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Thermodynamic behavior of the heavy-fermion compounds Ce_3X ($X = Al,In,Sn$)

Y.-Y. Chen
Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan

J. M. Lawrence
Physics Department, University of California–Irvine, Irvine, California 92717

J. D. Thompson and J. O. Willis
Physics Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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We have measured the resistivity $\rho(T)$ and susceptibility $\chi(T)$ of Ce_3Al, Ce_3In, and Ce_3Sn in the temperature range 1–350 K, the specific heat $C(T)$ for 1–25 K and the pressure dependence of the resistivity $\rho(P,T)$ for $0 < P < 16$ kbar and $1 < T < 300$ K. These are heavy-fermion systems that show no superconductivity above 0.4 K. In the ground state the linear coefficients of the specific heat γ are 0.70 and 0.26 J/mol Ce K^2 for Ce_3In and Ce_3Sn, respectively. The magnetic specific heat of Ce_3In shows two separated maxima: one at 4.3 K due to the heavy fermions and a second Schottky peak at 23 K arising from a Γ_7-Γ_8 crystal-field splitting of order $T_{CF} = 65$ K. For Ce_3Sn the crystal-field splitting is comparable. From $\chi(0)$ we obtain values of the Wilson ratio of 11.5 and 7.0 for Ce_3In and Ce_3Sn. We argue that these large values represent the presence of ferromagnetic correlations in the ground state. For Ce_3In the enhancement of the susceptibility and specific-heat coefficient and the rapid decrease of the resistivity all occur below the same temperature (7 K), suggesting that the onset of the heavy mass coincides with the onset of magnetic correlations and coherence. In addition, for Ce_3In an inflection point occurs in $\rho(T)$ at $T_{inf} = 2.2$ K, below which ρ varies as T^2, and there may be a peak in $C(T)/T$ at 2 K. Thus, it appears that there are two temperature scales for the onset of interaction effects: One coincides with the single-ion Kondo temperature T_K, and the other, a low-temperature scale T_L, obeys a rule $T_L = T_K / N_{deg}$, where N_{deg} is the degeneracy of the ground-state multiplet. The ground state of Ce_3Al is antiferromagnetic with $T_N = 2.5$ K. The specific-heat anomaly makes it impossible to determine γ but for $10 < T < 20$ K $\gamma = 0.085$ J/mol Ce K^2. From χ and the magnetic entropy we estimate $T_K = 10$–15 K. The magnetic entropy remains smaller than R ln2 even at 25 K; we conclude that the ordering occurs in a regime where the moment (at least on some sites) is strongly compensated by the Kondo effect. With application of pressure, the characteristic temperature increases in Ce_3Sn; it increases initially for Ce_3In, but for $P > 9$ kbar there is a structural transition with the unusual feature that the low-temperature phase has smaller characteristic energy than the high-temperature phase. A related transition occurs in Ce_3Al at ambient pressure, which disappears at higher pressure.

I. INTRODUCTION

The compounds Ce_3Al, Ce_3In, and Ce_3Sn form an interesting set of heavy-fermion materials.[1,2] At high temperatures and ambient pressure all have the cubic Cu_3Au crystal structure.[3–6] Ce_3Sn retains this structure at all pressures studied ($P < 16$ kbar) to low temperatures ($T > 1$ K).[1,6] Ce_3Al undergoes a phase transition at 520 K;[3] below this temperature it has the related hexagonal Ni_3Sn phase.[4] This transition is similar to the fcc-dhcp transition that occurs in cerium and other light rare earths. At $T_s = 115$ K it undergoes a second structural transition;[2] at first[2,7] the low-temperature phase was believed to be isostructural (Ni_3Sn) so that the transition would be analogous to the γ-α transition in cerium metal. More recent neutron work[8] reveals that the low-temperature phase of Ce_3Al has monoclinic symmetry ($P112_1/m$). This latter transition disappears for elevated pressures,[2] so that for $P > 12$ kbar the ground state has the Ni_3Sn structure. At $P = 0$, Ce_3In also retains the Cu_3Au structure to the lowest temperatures,[1,5] but at elevated pressures ($P > 9$ kbar) a structural transition occurs[1] at low temperature to an as yet unknown structure. The equilibrium structures are known[3,9] to be sensitive to the presence of interstitials, particularly carbon, and the degree of disorder in the Cu_3Au phase is sensitive to heat treatment.[5,6]

The resistivities reported earlier for these compounds have features in common with those of heavy-fermion compounds. Ce_3Al shows a peak in the resistivity[1,2,10] and susceptibility[10,11] at 2.7 K indicative of antiferromagnetic order. Between 2.7 and 20 K the slope $d\rho/dT$ is negative, suggesting the presence of the Kondo effect with a Kondo temperature of order 20 K. The resistivities of Ce_3Sn and Ce_3In (Ref. 1) are monotonic but rise rapidly at low temperatures in a manner characteristic of heavy fermions with small Kondo temperatures ($T_K < 20$ K). On application of pressure the resistivities of all three change more slowly with temperature; this is

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a general phenomenon observed in most cerium compounds and is attributed to the increase of T_K with increasing pressure.[12]

Because of the mentioned sensitivity[3,9] to the presence of interstitials we have remade[2] all three compounds with higher purity starting materials, giving some attention to the effects of stoichiometry and heat treatment on the thermodynamic properties. In this paper we report results for these new samples for the temperature and pressure dependence of the resistivity and in addition for the ambient pressure susceptibility and specific heat. The latter measurement allows us to prove unambiguously that these are heavy-fermion compounds, the hallmark[13] being large values of the linear coefficient of specific heat $\gamma = C(T)/T$. We present an analysis in terms of prevailing heavy-fermion theories,[14] for which the characteristic temperature scales are the single-ion Kondo temperature T_K and one or more temperatures for the onset of interaction effects. Crystal-field effects are also clearly present. Comparison between the different thermodynamic quantities leads to a determination of these parameters and their evolution with pressure. We conclude that ferromagnetic correlations are important in the ground state of Ce_3X. (Antiferromagnetic correlations have been observed[15] by neutron scattering in several heavy-fermion compounds.) Finally, we report phase diagrams for the low-temperature structural transitions.

II. EXPERIMENTAL DETAILS

All samples were prepared by arc melting. We obtained ultra-high-purity aluminum, indium, and tin from Alfa Ventron; but earlier studies[1,2] indicated that cerium obtained from commercial sources had a sufficiently large fraction of interstitial impurities, that the thermodynamic properties were affected. In this study we used high-purity cerium obtained from Ames Lab, and all sample fabrication steps were carried out in inert atmospheres. The samples of Ce_3In and Ce_3Sn were then annealed for one to two weeks at 5–700 °C and cooled slowly to room temperature, while samples of Ce_3Al were annealed first at 500 °C for three days followed by a three-week anneal at 200 °C to promote conversion from the cubic to the hexagonal phase.

Ce_3In oxidizes extremely rapidly in air, Ce_3Sn somewhat less rapidly, while Ce_3Al is quite stable against such oxidation. All three materials are highly ductile (particularly Ce_3Al) and can not be powdered. We performed x-ray diffraction on polished surfaces; because these materials are sensitive to strains, as evidenced in particular by the phase transitions reported below, the diffraction lines so obtained were broad. We also measured several samples which were filed to a fine powder, then annealed to remove strain; the diffraction patterns showed very sharp lines but with the same lattice constants as for the polished samples [see also Ref. 8]. This gives us confidence that the results for polished surfaces are essentially correct.

