Title

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Author

Phillips, N.E.

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PRESSURE DEPENDENCE OF THE SPECIFIC HEAT OF HEAVY-FERMION COMPOUNDS

N. E. Phillips[1], R. A. Fisher[1], S. E. Lacy[1], C. Marcenat[1],
J. A. Olsen[1], J. Flouquet[2], A. Amato[3], D. Jaccard[3],
Z. Fisk[4], A. L. Giorgi[4], J. L. Smith[4] and G. R. Stewart[4,5]

[1]MMRD, Lawrence Berkeley Laboratory, University of California,
Berkeley, CA 94720 USA
[2]CRTBT/CNRS, BP166X, 38042 Grenoble Cedex, France
[3]Physics Department, University of Geneva, Geneva, Switzerland
[4]MST, Los Alamos National Laboratory, Los Alamos, NM 87545 USA
[5]Present address: Physics Department, University of Florida,
Gainsville, FL 32611 USA

Measurement of the properties of materials as a function of pressure (P) provides an additional dimension for comparison with models and theoretical calculations. It also provides a relatively sound basis for establishing correlations between different properties. For example, if one looks for correlations between superconductivity and magnetic properties by studying series of different compounds or alloys, one is forced to resort to comparisons that are complicated, to a very substantial degree, by chemical and structural differences. If instead one studies the pressure dependence of the properties of a single material, only one relatively simple parameter, the volume (V), is changed. Measurement of the pressure dependence of the properties of heavy-fermion compounds (HFC) is particularly fruitful because the 4f and 5f electrons, which play the central role in the phenomenon, are extremely sensitive to pressure, and large effects are observed at modest pressures. Although the electrical resistivity (ρ) and the magnetic susceptibility (χ) of a number of HFC have been measured as a function of pressure, it is only recently that data for the specific heat (C) have become available for non-zero pressure. We describe here measurements of C(P) to $P \sim 9$ kbar for $CeAl_3$ [1], $CeCu_6$ [2], UBe_{13} [3], and UPt_3 [4]. Independent measurements of C(P) to $P \sim 6$ kbar have been reported for $CeCu_2Si_2$ [5].

All HFC have high values of C/T for $T<10K$, but the details of the temperature dependence of C/T vary significantly. Figure 1 shows the qualitatively different types of behavior that have been observed at zero pressure for the normal state of HFC that do not order magnetically. Also represented for comparison are data for α-Ce, for which γ, the value of C/T at $T=0$, is "high" (0.012 J/mole K^2) relative to those for ordinary metals. $CeAl_3$ is the prototypical example of an HFC that does not undergo a transition to an ordered state — neither superconductivity nor magnetic ordering are observed above 20mK [6]. Above 0.5K its properties, including the specific heat, are similar to those of a dilute (single-ion) Kondo system. Near 0.5K there is a conspicuous maximum in C/T, and in the low-temperature limit, $C/T = 1.20 + 1.96T$ J/mole K^2 [1]. The maximum in C/T has been associated with the development of coherence in a Kondo lattice [7]. There may also be a maximum in C/T for $CeCu_2Si_2$ but in that case the analysis of the experimental data is complicated by occurrence of superconductivity, by a strong field dependence of the normal state specific heat, and by sample-to-sample variations in the properties [7,8].

Another HFC that shows neither superconductivity nor magnetic ordering to the lowest temperatures of investigation is $CeCu_6$. In that case, the low-temperature limiting behavior is $C/T = 1.67 - 0.67T$ J/mole K^2, and there is no maximum in C/T above 60 mK [9]. (A maximum in C/T near 0.3K has been reported [10], but its existence is also inconsistent with other data [11]). With respect to the absence of a maximum in C/T, both UBe_{13} [12] and $CeRu_2Si_2$ [11,13] seem to be similar to $CeCu_6$, and this may be the more usual behavior for the normal state of an HFC that does not order magnetically.

UBe_{13} undergoes a transition to the superconducting state near 0.9K, but the curve in Fig. 1 represents the normal-state specific heat (C_n). The dashed part of the curve is an extrapolation of C_n data to T=0, $C_n = 1.31T - 1.58T^2 + 1.44T^3$ J/mole K, that is consistent with the temperature dependence of C_n between 0.5 and 1K, and also with the entropy calculated from data for the superconducting-state specific heat (C_s), which extend to lower temperatures [12]. Other similar results have also been reported [14,15]. The possibility of a maximum in C_n/T is not ruled out, but it seems unlikely.

As Fig. 1 makes clear, the specific heat of UPt_3 shows still another qualitatively different type of behavior. There is a shallow minimum in C_n/T in the vicinity of 10K. At lower temperatures there is an increase in C_n/T (which is barely perceptible in Fig. 1) and a gradual approach to a constant value in the T=0 limit. In the low temperature region, $C/T = \gamma + \delta T^2 \ln T + \varepsilon T^2$ [16,17,4]. A C/T of that form was originally predicted for ferromagnetic spin fluctuations [18,19]. It is now believed to arise more generally within Fermi-liquid theory, but there are only a very few systems in which it has been observed experimentally. UPt_3 is unique among HFC, unique among superconductors of all kinds, and very unusual among metals in general in exhibiting a specific heat of this form. It is now fairly generally believed that there are two characteristic energy scales, and two corresponding temperature scales that are important in understanding HFC behavior. One temperature scale, represented by T_K, is determined by the Kondo-like interactions of the 4f and 5f electrons with the conduction band; the other, corresponding to an energy that is one to two orders of magnitude smaller, and represented by T*,

