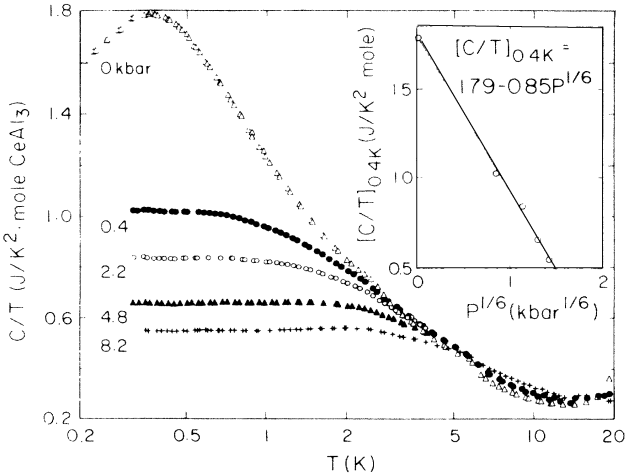

FIG. 2. Pressure dependence of the specific heat of $CeAl_3$. For clarity, only data for 0, 0.4, and 8.2 kbar are shown for $T > 4$ K.

sures (and to some degree the better purity of the sample) give interesting new information: In the vicinity of the maximum in C/T, i.e., near 0.4 K, C is reduced *by a factor of 3.2* at a pressure of 8.2 kbar, and more than half of the reduction occurs at 0.4 kbar; no indication of a maximum in C/T remains at even the lowest nonzero pressure, 0.4 kbar; and although C (and presumably other properties) is changed dramatically at 8.2 kbar, there is still no indication of superconductivity or magnetic ordering.

The nonlinearity of the pressure dependence of C is further illustrated in the inset to Fig. 2, where an empirical $P^{1/6}$ dependence of $[C/T]_{0.4\text{ K}}$ is demonstrated. With the assumption of a pressure-independent compressibility,[14] $\kappa = 2.16\times10^{-3}$ kbar^{-1}, one can use the relation given there to derive a Gruneisen parameter,

$$\Gamma_{C(0.4\text{ K})} = -\partial \ln[C/T]_{0.4\text{ K}}/\partial \ln V,$$

as a function of pressure. For the nonzero pressures at which C was actually measured, $\Gamma_{C(0.4\text{ K})}$ varies from -132 at 0.4 kbar to -19.4 at 8.2 kbar (see Table I). Use of the $P^{1/6}$ relation to interpolate between 0 and 0.4 kbar gives $\Gamma_{C(0.4\text{ K})} = -368$ and -220 at 0.1 and 0.2 kbar, respectively. The latter values must be taken with caution (the same interpolation gives $\Gamma_{C(0.4\text{ K})} = \infty$ at $P = 0$), but it is clear that there is an enormously strong pressure dependence near $P = 0$.

The thermal expansion has been measured from 0.3 to 10 K by Andres, Graebner, and Ott[1] (AGO) and from 20 mK to 1 K by Ribault *et al.*[6] AGO find a maximum positive value of α near 2 K, a nearly linear decrease at higher temperature, and negative values below 0.65 K. Below 0.2 K, Ribault *et al.* find the thermodynamically required approach to $\alpha = 0$ at $T = 0$, and negative values of α at all temperatures below 1 K with the minimum occurring near 0.4 or 0.5 K, depending on the sample. The thermodynamic relation $\partial\alpha/\partial T = -V^{-1}\partial(C/T)/\partial P$ permits an approximate calculation of values of $\partial\alpha/\partial T$ from $C(P = 0.4\text{ kbar}) - C(P = 0)$, and, thus, a comparison of the $\alpha(T)$ and $C(P)$ data. Near and above 1 K the agreement is reasonable. The calculated value of $\partial\alpha/\partial T$ changes sign near 2.5 K ; the measured value (AGO) changes sign near 2 K. Between 2.5 and 10 K the calculated value is temperature dependent, but its average value is roughly -0.5×10^{-5} K^{-1}; in this interval the measured value is roughly constant at -0.3×10^{-5} K^{-1}. Near 1 K the calculated value is 13×10^{-5} K^{-1}; the measured values are 3×10^{-5} K^{-1} (AGO) and 5×10^{-5} K^{-1} (Ribault *et al.*) At lower temperatures, however, the disagreement becomes conspicuous. *The measured values become negative again below about 0.5 K, but there is no indication of the corresponding change to positive values of* $\partial(C/T)/\partial P$. Irreversible pressure-induced changes in the sample

TABLE I. Parameters derived from $C(P)$ (see text for definitions).

P (kbar)	$\Gamma_{[C/T]_{0.4\text{ K}}}$	γ (mJ/mole·K^2)	m^*/m	Γ_{m^*}
0		1200	300	
				−183
0.4	−132	1024	256	
				−51.5
2.2	−41.3	838	209	
				−43.2
4.8	−25.8	657	164	
				−24.4
8.2	−19.4	549	137	

are ruled out as the cause of the apparent discrepancy between $\alpha(T)$ and $C(P)$ by the sequence of the $C(P)$ measurements. It is also worth noting that similar measurements of $C(P)$ on UPt_3 are in good agreement with $\alpha(T)$.[15] The uncertainty in the temperature at which $\partial\alpha/\partial T$ changes sign[1,6] leaves open the possibility that at temperatures slightly below the lowest reached in these measurements, and for $P \neq 0$, C/T rises sharply to cross the $P=0$ data and satisfy the thermodynamic relation. It seems more probable, however, that the required change in the behavior of C occurs within the temperature range of the measurements but at $0 < P < 0.4$ kbar. In either case, the results show that the negative values of $\partial\alpha/\partial T$, and probably the other Fermi-liquid properties that occur for $T < 0.5$ K and $P=0$, are characteristic of a state that is extremely sensitive to pressure and is completely suppressed at even relatively low pressures for $T > 0.35$ K.