The lattice constants for $Ce_{3+x}Sn$ ($-0.10 < x < 0.15$) were in the range 4.92–4.95 Å and for Ce_3In the value obtained was 4.96 Å. (The parameter x was determined from the starting composition after weight loss due to evaporation of indium or tin was accounted for.) These values are in good agreement with those reported[5,6] for the ordered Cu_3Au phase of both compounds (values for the disordered phase are reported to be in the range 5.01–5.05 Å). We saw no evidence of second phases in the diffraction patterns. Both susceptibility and resistivity are sensitive indicators of free tin and indium, which give characteristic signatures at their superconducting transitions; no such signature was observed. The resistance ratios $R(300\text{ K})/R(4.2\text{ K})$ were for Ce_3Sn in the range 12–14 for the range of stoichiometry already stated. For $Ce_{3+x}In$ for $-0.16 < x < 0.10$, the ratio $R(300)/R(1.8)$ varied from 4 to 6 for annealed samples, but was substantially smaller (1.5) for unannealed samples (see Table I). [$R(0)$ can be estimated by extrapolating the observed quadratic temperature dependence to $T=0$; see Fig. 10(a). In this case we find $R(300)/R(0)=27$ for the best sample.] The low-temperature susceptibility $\chi(1.8\text{ K})$ varied from 0.050 to 0.090 emu/mol Ce for annealed samples, but was 0.137 and 0.186 emu/mol Ce for unannealed samples. For unannealed samples and for a sample with $x = 0.16$ a peak was observed in the susceptibility between 2 and 3 K. We measured the susceptibility of the neighbor compound Ce_2In, which has a peak at 12 K; hence the observed peaks at 2–3 K do not arise from the presence of this compound. We draw the following conclusions: annealed $Ce_{3+x}Sn$ is single phase for the interval $-0.10 < x < 0.15$ and possibly for a larger interval; annealed $Ce_{3+x}In$ is single phase for the interval $-0.16 < x < 0.10$ but not for larger x; and that unannealed Ce_3In is disordered as evidenced by large susceptibility and small resistance ratio. Further, the disordered phase has a peak in the susceptibility near 2–3 K, indicating antiferromagnetic order.

For Ce_3Al we used optical metallography as well as x-ray diffraction, as the former technique proved quite sensitive to the presence of untransformed cubic phase. Two factors proved necessary to eliminate the cubic phase: long anneals at 200 °C (below the temperature of the cubic-hexagonal transition) and elimination of interstitials both in the starting materials and in the handling. For most such samples we obtained diffraction patterns for the hexagonal phase with $a = 7.03$ Å and $c = 5.44$ Å.[4] Two samples of $Ce_{3+x}Al$ with excess cerium did not show the characteristic splitting of the (002) and (201) lines; but showed a single line indicating $a = 7.03$ Å and $c = 5.33$ Å. However, for the whole range of composition $-0.05 < x < 0.05$ there are no observable differences in the temperature dependence of the resistivity reported below.

The electrical resistivity was measured using standard four-probe methods; for the pressure dependence of the resistivity we used a self-clamping cell.[16] The absolute values of the resistivities for Ce_3In and Ce_3Sn reported in the following are accurate to only about 30%, as determined from reproducibility (see Table I); for Ce_3Al the values reproduced to 10%. Two factors affected absolute accuracy: nonoptimal sample geometries and the existence of microcracks associated with oxidation in Ce_3In

TABLE I. Resistance ratio $\rho(300)/\rho(1.8\ \mathrm{K})$, susceptibility $\chi(1.8\ \mathrm{K})$ and room-temperature resistivity $\rho(300\ \mathrm{K})$ for varying stoichiometries and heat treatments for $Ce_{3+x}In$.

X	Heat treatment	$\chi(1.8\ \mathrm{K})$ (emu/mol Ce)	$\rho(300)$ ($\rho\Omega$ cm)	$\rho(300)/\rho(1.8)$	Comments
−0.156	500 °C	0.069	124	4.1	
−0.101	500 °C	0.093		3.6	
−0.050	As cast		101	1.5	
−0.032	600 °C		133	4.9	
−0.006	500 °C	0.063	121	5.2	
−0.004	As cast	0.186		1.9	
−0.004	700 °C	0.090		3.5	
−0.002	As cast	0.137		1.6	Peak in χ at $T=2.6$ K
−0.002	500 °C	0.097			No peak
+0.006	600 °C		139	4.2	
+0.045	600 °C	0.057	99	5.4	$\rho(300)/\rho(0)=27$ by extrapolation (see the text)
+0.064	As cast			2.6	
+0.064	500 °C	0.086		5.2	
+0.101	500 °C	0.054	91	5.8	
+0.161	500 °C	0.047	230	5.6	Peak in χ at $T=2.1$ K

and Ce_3Sn. The values reported following for the latter two compounds are thus upper limits. The relative accuracy is better than 0.1%, as can be seen from the scatter in the plots.

The susceptibility was measured several times for each sample using both the Faraday technique and a SQUID magnetometer. For Ce_3Al and Ce_3Sn and for Ce_3In for $T>20$ K the reproducibility was excellent. As can be seen from Table I, for Ce_3In the low-temperature susceptibility varies substantially from sample to sample. There appears to be an inverse correlation between $\chi(1.8\ \mathrm{K})$ and the ratio $R(300)/R(1.8)$ so that the intrinsic susceptibility should have the smaller value associated with large resistance ratios [$\chi(1.8)=0.05$ emu/mol Ce]. The obvious origin of this effect is that disordered samples have substantially larger susceptibilities, and corresponding smaller resistance ratios. As already mentioned, the extrapolated ratio $R(300)/R(0)$ is 27 for our best sample; this is sufficiently large that we think there will be no further reductions in $\chi(0)$ with improved sample quality. That is, we think the susceptibilities reported below have values close to the intrinsic value for Ce_3In.

The specific heat was measured using a time constant technique[17] and small (10-mg) samples. For Ce_3In and Ce_3Sn the surface oxide formed a barrier necessitating a correction for short times; this leads to scatter in the data at the lowest temperatures, visible in the plots given below. Two runs were performed for all three compounds; overall reproducibility was within the scatter.

Finally, we note that the presence of interstitials has a strong effect on the structural phase transitions reported in the following. This can be seen by comparing the resistivities for less pure samples, which were reported earlier,[1] to those reported in the following. The magnitude of the discontinuities, the temperature, and the pressure dependence of the transitions are all affected.

III. RESULTS AND ANALYSIS

The resistivity of the three compounds at ambient pressure is shown in Fig. 1. At room temperature the resistivity is of order $100\mu\ \Omega$ cm, a value typical of cerium compounds with large spin disorder scattering. For Ce_3Al three features are evident: The first-order transition at 110 K, the region of negative slope (2–20 K) suggestive of the Kondo effect, and the peak at low temperature indicating the onset of magnetic order. The resistivity of Ce_3In rises rapidly to large values for $T<10$ K, varying more slowly at higher temperature; such behavior is reminiscent of that of other heavy-fermion compounds with small characteristic temperature, such as UPt_3.[13] The behavior of Ce_3Sn is similar, but on a larger temperature scale. These facts give the first indication of the heavy-fermion nature of these materials. (It should be pointed out that polycrystalline averaging is important in Ce_3Al where the ground-state symmetry is low; single crystals would doubtless show very different behavior in different directions.)

The susceptibility of Ce_3In is shown in Fig. 2. It rises to a large value (0.057 emu/mol Ce) at 1.8 K, and appears to saturate. Above 100 K a Curie-Weiss law [$\chi(T)=C/(T+\Theta)$ with $C=0.807$ emu K/mol Ce and $\Theta=73$ K] is evident; the value of the Curie constant moment is that of a free $J=\frac{5}{2}$ cerium ion. Between 2 and 10 K a second region of Curie-Weiss behavior is evident, with $C=0.2$ emu K/mol Ce and $\Theta=1$ K. Here the Curie constant is essentially equal to the value for a ground-state doublet (0.193 emu K/mol Ce), suggesting the importance of crystal fields. This is supported by the plot of the effective moment $T\chi$; this has a plateau near $T=10$ K at the value 0.2 emu K/mol Ce, implying that the upper quartet is not yet excited but that the full moment of the ground-state doublet has been generated.

The susceptibility of Ce_3Sn (Fig. 3) is similar. The low-temperature value is smaller (0.013 emu/mol Ce) and the high-temperature Weiss constant larger ($\Theta = 87$ K). At low temperatures a Curie-Weiss law with $C = 0.21$ and $\Theta = 15$ K is evident; again crystal fields are in evidence, but in this case no plateau in $T\chi$ is evident. We also exhibit in the inset a plot of $T\chi$ at low temperature; were an impurity present so that

$$\chi(T) = \chi(0) + C_{\mathrm{imp}}/T$$

this curve would extrapolate to C_{imp} at $T = 0$. Evidently no such impurities are observed.

