Low-Temperature Specific Heat of $CeCu_2Si_2$ and $CeAl_3$: Coherence Effects in Kondo Lattice Systems

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Measurements of the specific heat as a function of temperature at varying magnetic fields for the Kondo lattice systems $CeCu_2Si_2$ and $CeAl_3$ reveal that, on an energy scale ~ 0.5 K $\ll T_K$, there is structure which is due to the periodicity and is qualitatively changed by disorder in the alloys $Ce_{0.9}Y_{0.1}Cu_2Si_2$, $Ce_{0.8}Y_{0.2}Cu_2Si_2$, and $Ce_{0.8}La_{0.2}Cu_2Si_2$. The results support the Fermi-liquid theory of Kondo lattices.

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The low-temperature properties of Kondo lattice systems found in many nearly trivalent Ce intermetallic compounds have continued to fascinate both experimentalists and theorists.[1] Among other phenomena, one finds magnetic ordering involving reduced Ce moments[2] as in $CeAl_2$, enhanced Fermi-liquid effects[3,4] as in $CeAl_3$, and heavy-fermion superconductivity[5] as in $CeCu_2Si_2$. In these systems there is an intermediate temperature range where the cerium atoms appear to act like independent spin-$\frac{1}{2}$ Kondo impurities with a characteristic "single-ion" Kondo temperature T_K. Although many aspects of the impurity Kondo problem are well understood,[6] the low-temperature properties of the Kondo lattice and disordered concentrated alloys are the subject of much current investigation and speculation.[1-5,7-9]

The purpose of this paper is to present results of new investigations of the low-temperature specific heat $C(T)$ as a function of magnetic field in $CeAl_3$, $CeCu_2Si_2$, and the disordered alloys $Ce_{0.9}Y_{0.1}Cu_2Si_2$ and $Ce_{0.8}Y_{0.2}Cu_2Si_2$, as well as $Ce_{0.8}La_{0.2}Cu_2Si_2$. These results show that the structure in $\gamma(T) = C(T)/T$ discovered in both $CeAl_3$[4] and $CeCu_2Si_2$[10] is a consequence of the periodicity of the Ce ions; the effect of a magnetic field in all concentrated systems studied is qualitatively different from the impurity case; and there is a characteristic temperature, $T_0 \sim 0.5$ K, associated with the lattice case, an order of magnitude smaller than T_K in these materials. These results are consistent with the Fermi-liquid arguments of Ref. 8, which suggested that in a lattice the "Kondo resonance" in the density of states near the Fermi energy would have structure and pronounced variations for energies $< k_B T_K$.

The specific-heat results of $CeCu_2Si_2$, $CeAl_3$, $Ce_{0.9}Y_{0.1}Cu_2Si_2$, and $Ce_{0.8}Y_{0.2}Cu_2Si_2$ are plotted as γ vs T in Figs. (1a)–(1c). There are four important aspects of the data to mention. First, two different $CeAl_3$ samples were studied. One was taken from the same batch as the sample studied in Ref. 3 and by Niksch, Lüthi, and Andres[11] [illustrated in Fig. 1(b)]. The other one was kindly supplied to us by E. Umlauf; for $B = 0$ its γ vs T dependence is qualitatively the same as that in Fig. 1(b) and is quantitatively very close to that published in Ref. 4 (cf. also Ref. 12). Second, we have chosen for this study $CeCu_2Si_2$ samples with $T_c < 0.5$ K: As discussed in Ref. 10 these samples (No. 10 and No. 11) behave as gapless superconductors. This is demonstrated in Fig. 1(a) by the very large value of γ (as $T \to 0$) in the superconducting ($B = 0$) state and the absence of a $C(T)$ jump at T_c. Third, the results for $Ce_{0.8}La_{0.2}Cu_2Si_2$ are close to those for $Ce_{0.9}Y_{0.1}Cu_2Si_2$ [Fig. 1(c)]. Fourth, as was already shown for $CeAl_3$ as well as $CeCu_2Si_2$,[10] the external magnetic field B gives rise to an upturn in C/T at low T, attributed to a nuclear term $C_N(t,B)$ arising from ^{63}Cu, ^{65}Cu, and ^{29}Si isotopes in $CeCu_2Si_2$[10] and ^{27}Al in $CeAl_3$.[3] We calculate $C_N(T,B)$ neglecting any hyperfine contributions and subtract it from the raw data to obtain specific heats represented by the solid lines in Fig. 1. This is purely electronic