The maximum in C/T at $P=0$ has been taken as defining the temperature, T^*, at which the interactions between the high-mass excitations in a coherent Kondo lattice become important.[2] Since the measurements of C at $P \neq 0$ do not extend below $T^*(P=0)$, they do not give a direct indication of the pressure dependence of T^*. However, the rapid decrease of C/T with increasing T at $T > 0.35$ K and $P=0$ contrasts sharply with the $P \neq 0$ data and suggests a huge decrease with increasing pressure of the interaction between particles. Extrapolation of C/T to $T=0$ gives γ, the coefficient of the linear term in C, and m^*/m, the corresponding effective mass ratio of the f electrons. These quantities and average values of a Gruneisen parameter, $\Gamma_{m^*} = -\partial \ln m^* / \partial \ln V$, evaluated for successive pairs of the pressures at which m^* was determined, are given in Table I.

The $C(P)$ data can also be compared with $\rho(P)$ data[7] by use of the empirical rule that γ is approximately inversely proportional to the temperature T_M^ρ at which ρ reaches a maximum.[16] For 0 and 16 kbar, T_M^ρ is 34 and 70 K, respectively. This leads to a predicted decrease by a factor of 2 in γ at 16 kbar, i.e., to $\gamma(16 \text{ kbar}) \simeq 600$ mJ/mole$\cdot$K^2. For $P \geqslant 0.4$ kbar, $\gamma \approx [C/T]_{0.4\text{ K}}$, and extrapolation of the $P^{1/6}$ relation illustrated in Fig. 1 gives $\gamma(16 \text{ kbar}) = 440$ mJ/mole$\cdot$K^2, in quite reasonable agreement with the value predicted from the correlation with T_M^ρ, considering the crudeness of the approximations.

For "intermediate valence compounds" (IVC), such as $CeSn_3$, $CeBe_{13}$, and $CePd_3$, Γ_{m^*} is typically[17] of order of magnitude -10, and the rapid decrease in magnitude of Γ_{m^*} for $CeAl_3$ with increasing pressure may indicate an approach to IVC behavior. With that assumption, the $2J+1$ channels of the $4f^1$ configuration must be recovered under pressure, favoring the mixing with the $4f^0$ configurations, and decreasing strongly the intersite coupling.[18] With the further somewhat arbitrary assumption that extrapolation of the $P^{1/6}$ pressure dependence to 20 kbar gives values of properties that are at least rough approximations to the IVC limit (and vanishing interactions between particles), one obtains $\Gamma_{m^*}(20 \text{ kbar}) = -13.8$, $\gamma(20 \text{ kbar}) = 390$ mJ/mole$\cdot$K^2, and $m^*(20 \text{ kbar})/m = m_b(20 \text{ kbar})/m = 98$, for the contributions of the renormalized band mass (m_b) alone. Extrapolation of these quantities back to $P=0$ (using the *constant* value $\Gamma_{m^*} \approx -13.8$ to represent the volume dependence exclusive of that of the intersite coupling) gives $m_b(P=0)/m = 177$, and a mass enhancement due to interactions of $m^*/m_b \approx \frac{300}{177} \approx 1.7$ at $P=0$. Another estimate of the same quantity is provided by a comparison with $CeAl_2$, for which the paramagnetic phase has a Kondo temperature similar to that of $CeAl_3$ (as shown by the similarity of the $\log T$ terms in ρ and of the quasielastic neutron scattering[19]). The entropy drop below the Néel temperature in $CeAl_2$ corresponds mainly to the quenching of the interactions between the heavy fermions. Thus the quasiconstant values[20] of $\gamma \approx 150$ mJ/mole$\cdot$K^2 below the Néel temperature and at higher temperatures can be regarded as mainly due to normalized band effects and give $m_b/m \sim 40$. If it is assumed that these effects are, very roughly, the same as for $CeAl_3$, one obtains $m^*/m_b \approx \frac{300}{40} \approx 7$. These two rough estimates suggest that in cerium heavy-fermion compounds the interactions between the renormalized particles give a ratio m^*/m_b of the order of 1.7 to 7. [It is interesting to note that in UPt_3 an almost pressure-independent value $m^*/m_b \sim 1.6$ has been found[15] by comparison of $C(P)$ data with spin-fluctuation theory. Thus, in this material as well, the high value of m^* is the result of a large renormalization effect and a relatively small effect of interactions.] The huge values of m^* and Γ_{m^*} are due to a low value of T^* ($T^* \propto 1/m^*$). The ratio Γ_{m^*}/m^*, however, which represents the variation of T^* with volume, has a value comparable to that of a normal metal. The coupling constant derived from ultrasonic-attenuation data, which is also of the same order of magnitude as found for normal metals, has led to a similar conclusion.[21,22] The physical origin of m_b must be attributed to a weak delocalization of the f electrons arising from a small deviation from the integer trivalent state in quasitrivalent compounds: The low number of moving particles leads to the apparent high mass.[23,24]

In conclusion, the $C(P)$ measurements show a dramatic pressure dependence at temperatures in the vicinity of the $P=0$ maximum in C/T. Although a complete characterization of the effect requires an extension of the measurements to lower pressures and temperatures, it can be expected to be reflected in other properties, notably transport properties, and measurement of such properties in the same region of pressure and temperature would be of considerable interest. Estimates of the contribution to m^*/m_b of interactions between the heavy particles give values comparable to those found[25] for ^{3}He, emphasizing the similarity with that quantum fluid.

The work at Berkeley was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

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