For Ce_3Al (Fig. 4) the high-temperature Curie constant ($C = 0.88$ emu/mol Ce) is larger than the free-ion value and the Weiss constant (108 K) even larger than in Ce_3Sn. The structural phase transition is manifest through a small discontinuity at 110 K. A peak in χ at 2.8 K correlates with the mentioned peak in resistivity. Above this temperature the susceptibility has Curie-Weiss form with $C = 0.32$ emu/mol Ce and $\Theta = 10$ K. The temperature of the peak decreases with increasing magnetic field, as expected for an antiferromagnetic transition. For $T > T_N$ the plot of $M(H)$ is linear; but for

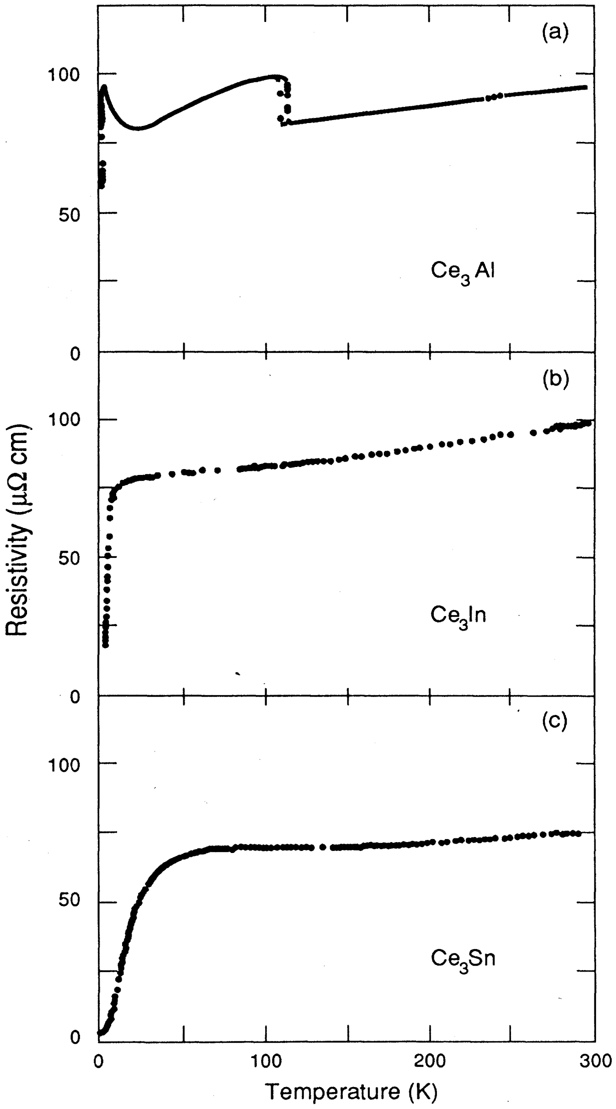

FIG. 1. Resistivity of Ce_3Al, Ce_3In, and Ce_3Sn for 1–300 K.

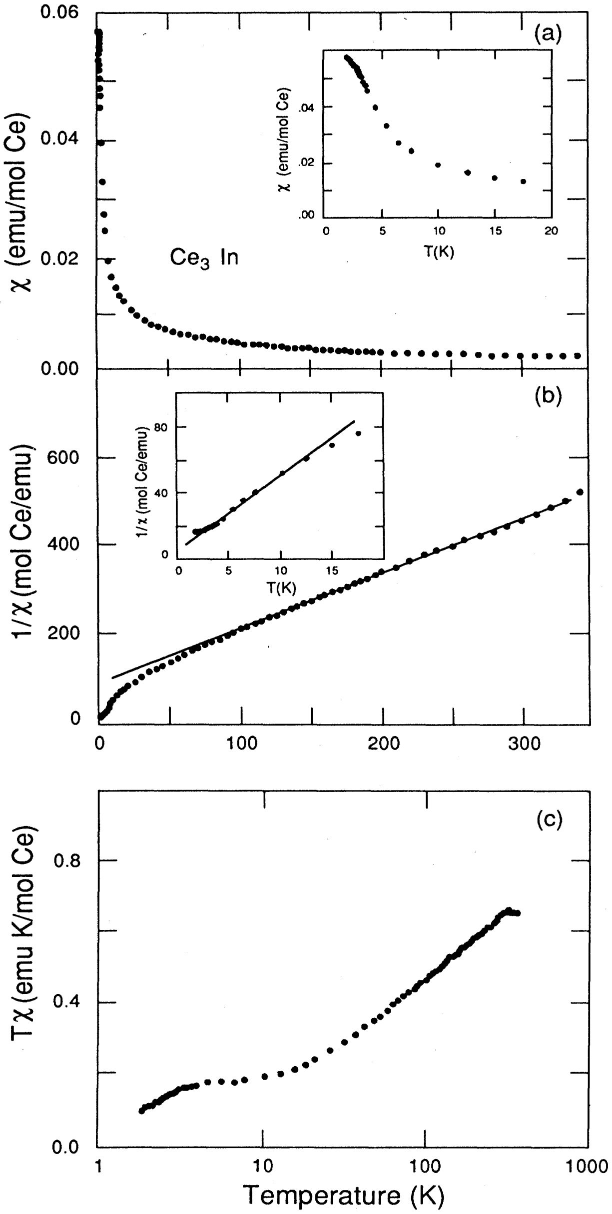

FIG. 2. (a) Susceptibility $\chi(T)$ of Ce_3In for 0–350 K. (Inset: Susceptibility for 0–20 K.) (b) Inverse susceptibility, 0–350 K. The solid line represents the fit $\chi = C/(T + \Theta)$ with C equal the free-ion value and $\Theta = 73$. (Inset: $1/\chi$ for 0–20 K.) The solid line is $C = C/(T + \Theta)$ with $C = 0.21$ emu K/mol Ce and $\Theta = 0.9$ K. (c) Effective moment $T\chi(T)$ vs $\log_{10}(T)$.

$T=2$ $K<T_N$ the curve is nonlinear, suggesting that a field induced transition occurs near 40 kG. The magnitude of the susceptibility at $T=T_N$ is 0.023 emu/mol Ce.

The specific heat of Ce_3In is shown in Fig. 5. Between 10 and 20 K the data follow the law $C(T)=\gamma T+\beta T^3$ where $\gamma=300$ mJ/mol Ce K and $\beta=0.33$ mJ/mol Ce K^4. At lower temperatures $C(T)/T$ increases to 700 mJ/mol Ce K^2. This is typical behavior for a heavy-fermion system. There is a peak in C/T at 2 K [Fig. 5(b)]; it is possible that this is an artifact of the short-time correction already mentioned. Under the assumption that the βT^3 term arises from phonons (the corresponding Debye temperature is 200 K), we subtract it, plotting the magnetic specific heat $C_{\mathrm{mag}}(T)$ in Fig. 5(c). The solid lines represent calculations[18] for a spin $\frac{1}{2}$ Kondo ion with $T_K=4.8$ K and for a Schottky anomaly due to an excited quartet at $T_{\mathrm{cf}}=65$ K. The data is approximately the sum of these two curves; and in particular the Kondo and Schottky peaks are fairly well separated in the data. (Other choices of the coefficient β of the phonon term have the following effect: For smaller β the magnitude of the magnetic specific heat comes out too large compared