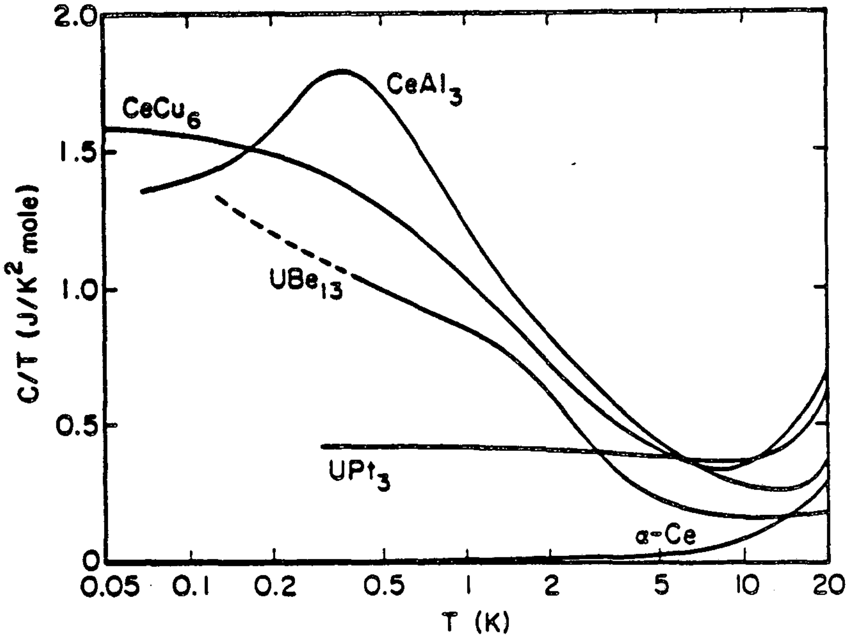


Fig. 1. The specific heats of four HFC, and for comparison that of α-Ce, as C/T vs. log T. For UPt_3 and UBe_{13}, it is C_n that is represented.

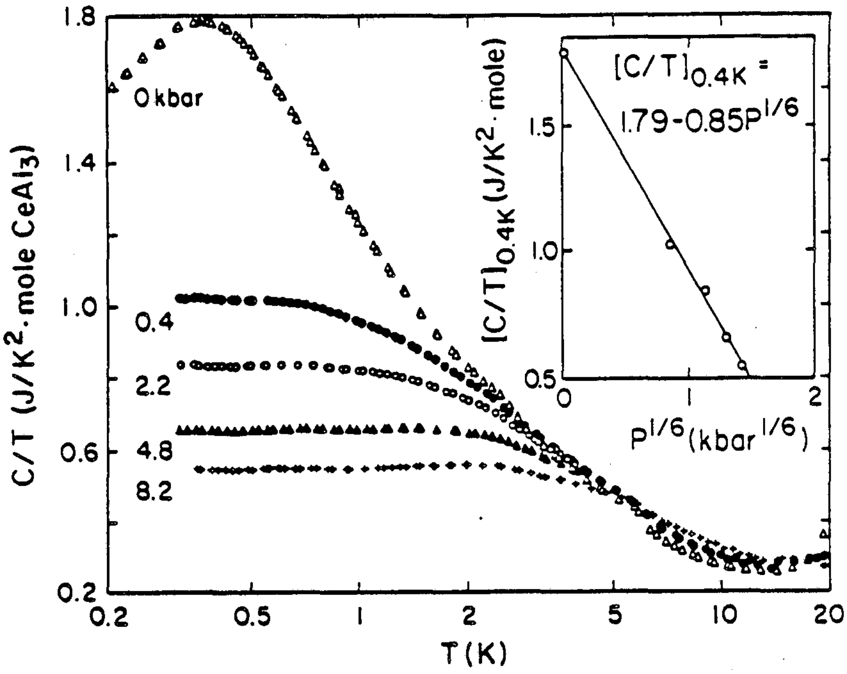
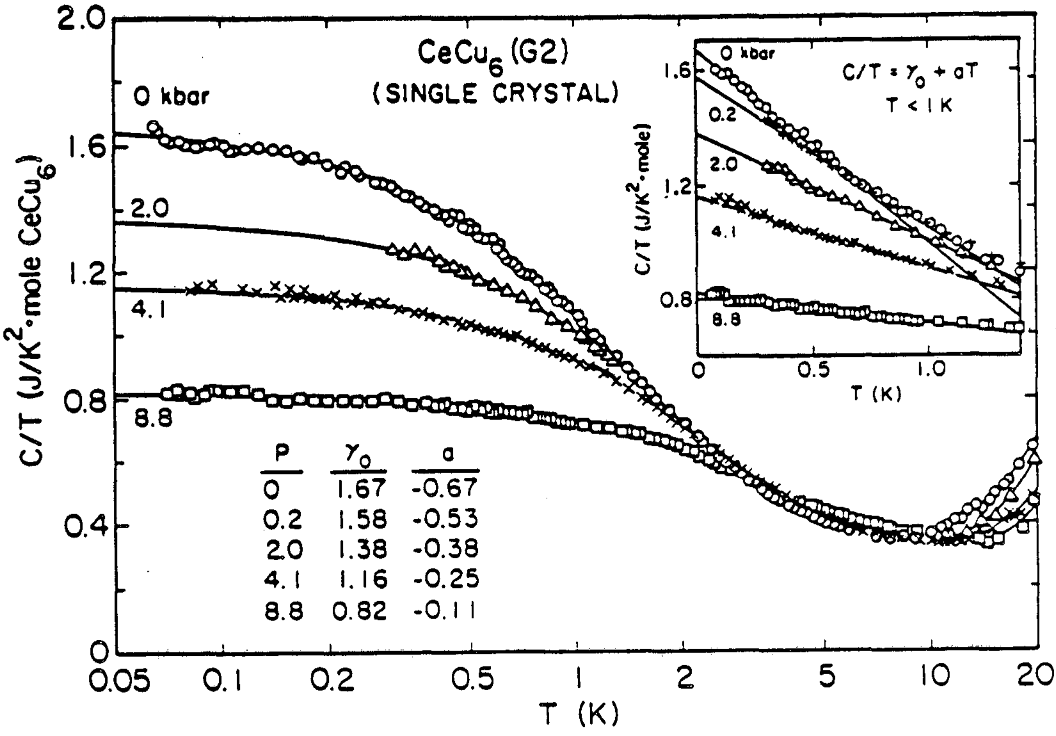