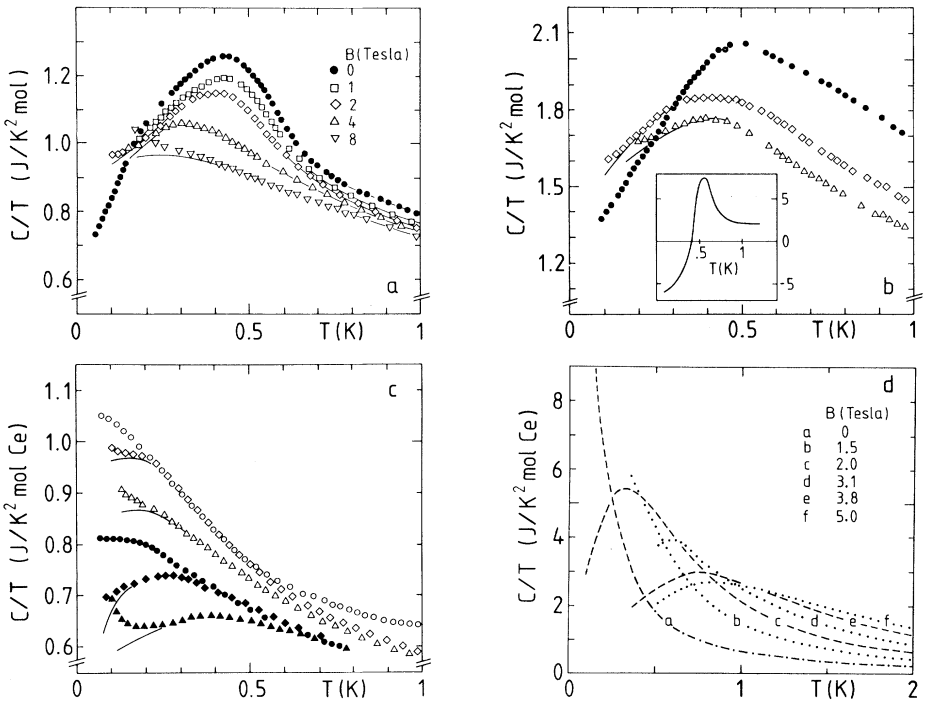

FIG. 1. C/T vs T for (a) $CeCu_2Si_2$, (b) $CeAl_3$, (c) $Ce_{1-x}Y_xCu_2Si_2$, and (d) $La_{1-x}Ce_xAl_2$, as a function of magnetic field B. The symbols are explained in (a); in (c) open symbols were chosen for $x=0.1$ and closed symbols for $x=0.2$. The maximum experimental error is indicated by the symbol size. Solid lines in (a)–(c) display electronic specific heats after subtraction of a nuclear term (see text). The results in (d) are taken from Ref. 13 (dashed lines, $x=0.0064$) and Ref. 14 (dotted lines, $x=0.0149$). Note that T_K is much larger (~ 5–10 K) in (a)–(c) than in (d), where $T_K \sim 0.4$ K. The inset in (b) shows $\partial \ln\gamma/\partial \ln V$ vs T for $CeAl_3$ (see text).

since below 1 K any phonon contribution is completely negligible for these materials.

We begin with a discussion of the zero-field results. Above 0.5 K the $\gamma(T)$ dependence for each compound and alloy studied is qualitatively the same as for the spin-$\frac{1}{2}$ impurity Kondo problem, which has been extensively investigated, e.g., for Ce in $LaAl_2$.[13,14] All these systems exhibit spin $\frac{1}{2}$ (crystal-field ground-state doublet) and the thermodynamics can be understood in terms of a model invoking a resonance level[15] of width k_BT_K centered on the Fermi energy as shown schematically in Fig. 2. The results of this model are close to those of the Bethe-*Ansatz* calculations[6] and yield a continuous increase in $\gamma(T)$ as T decreases. In this single-ion theory the Kondo temperature is related to the maximum value of γ (at $T=0$) by[6] $\gamma_{max}T_K \simeq 0.68R$, where R is the gas constant. The T_K values of the compounds obtained from γ_{max} (at $T_0 \simeq 0.5$ K) in this way are $T_K \sim 3$ K for $CeAl_3$ and $T_K \sim 4.5$ K for $CeCu_2Si_2$, compared to ~ 6 and ~ 10 K as obtained[16,17] from neutron scattering. For the concentrated alloys, $\gamma(T)$ is seen to be somewhat smaller than in $CeCu_2Si_2$. T_K obtained from γ_{max} (at the lowest accessible temperature) increases with Y concentration, but decreases on going from $Ce_{0.8}Y_{0.2}Cu_2Si_2$ to $Ce_{0.8}La_{0.2}Cu_2Si_2$, in accordance with the well-known fact[18] that in Ce-based systems T_K usually rises with decreasing volume and vice versa. For a Kondo impurity with spin $\frac{1}{2}$, $\gamma(T)$ continues to increase monotonically