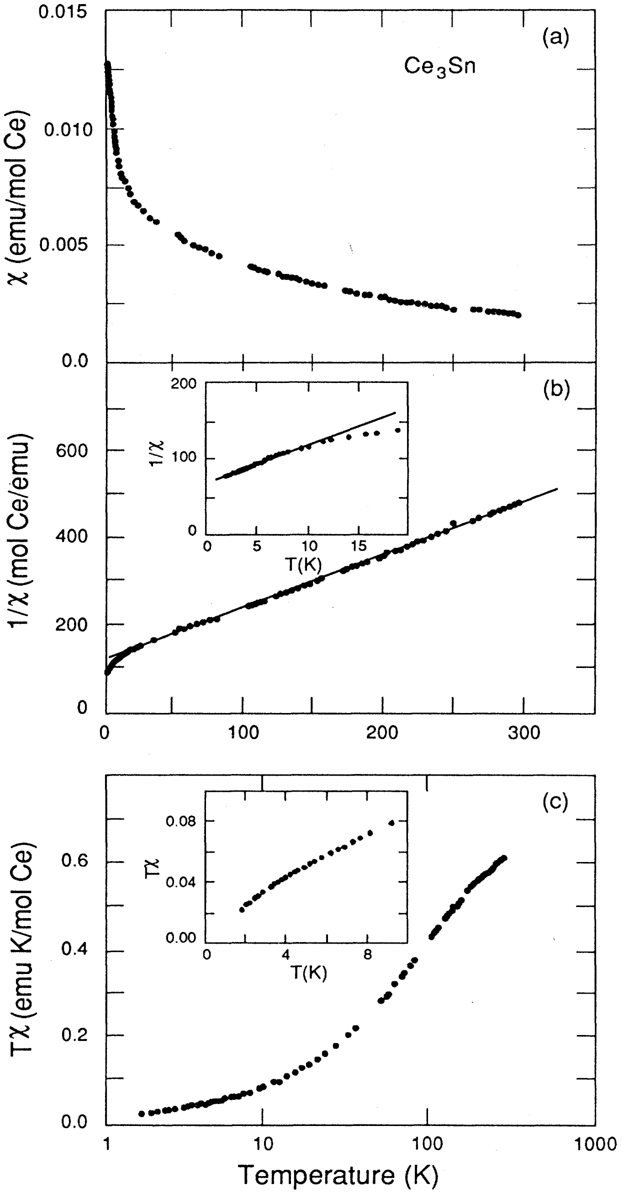

FIG. 3. (a) Susceptibility for Ce_3Sn for 0–350 K. (b) Inverse susceptibility, 0–350 K. The solid line is $\chi=C/T+\Theta)$ with C equal the free-ion value and $\Theta=87$ K. Inset: $1/\chi$ for 0–20 K. The solid line is $C/(T+\Theta)$ with $C=0.21$ emu K/mol Ce and $\Theta=15$ K. (c) Effective moment $T\chi$ vs $\log_{10}(T)$. (Inset: $T\chi$ vs T for 0–10 K).

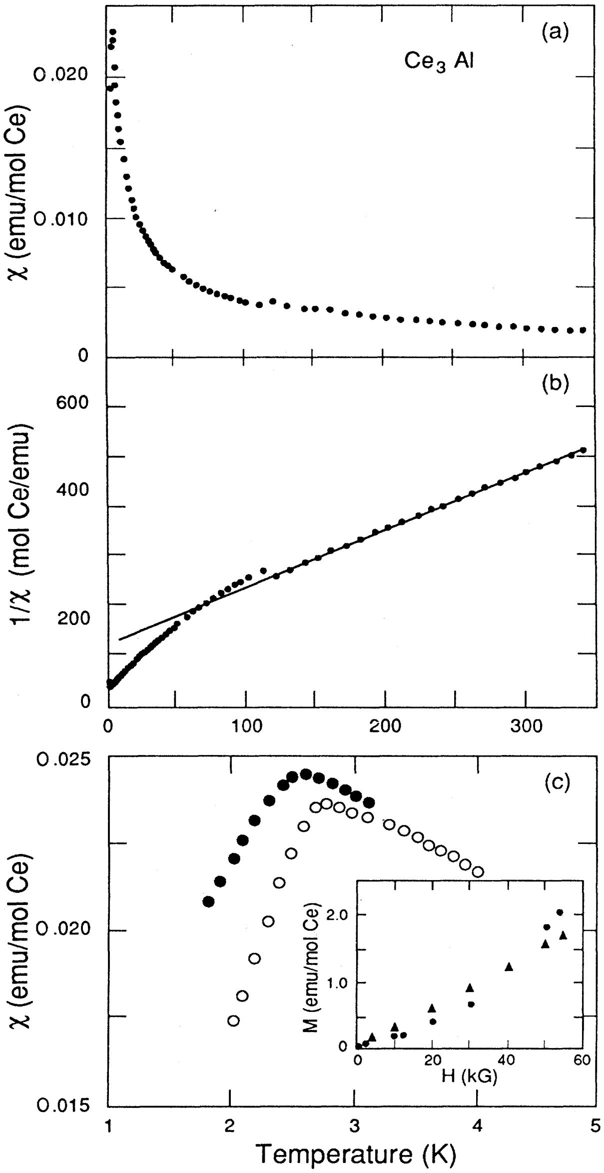

FIG. 4. (a) Susceptibility of Ce_3Al for 0–350 K. (b) Inverse susceptibility for 0–350 K. (c) χ vs T near T_N; open circles $H=2$ kG, closed circles $H=25$ kG. (Inset: M vs H; points $T=2$ K, triangles $T=5$ K.)

to the peak in the Schottky contribution; for larger β the peak in C_{mag} becomes too sharp and the magnitude too small.)

For Ce_3Sn (see Fig. 6) the specific heat is similar except that there is no increase in C/T at low temperature. The value of the coefficient β is the same as in Ce_3In, which strengthens our assumption that this represents phonons; that is, the crystal structures, lattice constants, and atomic weights are virtually identical in the two cases so that the phonon contribution should be identical. Because of the smaller value of γ at $T=0$ the fermions are not as heavy in Ce_3Sn as in Ce_3In. The magnetic specific heat does not separate cleanly into a Kondo and Schottky contribution; and indeed the value of specific heat at the apparent peak near 25 K is too low to be fit by a simple Schottky anomaly. This is discussed in the following.

For Ce_3Al the specific heat for the interval $10 < T < 20$ K fits to $C(T)=\gamma T+\beta T^3$ with $\gamma=85$ mJ/mol Ce K^2 and $\beta=0.66$ mJ/mol Ce K^4. The very different value of β (the Debye temperature is 160 K) arises from the different crystal structure for Ce_3Al. The linear coefficient, while smaller than in the other cases, is still very much larger than in ordinary metals. A peak in $C(T)$ occurs at 2.5 K; this represents the onset of magnetic order. After subtracting the phonon term we plot the magnetic contribution to the entropy in Fig. 7(c). This is substantially smaller than R ln2 at all temperatures shown; hence only a fraction of the entropy of a doublet is liberated at the phase transition, the rest being generated slowly on a much broader temperature scale.

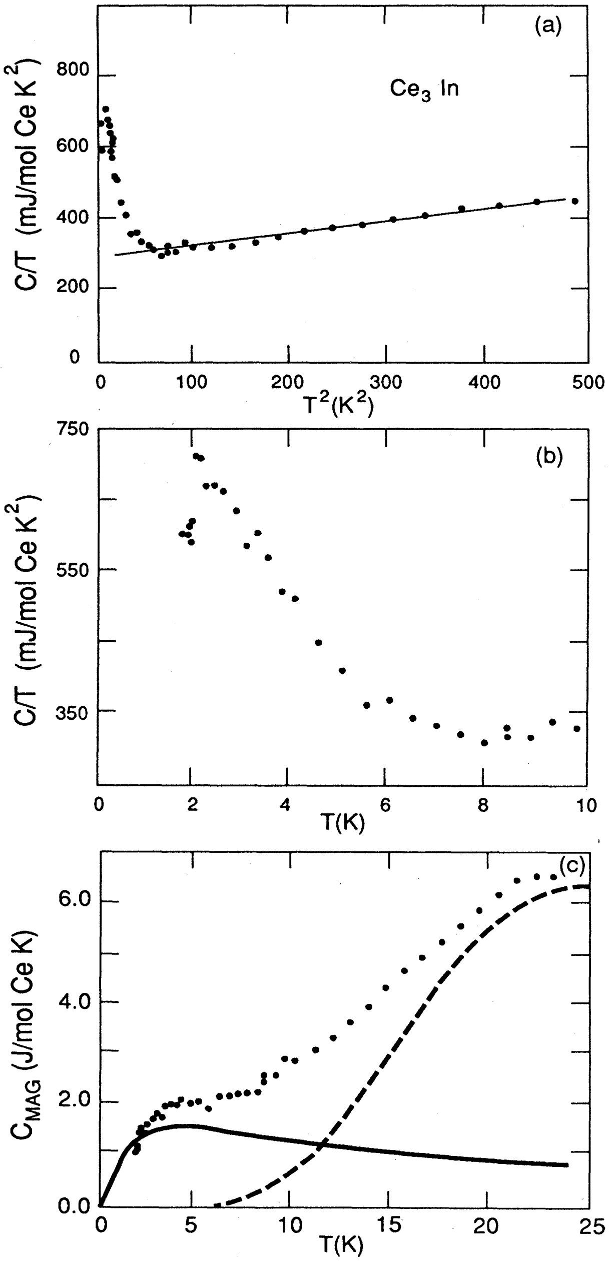

FIG. 5. (a) The coefficient of specific heat $C(T)/T$ vs T^2. The solid line estimates the phonon contribution, 0.33 mJ/mol Ce K^4. (b) C/T vs T for 0–10 K showing a peak near 2 K. (c) The magnetic specific heat vs T for 0–25 K. The solid line represents the specific heat of a spin-$\frac{1}{2}$ Kondo ion with $T_K=4.8$ K; the dashed line represents a Schottky anomaly from a quartet at $T_{\mathrm{cf}}=65$ K.