Fig. 2. Pressure dependence of C/T for CeAl$_3$.

is determined by the interactions between the f electrons, and is related to the development of coherence for the Kondo lattice. The transition from one regime to the other is marked, for example, by a maximum in ρ, which occurs at a temperature T_M. For most HFC T_M is of the order of a few tens of K or less, but for UPt$_3$ it is above room temperature [20]. Thus, it seems probable that the difference between UPt$_3$ and the other HFC for which C/T is displayed in Fig. 1 reflects differences in the values of T* and T_K, and the fact that, in contrast with the others, data for UPt$_3$ are well within the region in which C/T is dominated by the intersite interactions. From this point of view, it seems possible that the $T^3\ln T$ terms observed in UPt$_3$ exist in the other HFC as well, but would be observed only at temperatures below



P	γ_0	a
0	1.67	-0.67
0.2	1.58	-0.53
2.0	1.38	-0.38
4.1	1.16	-0.25
8.8	0.82	-0.11

Fig. 3. Pressure dependence of C/T for CeCu$_6$.

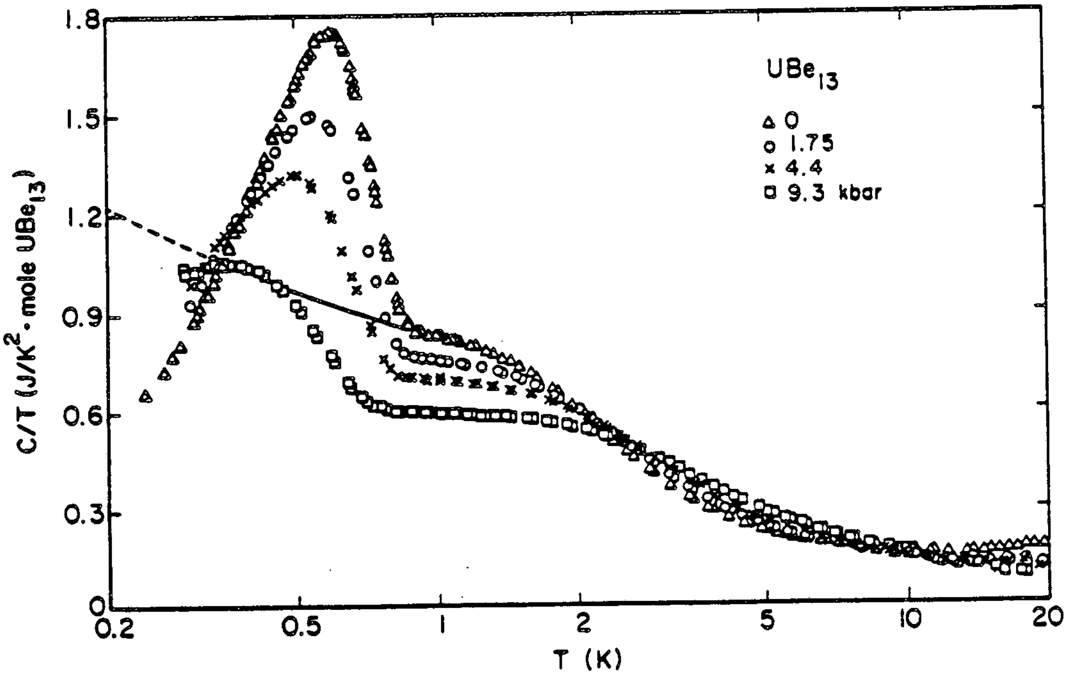


Fig. 4. Pressure dependence of C/T for UBe_{13}.

those to which measurements have been made to date.