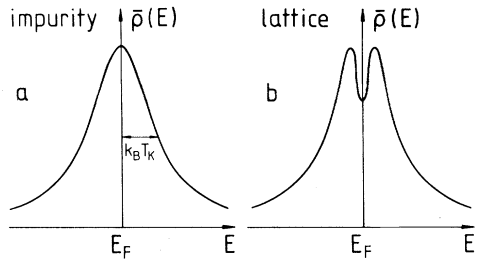

FIG. 2. Schematic drawings of the resonance density of states near the Fermi energy for the spin-$\frac{1}{2}$ Kondo problem with $B=0$: (a) impurity case; (b) the form indicated by the experiment for the present lattices. In the lattice, the resonance is *not* in general symmetric; however, only the symmetric part $\bar{\rho}$ enters the specific heat.

as T decreases[13-15] as shown in Fig. 1(d). However, in the compounds $CeCu_2Si_2$ and $CeAl_3$ there is decrease in $\gamma(T)$ below $T_0 \simeq 0.5$ K as shown in Figs. 1(a) and 1(b) and in Refs. 4 and 10.

To show that the periodicity of the Ce ions is directly responsible for the observed structure, we have attempted to destroy coherence in $CeCu_2Si_2$ in a controlled way, i.e., by substituting up to 20 at.% Ce by either Y or La. The resulting $\gamma(T)$ dependences are shown for the Y-doped samples in Fig. 1(c). Down to the lowest accessible temperature (0.07 K) no maximum can be resolved in the $B=0$ data. Rather, $\gamma(T)$ of the concentrated alloys resembles that of the dilute Kondo alloys [Fig. 1(d) and Refs. 6, 13, and 14]. This forms a convincing case that the $(B=0)$ $\gamma(T)$ maximum found at a finite temperature well below T_K is a unique feature of Kondo *lattices*, which signals a transition to the coherent coupling of the Kondo resonances at the periodic Ce sites.

The results for $\gamma(T)$ as a function of magnetic field provide further evidence for cooperative behavior in the concentrated systems. In the case of a single spin-$\frac{1}{2}$ Kondo ion, the twofold resonance at E_F becomes split by the external field. If the Zeeman energy $k_B T_B = \mu_s B$ is greater than $0.5 k_B T_K$, $\gamma(T)$ has a maximum[6,15] at a temperature T_{max} which is shifted *upwards* with increasing field as is shown in Fig. 1(d) for $(La,Ce)Al_2$. Although no results on dilute Kondo systems exist at fields much lower in proportion to T_K, the theory indicates clearly that there is no maximum (at finite temperature) in $\gamma(T)$ for $T_B \leq 0.5 T_K$. In the concentrated systems, however, the largest values of T_B/T_K, obtained at $B=8$ T, are ~ 0.8 in $CeAl_3$ and ~ 0.4 in $CeCu_2Si_2$ choosing the average value of the saturation moment $\bar{\mu}_s \simeq \frac{1}{3}\langle \mu_z \rangle = 0.43 \mu_B$ and $0.36 \mu_B$, respectively, calculated from the known crystal-field schemes of Ce^{3+} (Ref. 17). The present observation of maxima in $\gamma(T)$ (even at $B=2$ T) for all concentrated systems studied shows that there are low-energy effects in the concentrated alloys as well as in the lattices. However, the field dependence of the $\gamma(T)$ maximum for both $CeAl_3$ and $CeCu_2Si_2$ is different from that of the concentrated alloys. One clearly sees that the peak height γ_{max} is reduced more slowly and the peak temperature T_{max} decreases, rather than increases, with field.