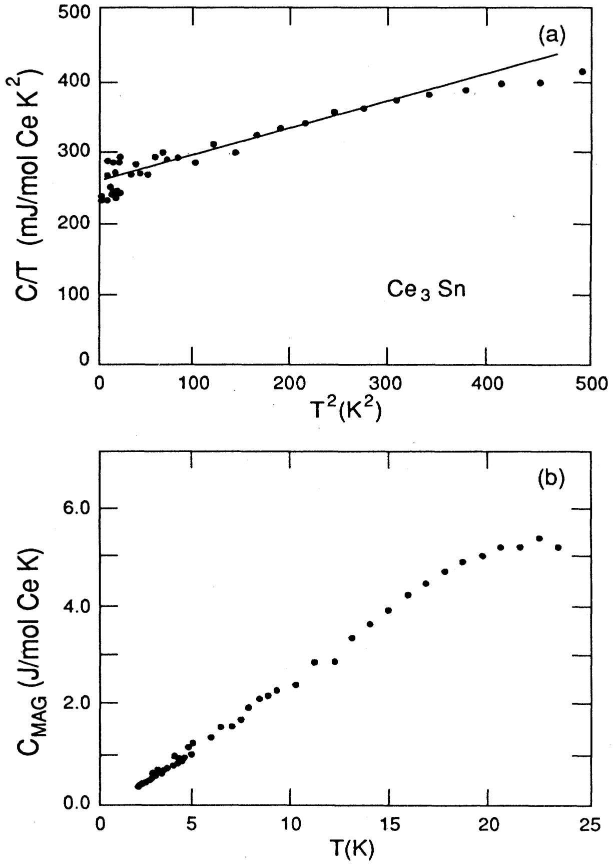

FIG. 6. (a) $C(T)/T$ for Ce_3Sn; the solid line represents a phonon term with the same magnitude as in Ce_3In. (b) The magnetic specific heat 0–25 K.

In Fig. 8 we show the resistivity of Ce$_3$Sn at several pressures. (The sample used for this plot was not as free of oxygen as the samples used for the rest of this paper, and hence has a smaller resistance ratio.) The major effect of pressure is to decrease the rate of increase of $\rho(T)$; this we attribute to an increase of characteristic temperature. The concept of characteristic temperature is discussed further in the Discussion. We give two estimates: the temperature T_{inf} of the inflection in $\rho(T)$ and the temperature T_* obtained by fitting the data at the lowest temperatures to the phenomenological formula

$$\rho(T)=\rho_0+\rho_{\mathrm{sat}}(T/T_*)^2 . \qquad (1)$$

That the temperature dependence is quadratic can be seen in Fig. 8(b). The saturation resistivity ρ_{sat} is found by extrapolating the resistivity at high temperatures in the region where it is approximately linear to $T=0$. In Fig. 8(c) we plot both T_{inf} and T_* as a function of pres-

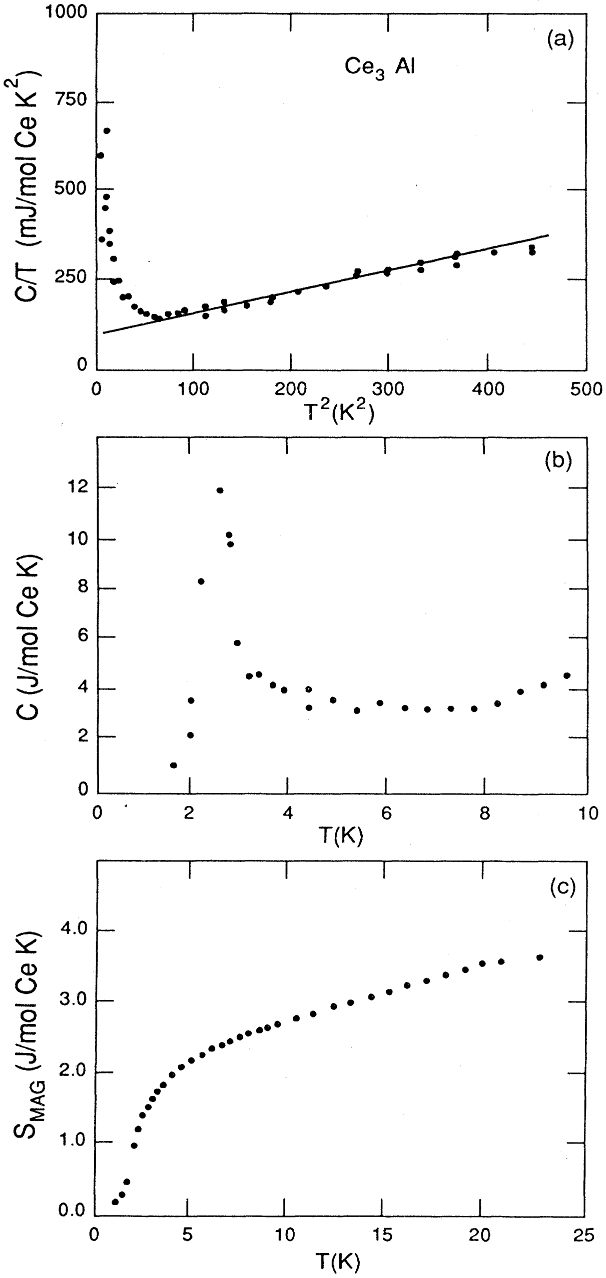

FIG. 7. (a) $C(T)/T$ for Ce$_3$Al. The solid line estimates the phonon contribution as 0.66 mJ/mol Ce K^4. (b) $C(T)$ vs T. (c) The magnetic contribution to the entropy, 0–25 K.

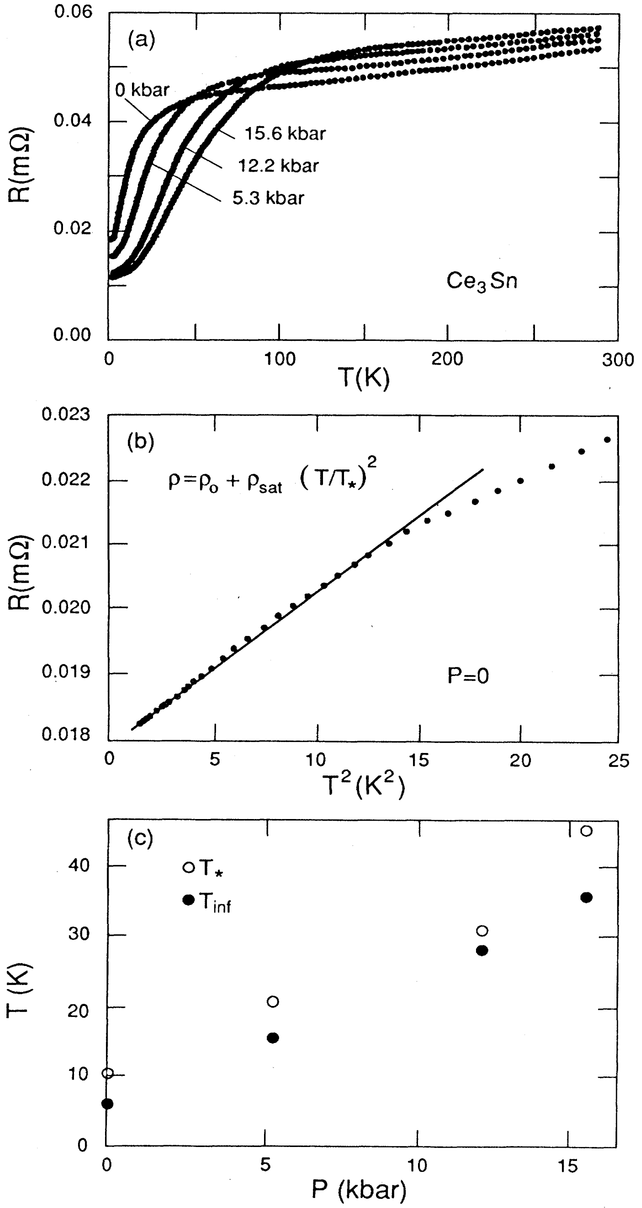

FIG. 8. (a) The resistance vs temperature for Ce$_3$Sn, 0–300 K for four pressures (0, 5.3, 12.2, and 15.6 kbar). (b) The resistance vs the square of the temperature at ambient pressure. (c) The inflection temperatures T_{inf} and the temperatures T_* obtained from the coefficient of the quadratic contribution vs pressure.

sure, where it is seen that both increase linearly with pressure and that T_* is similar in magnitude to $T_{\rm inf}$. We note that at $P=0$ we obtain $T_{\rm inf}=6.2$ K and $T_*=10.4$ K and that the slope $dT_{\rm inf}/dP$ is 1.8 K/kbar.