The experimental data for C(P) for $CeAl_3$, $CeCu_6$, UBe_{13} and UPt_3 are shown in Figs. 2-5, respectively. To show more clearly the relations between the data at different pressures in the 2-20K region, smoothed representations of $[C(P)-C(0)]/T$ are plotted in Figs. 6-9. The error bars represent the indicated percentage of the total measured heat capacity (i.e., including that of the pressure cell). In most cases the precision of the measurements is such that the uncertainty in the heat capacity of the sample is of the order of 0.1% of the total. For $CeAl_3$ the uncertainty is about 0.5%, and above 15K, not much more than the sign of $(\partial C/\partial P)_T$ is determined. For discussion of the pressure or volume dependence of a property X, it is convenient to introduce the Gruneisen parameter defined as $\Gamma_X \equiv -(\partial \ln X/\partial \ln V)_T$

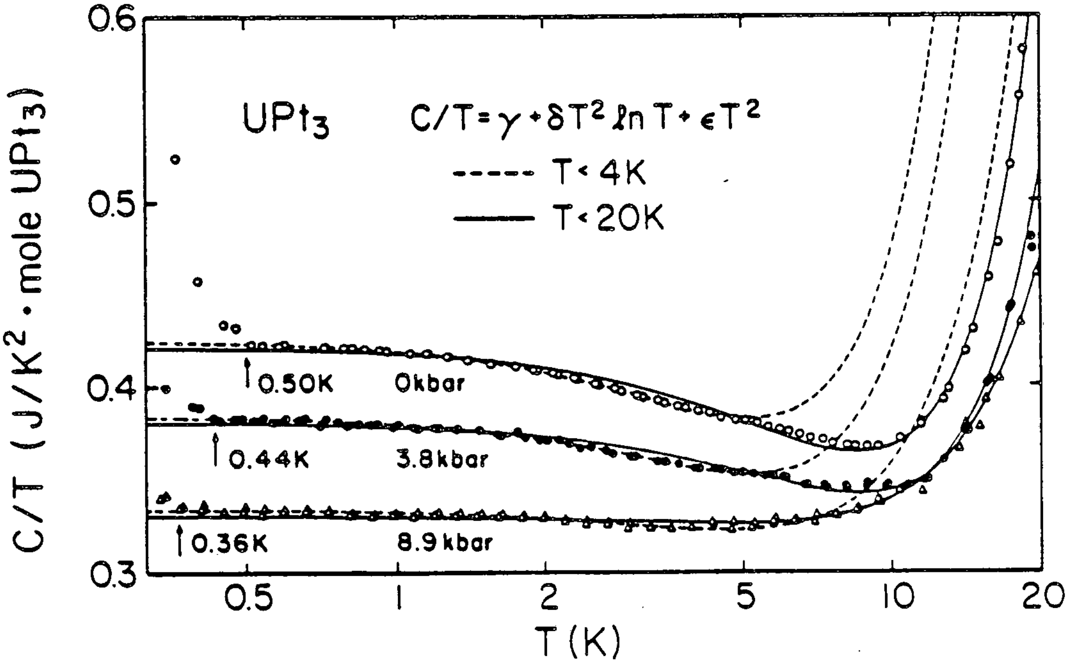


Fig. 5. Pressure dependence of C/T for UPt_3.

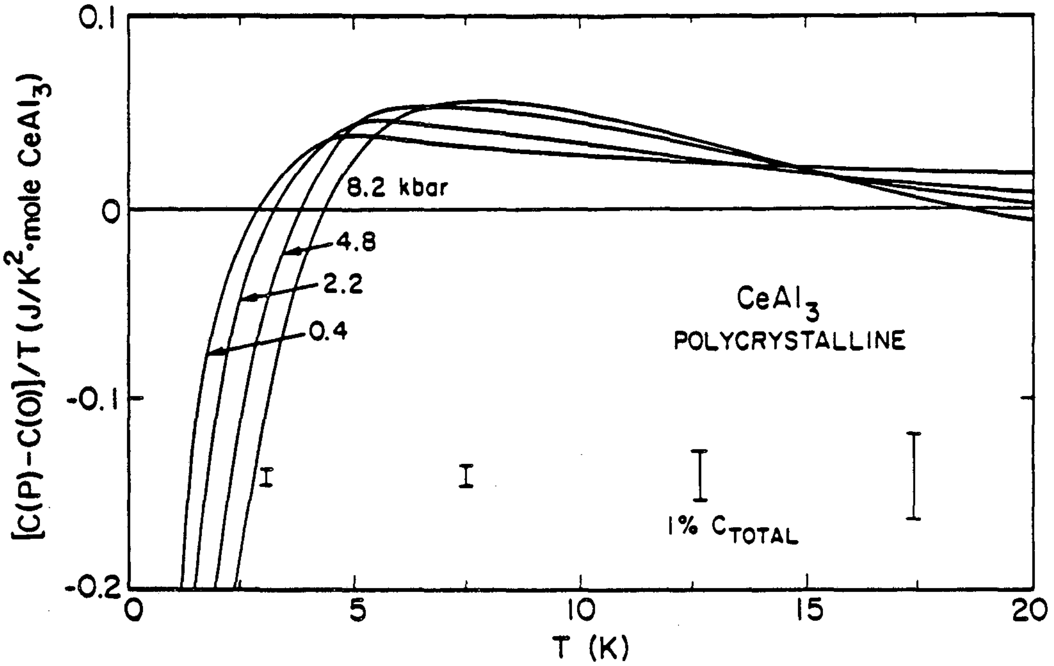


Fig. 6. Pressure dependence of $[C(P)-C(0)]/T$ for CeAl$_3$.