The present results for the Kondo lattices are consistent with the qualitative arguments of Ref. 8 that coherence leads to structure developing in the Kondo resonance density of states $\rho(E)$ at the Fermi energy. The observed minimum for $\gamma(T)$ at $T=0$ shows that there is a minimum at E_F in the symmetrized density of states $\bar{\rho} = \frac{1}{2}[\rho(E-E_F) + \rho(E_F-E)]$ as illustrated in Fig. 2(b). This can be understood as the tendencey to form a gap at E_F. However, there cannot be a true gap in these systems because of band crossings in symmetry directions.[8] Magnetic fields modify the structure but do not destroy it for $T_B < T_K$, because sum rules[8] require the coherent resonance near E_F unless T_B is so large that the spins are "frozen." The effects of disorder in a dense Kondo system have not been addressed theoretically. The present results suggest that the coherence is modified but there still remain cooperative interactions between different sites.

There are other indications of a low-T regime in which the Ce atoms act coherently in a Kondo lattice. Resistivity (ρ) experiments show that, at low temperature, ρ increases with T (Refs. 1–5, 7, and 8) and B (Remenyi *et al.*[19]), whereas the opposite occurs for a spin-$\frac{1}{2}$ Kondo impurity.[1,6,20] The coherent Fermi surface has the observed directly in $CeSn_3$.[21] For $CeAl_3$, anomalies near $T_0 \simeq 0.5$ K have been observed in various thermodynamic quantities, i.e., a flat minimum in the susceptibility $\chi(T)$,[3] a flat minimum in the bulk modulus $c_B(T)$,[11] and a pronounced peak in the coefficient of the thermal expansion $\alpha(T)$. This latter quantity is very large, changes sign at $T \sim 1$ K,[3,22] and gives rise to giant negative values of the electronic Grüneisen constant.[23,24] It has still to be clarified by experiments on concentrated Ce alloys lacking coherence which of these features, like the $\gamma(T)$ maximum, occurs only in a lattice.

Knowing $\alpha(T)$, $c_B(T)$, and $\gamma(T)$, one can predict the volume dependence of γ by $\partial \ln \gamma / \partial \ln V = \gamma^{-1} \partial(c_B \alpha)/\partial T$.[22,23] The thermal variation of this quantity for $CeAl_3$ is displayed in the inset of Fig. 1(b). Obviously, there are two mechanisms for the volume dependence of γ. At high T, $\partial \ln \gamma / \partial \ln V$ is almost constant and has the sign expected for the single-ion Kondo effect, but at low T there is an entirely new mechanism as indicated by the distinct structure, including a change of sign, near T_0. This suggests that under pressure the structure in $\gamma(T)$ will become less pronounced since γ should decrease for $T \gtrsim T_0$, but increase for $T < T_0$. Note that the results on $(Ce,Y)Cu_2Si_2$ are *not* simply an internal pressure effect, since La atoms (larger than Ce) in place of Y (smaller than Ce) cause a similar monotonical $\gamma(T)$ dependence at low T.

It is interesting to speculate why E_F is near a minimum in the density of states in these Kondo lattice systems. One possibility is that the nonmagnetic ground state of the lattice is in fact *stabilized*

by the opening of the pseudogap, and that other systems which do not have the decreased density of states at E_F will have a greater tendency to order magnetically. This could explain the absence of order in these noncubic spin-$\frac{1}{2}$ systems in contrast to recent arguments[24] that require higher spin to suppress magnetic order. Further, in the *cubic* spin-$\frac{1}{2}$ systems like $CeAl_2$ and CeB_6 the tendency to open the pseudogap might be weaker as a result of symmetry reasons and, thus, magnetic order might be favored.

In summary, the anomalous temperature dependence of the linear specific-heat coefficient $\gamma(T)$ of the nearly trivalent intermetallic compounds $CeAl_3$ and $CeCu_2Si_2$ can be viewed as a transition, at $T_0 \simeq 0.5$ K, from a "single-ion Kondo regime" to a "Kondo lattice regime." At low temperature coherence effects of the lattice lead to structure in $\gamma(T)$, which is consistent with a pseudogap structure[8] within the "single-ion Kondo resonance" at E_F. Finite-field data show that a cooperative low-energy scale persists also in the concentrated alloys, which differ qualitatively from dilute Kondo systems.

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Note added.—Recently, the one-particle excitation spectrum of a Kondo lattice has been calculated by renormalized perturbation theory for the Anderson model: see N. Grewe, Solid State Commun. **50**, 19 (1984). In fact, this calculation demonstrates the formation of a (pseudo) gap due to coherence.

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