For pressures up to 10 kbar the resistivity of Ce_3In behaves similar to that of Ce_3Sn (Fig. 9). The resistivity is again quadratic at the lowest temperatures [Fig. 10(a)], with $T_{\rm inf}=2.2$ K and $T_*=4.1$ K and with $dT_{\rm inf}/dP=1.5$ K/kbar; so that the characteristic temperature appears to be about three times smaller than in Ce_3Sn, but the pressure dependence is similar. In addition as P increases a maximum appears in $\rho(T)$ indicative of the presence of the Kondo effect. For $P>9$ kbar a structural phase transition occurs; the phase boundary, found by taking the midpoint of the hysteresis loops, is shown in Fig. 10(c). From the shape of the phase boundary it is clear that the high-temperature phase is the original Cu_3Au phase; note that the maxima in $\rho(T)$ observed at lower pressure are still clearly observed in the high-temperature phase, especially at 10.6 kbar. On the other hand, in the low-temperature phase both the inflection temperature $T_{\rm inf}$ and the coefficient T_* of the quadratic term are quite small.

In Fig. 11 we exhibit the pressure dependence of the resistivity of Ce_3Al. Pressure has very little effect on the resistivity of the high-temperature phase. Its effect on the structural phase transition, shown in detail in Fig. 12, is to decrease the magnitude of the discontinuity and shift the temperature of the phase transition. We plot the phase boundary in Fig. 13; the extrapolation to $T=0$ is based on the observation that no hysteresis was observed for $P>12$ kbar. It appears that the Ni_3Sn phase is stable at high pressure. The shape of the resistivity at the phase transition is similar to that in the case of Ce_3In (note in particular the similarity of the curves for Ce_3Al at $P=7.12$ kbar and for Ce_3In at $P=16.5$ kbar) leading us to speculate that the high-pressure low-temperature phase of the latter compound may be similar to the low-pressure low-temperature phase of Ce_3Al. The effect of pressure on the low-temperature phase of Ce_3Al is as follows: The region of negative $d\rho/dT$ is suppressed, and for $P>6$ kbar the low-temperature resistivity is monotonic, with $T_{\rm inf}$ initially increasing rapidly ($dT_{\rm inf}/dP=3.6$ K/kbar) but then saturating at a value 32 K in the high-pressure phase. At the same time the temperature and magnitude of the resistance drop at the antiferromagnetic transition change rapidly with pressure (Fig. 14). We have not attempted to quantify the magnetic phase boundary, but it is clear that the transition disappears at about the same pressure as the $T=0$ phase transition to the Ni_3Sn phase.

We tested samples of Ce_3In and Ce_3Sn for superconductivity; the samples remained normal above 0.4 K.

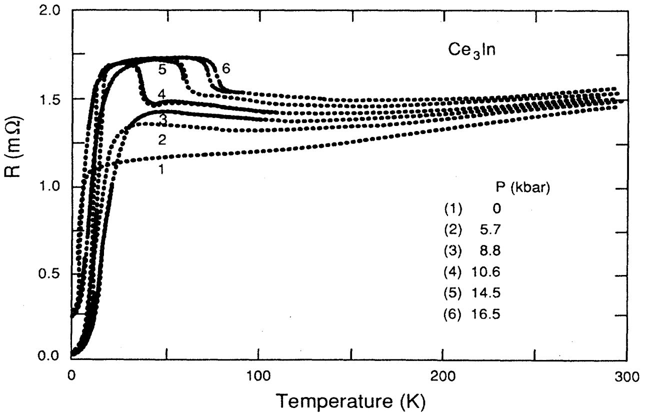

FIG. 9. The resistance vs temperature for Ce_3In for several pressures in the range 0–16.5 kbar and 0–300 K.

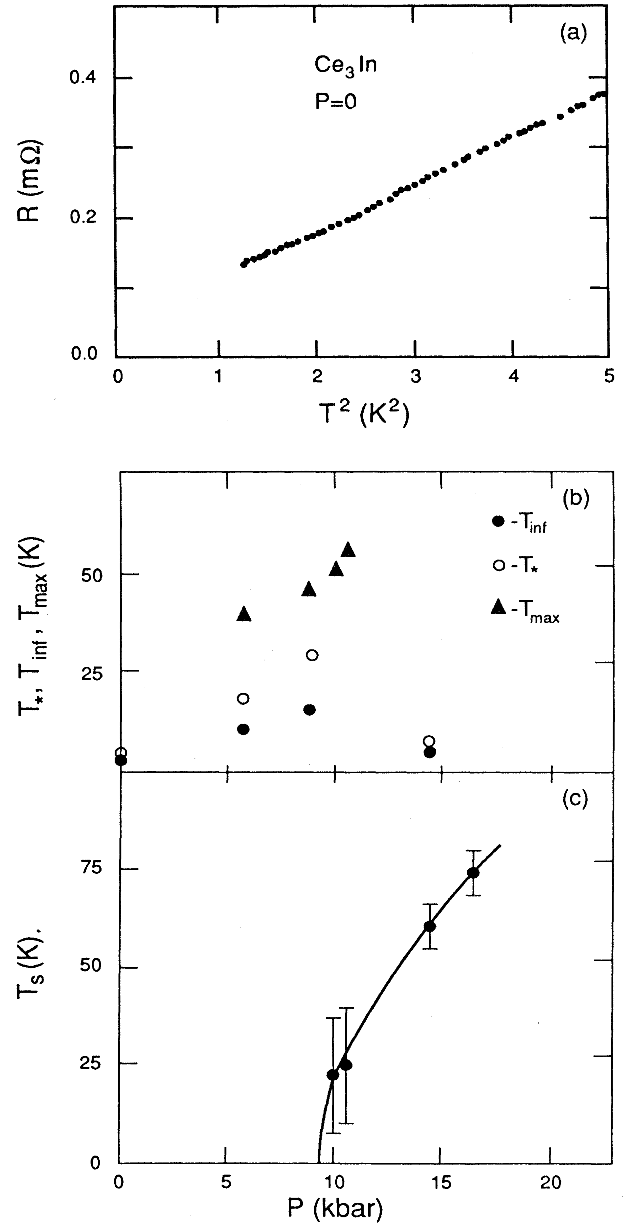

FIG. 10. The resistance vs T^2 for Ce_3In. (b) The inflection temperature $T_{\rm inf}$, the quadratic coefficient T_*, and the temperature of the maximum $T_{\rm max}$ vs pressure. (c) The phase diagram for the structural transition. The error bars give the width of the hysteresis.

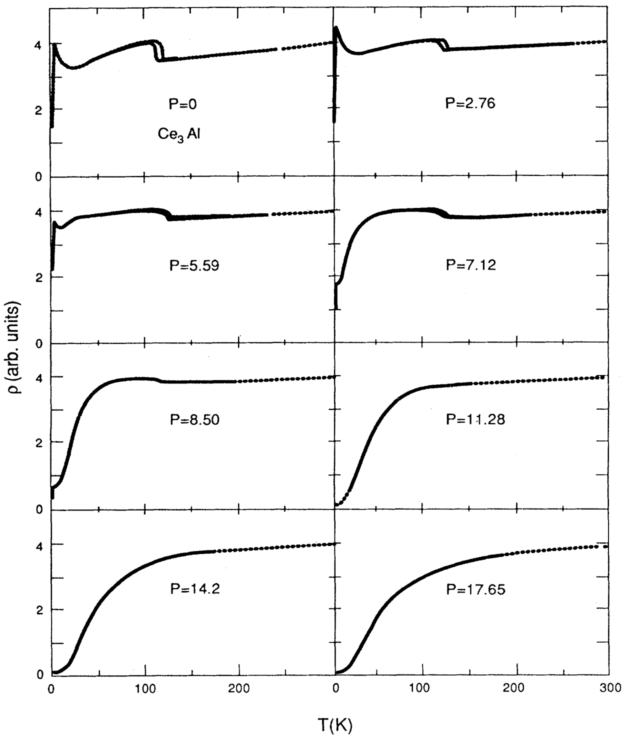

FIG. 11. The resistance vs temperature for Ce$_3$Al for several pressures in the range 0–17.65 kbar.