$= \kappa^{-1}(\partial \ln X/\partial P)_T$ where κ is the compressibility. Smoothed values of Γ_C are given in Tables 1-4.

As noted above, the temperature dependence of the specific heat of UPt$_3$ is qualitatively different from those of CeAl$_3$, CeCu$_6$ and UBe$_{13}$. Figs. 2-5 and particularly Figs. 6-9 show that the pressure dependences are also very different. For CeAl$_3$, CeCu$_6$ and UBe$_{13}$, there is a low temperature region in which $(\partial C/\partial P)_T$ is predominantly negative, an intermediate temperature region in which it is positive, and a higher temperature region in which it is negative again. The changes in sign depend on pressure as well as temperature, but they occur, very approximately, at 3 and 17K for CeAl$_3$, at 2 and 10K for CeCu$_6$, and at 3 and 10K for UBe$_{13}$. For UPt$_3$, in contrast, $(\partial C/\partial P)_T$ is negative, except for $P \sim 4$-9 kbar and $T \sim 12$K where it is approximately zero. This difference between UPt$_3$ and the others is probably also asso-

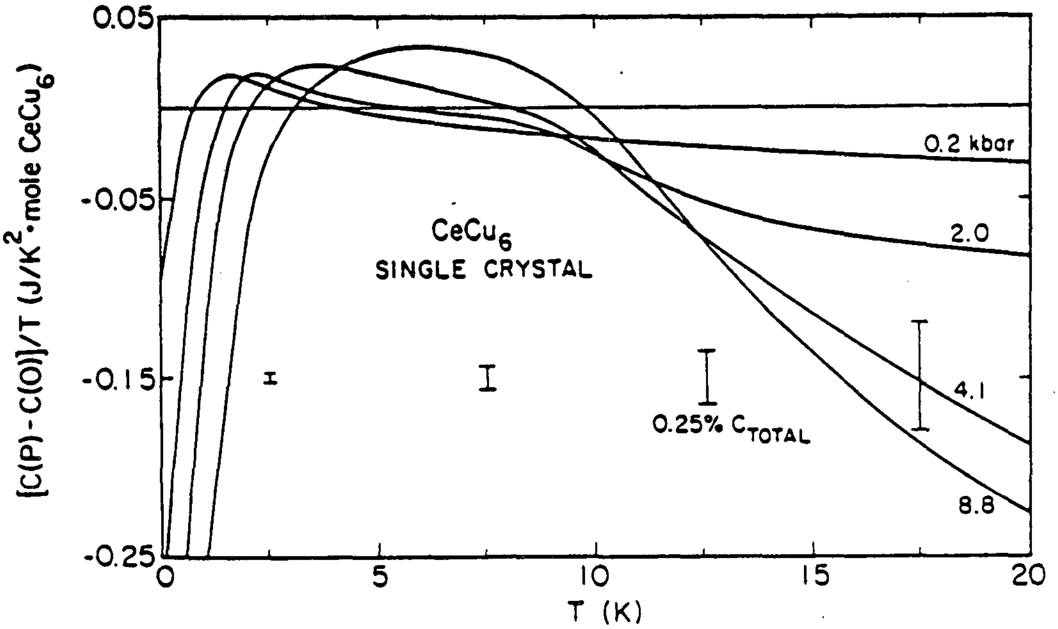


Fig. 7. Pressure dependence of $[C(P)-C(0)]/T$ for CeCu$_6$.

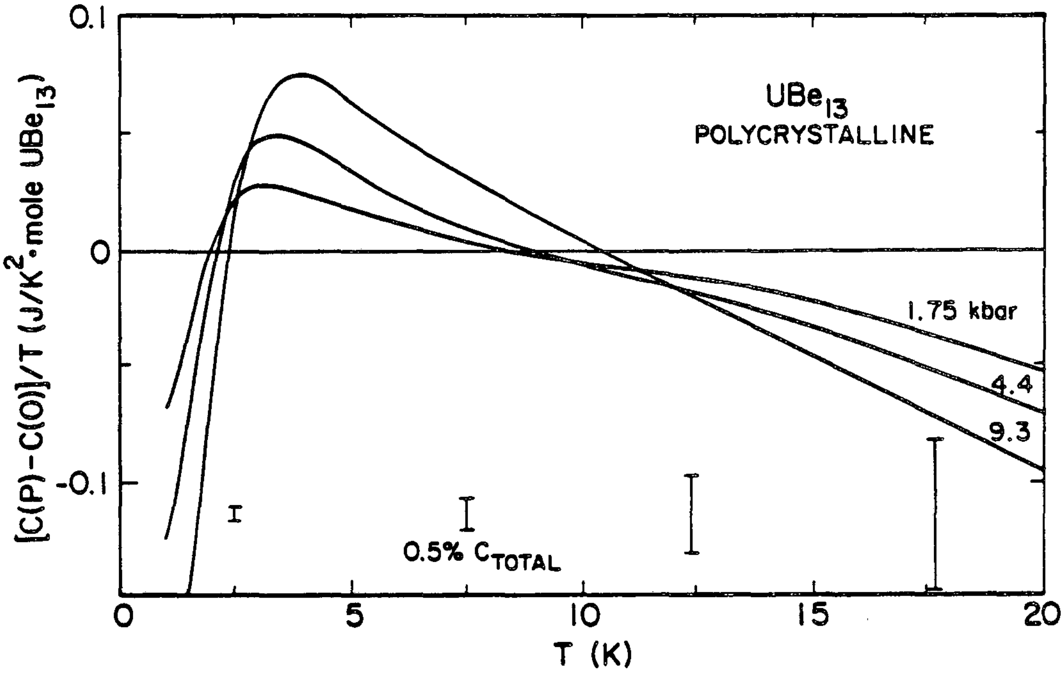


Fig. 8. Pressure dependence of $[C(P)-C(0)]/T$ for UBe_{13}.

ciated with a difference in relative importance of the interactions represented by T^* and T_K in the temperature region of the measurements. There is substantial non-linearity in the pressure dependence of C for all four materials, but it is particularly extreme for $CeAl_3$ for which $[C/T]_{0.4K} = 1.79 - 0.85\,P^{1/6}$ (P in kbar and C in J/mole K^2) for the non-zero pressures at which C was measured [1]. (There must be deviations from that relation near zero pressure [1].) The deviations from linearity are apparent in Figs. 2-9 and Tables 1-4.

The pressure dependence of C is related to the temperature dependence of the thermal expansion (α) by the thermodynamic expression $(\partial\alpha/\partial T)_P = -(VT)^{-1}(\partial C/\partial P)_T$. Experimental values of α are available for both $CeAl_3$ [6,25] and UPt_3 [26], at zero pressure, and can be compared with $(\partial C/\partial P)_T$ in the

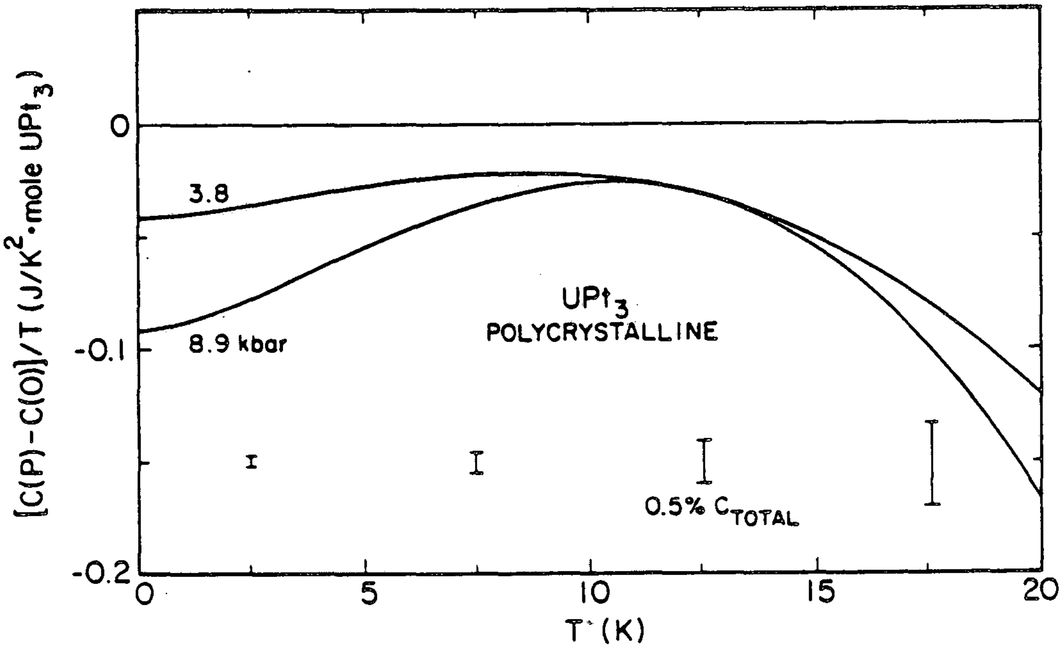


Fig. 9. Pressure dependence of $[C(P)-C(0)]/T$ for UPt_3.

Table 1. Γ_C for $CeAl_3$ (hexagonal), based on $\kappa = 2.16 \times 10^{-3}$ $kbar^{-1}$ [21].

T(K) P(kbar)	0	0.4	1	2	4	10	15	20
0.2	-160	-710	-340	-80	70	100	110	80
1	-52	-51	-37	-14	6	17	0	-5
2	-50	-48	-40	-19	-2	6	-5	-14
4	-41	-40	-38	-24	-6	4	0	-3
6	-27	-27	-26	-21	-8	1	0	-3
8	-15	-15	-14	-13	-9	0	0	-3

Table 2. Γ_C for $CeCu_6$ (which undergoes a change in crystal structure from orthorhombic to monoclinic near 200K), based on $\kappa = 1.1 \times 10^{-3}$ $kbar^{-1}$ [22].

T(K) P(kbar)	0	0.5	1	1.5	2	5	10	20
0	-115	-52	0	20	40	-8	-56	-90
1	-88	-54	-19	0	10	4	-28	-72
3	-73	-60	-41	-23	-13	14	-4	-54
5	-68	-60	-46	-31	-18	12	6	-37
7	-66	-57	-48	-35	-20	5	12	-17
9	-63	-55	-50	-38	-22	0	18	0

Table 3. Γ_C for UBe_{13} (cubic), based on $\kappa = 0.97 \times 10^{-3}$ $kbar^{-1}$ [23].