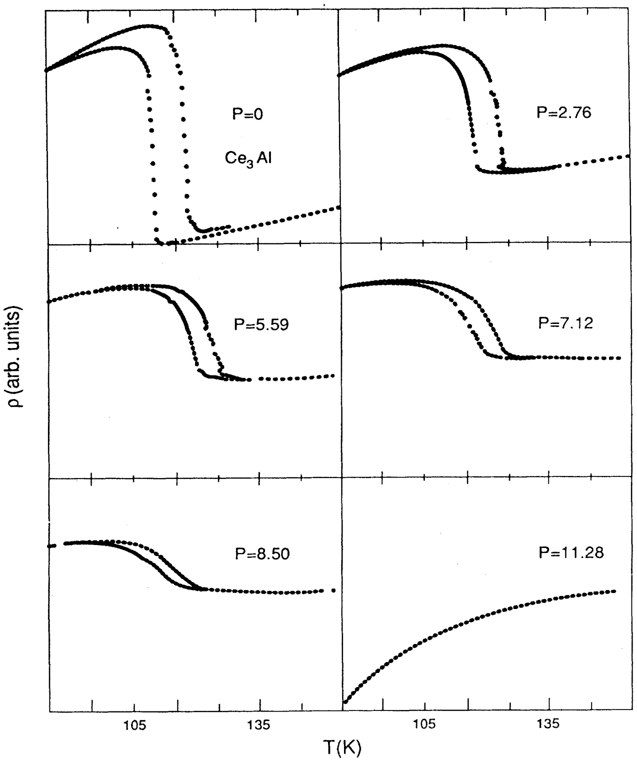

FIG. 12. Detail of the resistance vs temperature of Ce$_3$Al in the vicinity of the structural phase transition for several pressures in the range 0–11.28 kbar.

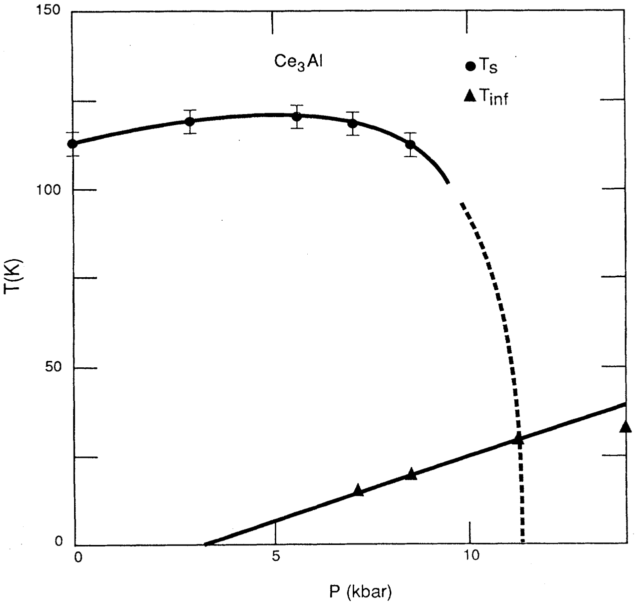

FIG. 13. The phase diagram of the structural transition $T_s(P)$ for Ce$_3$Al and the temperature $T_{\rm inf}(P)$ of the inflection in the resistivity.

IV. DISCUSSION

The physics of heavy-fermion compounds[13,14] involves an interplay between spin fluctuations (Kondo effect), interactions which are responsible for the development of coherence and can cause magnetic order or spin-spin correlations in a nonmagnetic ground state, and crystal-field effects. We discuss the latter first.

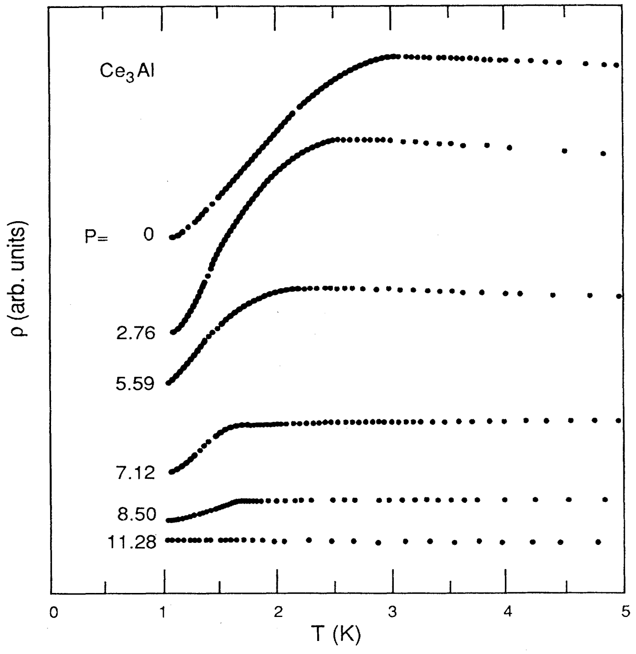

FIG. 14. The low-temperature resistivity of Ce$_3$Al in the vicinity of the magnetic transition for several pressures in the range 0–11.28 kbar.

For both Ce_3In and Ce_3Sn the high-temperature Curie constant is close to the free-ion value; but at low temperatures the data fit a Curie-Weiss law with Curie constant equal to the value (0.194 emu K/mol Ce) for a Γ_7 doublet as expected for $J=\frac{5}{2}$ Ce ions in cubic symmetry. For Ce_3In the effective moment $T\chi(T)$ has a plateau at this value near $T=10$ K; our interpretation is that at these temperatures the moment of the doublet has been generated (i.e., the Kondo compensation overcome) but the higher Γ_8 quartet not yet excited. To estimate the crystal-field splitting we plot the magnetic specific heat of Ce_3In in Fig. 5(c). A reasonable fit to the data is obtained by assuming the specific heat has a contribution from a Kondo doublet, and a Schottky anomaly arising from the excited quartet located 65 K above the ground doublet. Because the Kondo temperature is small compared to the crystal-field splitting a clean separation in the data between the Kondo maximum and the Schottky contribution occurs at temperatures comparable to the plateau in the effective moment, and for the same reason. For Ce_3Sn the Kondo temperature is large enough that the Kondo peak merges with the Schottky anomaly and no maximum is resolved. There appears to be a peak near 25 K suggesting a comparable crystal-field splitting as for Ce_3In. However, the peak value is smaller than expected for a simple Schottky anomaly. This is consistent with our expectation that the specific-heat peak from an excited quartet which itself scatters electrons via Kondo processes should be smaller and broader than for the simple local moment case. The inverse susceptibility of Ce_3In and Ce_3Sn deviates from the high-temperature Curie-Weiss law near 100 K; this deviation is also a crystal-field effect. For Ce_3Al we make no estimate of the splitting, as the symmetry is not cubic; but the reduced Curie constant (0.32 emu K/mol Ce) at low temperature is doubtless a crystal-field effect.

With the existence of crystal fields firmly in place we can now estimate the characteristic energies of the heavy-fermion ground state. One way to do this is with single-impurity theory. Bethe-Ansatz calculations[18] for a Kondo doublet predict a peak in the magnetic specific heat at 0.9 T_K and a linear coefficient $\gamma=\pi R/6\ T_K$ where R is the gas constant. From the observed maximum at 4.3 K in Ce_3In we estimate $T_K=4.8$ K; from the observed $\gamma=0.7$ J/mol Ce K^2 we estimate $T_K=6.2$ K, in good agreement. For Ce_3Sn the observed linear coefficient $\gamma=0.26$ J/mol Ce K^2 gives $T_K=16.7$ K; this is comparable to the value of the Weiss parameter $\Theta=15$ K observed in the low-temperature susceptibility.