T(K) P(kbar)	1	2	5	10	15	20
0	-63	11	56	-41	-125	-230
1	-50	0	40	-26	-88	-190
3	-32	-10	-27	-2	-36	-65
5	-30	-14	-23	10	-18	-60
7	-33	-17	21	16	-19	-55
9	-34	-18	18	18	-20	-60

Table 4. Γ_C for UPt_3 (hexagonal), based on $\kappa = 0.48 \times 10^{-3}$ $kbar^{-1}$ [24].

T(K) P(kbar)	0[a]	1	2	5	10	15	20
0	-59	-62	-64	-69	-75	-82	-140
1	-58	-58	-57	-54	-49	-73	-127
3	-56	-53	-48	-40	-24	-46	-95
5	-56	-53	-47	-36	-9	-14	-58
7	-57	-55	-50	-36	-2	-3	-32
9	-58	-57	-55	-36	0	0	-19

[a] Values of Γ_C at T=0 are from extrapolated C_n.

same limit. For CeAl$_3$, the measured values of α are in reasonable agreement with $(\partial C/\partial P)_T$ above 1K, but there is a conspicuous discrepancy at lower temperatures where $(\partial\alpha/\partial T)_P$ becomes negative (again) but there is no indication of the corresponding change to positive values of $(\partial C/\partial P)_T$. The resolution of the discrepancy may lie in a further change in sign of $(\partial C/\partial P)_T$, either at lower temperatures or at lower, but still non-zero, pressures than those at which C has been measured [1]. For UPt$_3$, the C and α data are consistent to within the probable experimental errors [4,27,28].

The C(P) data can be compared with $\rho(P)$ by use of the empirical rule that γ is approximately proportional to T_M^{-1} [29]. For CeAl$_3$, T_M (16 kbar)/ $T_M(0) = 2$ [6] and, by extrapolation, $\gamma(0)/\gamma(16\text{ kbar}) = 2.3$ [1]. For CeCu$_6$ $\gamma(0)/\gamma(9\text{ kbar}) = 2.0$ [2] and $T_M(9\text{ kbar})/T_M(0) = 2.2$ [30]. For UBe$_{13}$ the comparison is less clear both because measurements under pressure and in magnetic field, necessary to determine $C_n(P)$, have not been made, and because of the uncertainty in the extrapolation of C_n/T to T=0. Nevertheless, at least the qualitative applicability of the correlation is obvious: $T_M(9\text{ kbar})/T_M(0) = 1.8$ [31]; $[C_n(0)/C_n(9\text{ kbar})]_{1K} \sim 1.5$ and, if one makes a rough extrapolation of $C_n(9\text{ kbar})/T$ to T=0 from T>1K and accepts the value of $\gamma(0)$ reported above, $\gamma(0)/\gamma(9\text{ kbar}) = 2.0$ [3]. Presumably both T_M and γ depend in a complicated way on the interplay between the interactions related to T* and T_K, and the correlation between γ and T_M^{-1} seems to point to the existence of some kind of scaling relation that involves both of these characteristic temperatures.

From the pressure dependence of the $T^3\ln T$ and T^3 terms in the specific heat of UPt$_3$, one can derive the pressure dependence of the associated characteristic temperature. Application of expressions derived for spin fluctuations [18,19] gives a spin fluctuation temperature (T_{sf}) and a Fermi temperature (T_F) that vary from $T_{sf} = 6.4$K and $T_F = 154$K at P=0 to $T_{sf} = 88.1$K and $T_F = 196$K at 8.9 kbar [4]. That analysis suggests that the pressure dependence of the band structure is more important than that of the Stoner enhancement in determining the macroscopic properties. Another interpretation of the same data within the framework of Fermi-liquid theory has led to similar conclusions [27]. The data have also been compared with the pressure dependence of ρ and χ to demonstrate consistency with a Kondo lattice model, rather than ferromagnetic spin fluctuations [32].

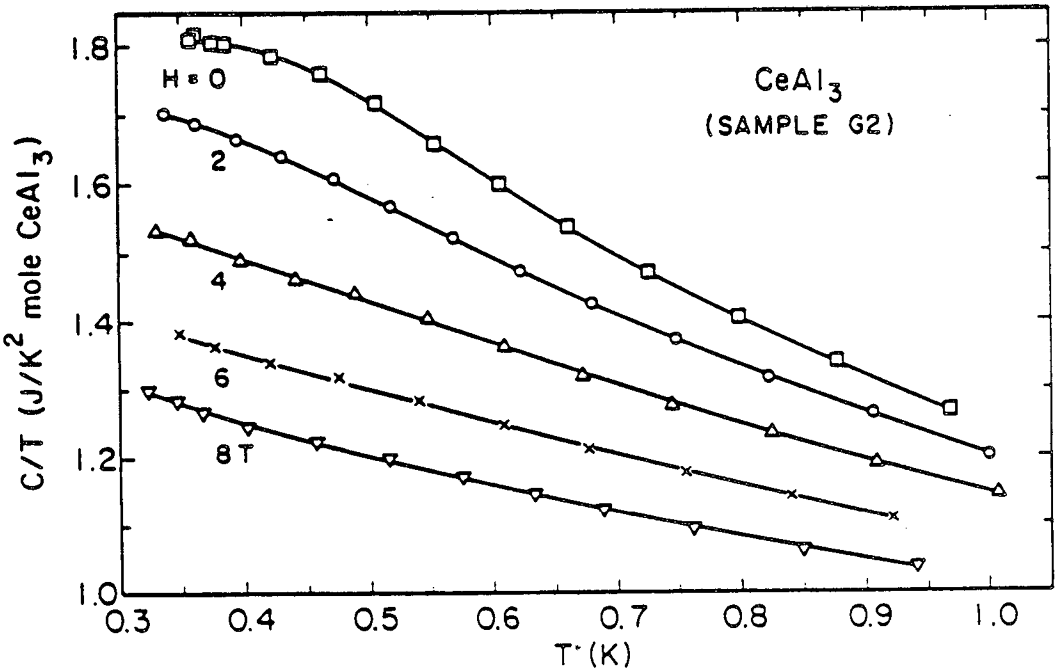


Fig. 10. Magnetic field dependence of C/T for polycrystalline CeAl$_3$.

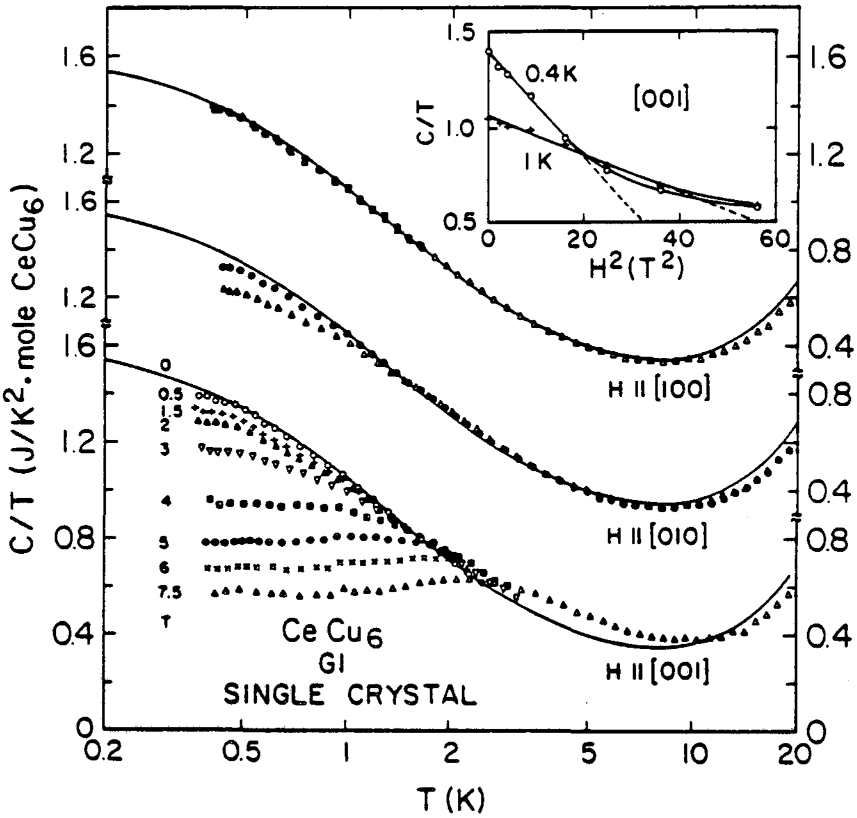


Fig. 11. Magnetic field dependence of C/T for single crystal $CeCu_6$.

The pressure dependence of C has also been measured for $CeCu_2Si_2$ [5] and $\Gamma_\gamma \sim -70$, similar to the values for the two U-based superconductors, $\Gamma_\gamma \sim -60$ for UBe_{13} and $\Gamma_\gamma = -57$ for UPt_3. One might think of looking for correlations between Γ_γ and Γ_{Tc} (where Tc is the critical temperature for superconductivity) and a comparison with BCS superconductors for clues to the origin of superconductivity. Such a comparison has been made for UPt_3 [4] on the basis of spin fluctuation theory, but there is now some reason to question the applicability of that theory. The values of Γ_{Tc} for the three heavy-fermion superconductors are not very similar: $\Gamma_{Tc} \sim 7$ for $CeCu_2Si_2$ [5], ~ -76 for UPt_3 [4] and ~ -48 for UBe_{13} [3].

There are interesting qualitative similarities between the effects of magnetic field (H) and P on C for both $CeAl_3$ and $CeCu_6$. The effect of H on C/T is shown in Figs. 10 and 11 for $CeAl_3$ [33] and $CeCu_6$ [9], for comparison with the P dependences shown in Figs. 2 and 3. For $CeCu_6$, the effect of a 5T field along [001] (the direction of strong H dependence) is strikingly similar to that of 8.8 kbar pressure. For $CeAl_3$ the similarity is less pronounced, but that could be a consequence of anisotropy of the field dependence and the distribution of orientations in the polycrystalline sample (cf. data for other orientations in Fig. 11). (For $CeAl_3$ below 0.4K, C increases with H [7] but, as noted above, there is some reason to expect an increase with P in this region.) These similarities are suggestive, but in the region in which they occur C is presumably determined by the superposition of intersite interactions on a Kondo lattice, and we have not recognized any simple rationale for them. By contrast with $CeAl_3$ and $CeCu_6$, both UBe_{13} and UPt_3 exhibit only a weak dependence of C on H at any temperature.

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