The properties of a periodic heavy-fermion compound should not simply be those of a Kondo ion, however, but should show effects due to interactions. One way these can show up is in the susceptibility; magnetic correlations can increase or decrease the value of $\chi(0)$ from that expected for an isolated Kondo ion. A measure of this is the Wilson ratio[13,14]

$$R=\pi^2 N_A k_b \chi(0)/3C_{\mathrm{eff}}\gamma \ .$$

For a Kondo doublet ion this should have the value 2. For Ce_3In where $\chi(0)=0.57$ emu/mol Ce we obtain $R=11.5$; for Ce_3Sn where $\chi(0)=0.013$ emu/mol Ce we get $R=7.0$. In obtaining these we use for C_{eff} the value 0.193 emu K/mol Ce appropriate for the Γ_7 doublet. These are large values of R (For comparison,[13] the susceptibility of $CeAl_3$ is 0.025 emu/mol Ce, a factor of two smaller than that of Ce_3In, but the specific-heat coefficient is 1.7 J/mol Ce K^2, two and a half times larger; hence $\chi(0)/\gamma$ is 5 times smaller.) These large values of the Wilson ratio reflect ferromagnetic correlations in the heavy-fermion ground state. The presence of a field induced transition observed in the $M(H)$ curve for Ce_3Al [Fig. 4(c) inset] is also consistent with the existence of ferromagnetic correlations. Such correlations are to be expected in heavy-fermion compounds in addition to the antiferromagnetic correlations recently observed by neutron scattering.[15] They can arise in principle if the heavy-fermion phase is close in energy to a magnetic phase where ferromagnetic sheets are antiferromagnetically coupled;[19] such magnetic phases are quite common in cerium compounds.

Another important effect of interactions is that the resistivity of a periodic heavy-fermion compound vanishes as $T\rightarrow 0$. For Ce_3In the resistivity decreases rapidly below about 7 K (Fig. 1). It should be noted that there is a rapid increase in the susceptibility, presumably due to increasing ferromagnetic correlations [Fig. 2(a) inset], and that the specific-heat coefficient also increases to its large values [Fig. 5(a)] below this same temperature. This implies that the onset of coherence in the resistivity, of magnetic correlations in the susceptibility and heavy mass in the specific heat all occur simultaneously.[19]

A peak is observed in the specific-heat linear coefficient C/T at 2 K; while this may be an artifact of the short-time correction already discussed, if real it accords nicely with the observation of similar peaks in other heavy fermions,[20] where it has been attributed to the growth of a hybridization gap. It coincides with the inflection in the resistivity at 2.2 K below which the resistivity varies at T^2.

There is no reliable theory at present for the coherent heavy-fermion ground state of a lattice of cerium atoms. The fact that Kondo impurity theory describes the data for certain compounds at elevated temperatures[14] is not understood very well. We have compared the specific heat of Ce_3In to that of the Kondo impurity model; the comparison is reasonable above 2 K, the temperature of the maximum in C/T (the Kondo ion model does not predict such a maximum). On closer examination the single-impurity model is clearly inadequate below 7–10 K because interaction effects are clearly observed in the decrease of the resistivity and the enhancement of the susceptibility. Indeed there is no region of negative $d\rho/dT$ as predicted by the impurity model.

The concept of characteristic temperature is unclear for a periodic compound. We can distinguish at least three temperatures for Ce_3In: the single-ion Kondo temperature obtained from fits to the specific heat ($T_K=5-6$ K); the temperature scale for the decrease in resistivity and enhancement of the susceptibility whose value (≈ 7 K) is here equal to the Kondo temperature; and the temperature of the maximum in C/T and inflection in the resistivity (2 K). [The temperature T_* obtained from fits to Eq. (1) is purely phenomenological; it is convenient for determining the pressure dependence.] The situation is analogous to $CePd_3$ (Ref. 21) where the single-ion scale is $T_K=250$, where the resistivity begins to decrease at 125 K and where there appears to be a third scale ($T_L=40$ K) below which anomalies in resistivity and susceptibility occur. For Ce_3In the low-temperature scale ($T_L=2$ K) obeys a rule discussed earlier[21] for $CePd_3$, namely that in comparison in the Kondo temperature (5–6 K for Ce_3In and 250 K for $CePd_3$) it is approximately true that $T_L=T_K/N_{\text{deg}}$ where the degeneracy N_{deg} is 2 for the doublet ground state in Ce_3In and 6 for the $J=\frac{5}{2}$ multiplet in $CePd_3$. On the other hand, it is quite possible that the temperature scales for the onset of various interaction effects (coherence in electron scattering, magnetic correlations, and the hybridization gap) do not exhibit a universal relationship to each other nor to the single-ion Kondo temperature.

If we apply single-impurity analysis to Ce_3Al, using the value $\gamma=0.085$ J/mol Ce obtained for $10<T<20$ K, we obtain $T_K=51$ K; using $\chi(0)=0.023$ emu/mol Ce and using $C_{\text{eff}}=0.32$ emu K/mol Ce (the value observed in low-temperature Curie-Weiss plots) we obtain $R=23.1$, a value which is absurdly large. The problem is that the above value of γ is too small: in Ce_3In the large value of γ only builds up below 10 K; this probably also occurs for Ce_3Al, but the phase transition makes it impossible to extract γ. An estimate $T_K=10-15$ K for Ce_3Al can be obtained using the phenomenology

$$\chi(T)=C_{\text{eff}}/(T+T_K)\ .$$

A second estimate of T_K is the temperature where the magnetic entropy S reaches one half the value R ln2; this gives $T_K=12$ K. This is comparable to the value for Ce_3Sn and is in accord with the temperature of the resistance minimum (20 K).

The interactions responsible for coherence can lead to ordering, as observed for Ce_3Al. There is a feature of the transition in Ce_3Al which is quite unusual; namely that the entropy remains substantially smaller than the value R ln2 expected above T_N for ordering in a doublet, even at temperatures well above T_N [Fig. 7(c)]. It appears that the Kondo effect reduces the entropy below its free-ion value for $T>T_N$. Since T_K (12 K) is larger than T_N in this compound we expect that the ground-state moment should be substantially reduced by the Kondo spin fluctuations. This reduction need not be uniform on all sites; it is possible that ordering occurs with full moment on some sites but that the Kondo effect quenches the moment on an inequivalent set of sites.

At high temperatures both Ce_3In and Ce_3Sn exhibit properties similar to other cerium compounds. The magnitude of the resistivity at 300 K is close to 100 $\mu\Omega$ cm and increases with increasing pressure.[12] Since the high-temperature spin disorder resistivity should vary as J_K^2 where J_K is the Kondo coupling constant we attribute the increase to an increase of J_K with pressure. This also causes the Kondo temperature to increase as is clearly evident [Fig. 8(c) and 10(b)] at least at low temperatures. The Kondo temperatures observed at high temperatures when the full $J=\frac{5}{2}$ manifold is excited are usually larger than at low temperatures when only the ground-state doublet contributes to the Kondo scattering. Here we can estimate the high-temperature characteristic energy from the Weiss parameter, which is 73 K for Ce_3In and 87 K for Ce_3Sn. These values are comparable to the crystal-field splitting; and hence somewhat uncertain, as crystal fields can also affect the Weiss parameter. To clarify this requires inelastic neutron scattering.

The high-temperature behavior is Ce_3Al is different. Very little pressure dependence is observed in the interval 150–300 K until the highest pressures $P>12$ kbar are reached. This would be expected if the characteristic energy of the Ni_3Sn phase remained very much smaller than 100 K at these pressures. The high-temperature Curie-Weiss law exhibits a Curie constant (0.88 emu K/mol Ce) which is larger than the free-ion value and a large (108 K) Weiss parameter; it is unclear to what extent these enhancements reflect crystal fields, whose magnitudes are unknown for this material.

The evolution with pressure of Ce_3X is quite interesting. The simplest case is Ce_3Sn, where there is a uniform increase in characteristic temperature; the inflection temperature increases at a rate 1.8 K/kbar. At low pressures Ce_3In evolves in a similar fashion, with the additional feature that a Kondo maximum becomes visible as the pressure increases. This evolution is cut off by the phase transition which sets in at 9 kbar. The resistivity at high pressure has a much smaller inflection temperature than at pressures just preceding the transition (e.g., 8.8 kbar); thus at high pressure Ce_3In returns to a ground state with smaller characteristic energy T_K. This is remarkable since the overall trend in cerium compounds is, as already stated, to evolve towards states of larger T_K with increasing P. The resistivity at 16.5 kbar is very similar to that of Ce_3Al at 6–8 kbar suggesting that the transition is similar and that the ground state of Ce_3In at high pressure may be similar to that of Ce_3Al at low pressure. In Ce_3Al, as for Ce_3Sn, the characteristic energy clearly increases with pressure at all P and at $P>11$ kbar the system reverts to a nonmagnetic ground state with resistivity very similar to that of high pressure Ce_3Sn.

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