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Ce valence mixing and strong $3d$ antiferromagnetism in $CeMn_2Si_2$

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Transport, specific-heat, x-ray-absorption, and magnetic measurements on $CeMn_2Si_2$ are presented. These results indicate that $CeMn_2Si_2$ is the first example of a system where low-energy-scale ($T < 100$ K) Ce valence-mixing effects coexist with much higher-energy-scale (400 K) $3d$ magnetism. The case for this novel confluence of Ce demagnetization with Mn magnetic order is presented partially through analogy with the prototype mixed-valent system $CePd_3$.

In mixed-valent (MV) and heavy-fermion Ce systems, local-moment magnetism is typically quenched on a moderately low energy (temperature) scale (i.e., in the 1-500 K range).[1] This rapid low-temperature removal of the Ce $4f$ degeneracy and the strongly renormalized Fermi-liquid ground state which accompany it have been the center of a great deal of experimental and theoretical work in recent years.[1-3] The efficiency of $3d$, $4d$, and $5d$ transition-metal atoms in varying the Ce valence and Fermi-liquid parameters have made Ce and transition-metal-containing compounds the focus of much of the experimental work in this field.[2,4] Heretofore, however, no low-energy-scale mixed-valent Ce compounds in which the transition metals are strongly magnetic have been found.

In this paper, we show that a mixed-valent Ce state with a characteristic energy scale below 200 K is possible in a strongly magnetic $3d$ transition-metal compound. Specifically, we will show that $CeMn_2Si_2$ (in which the Mn sublattice orders antiferromagnetically near 376 K) is a MV Ce compound, analogous, in a number of ways, to the prototype MV $CePd_3$ system.[4-6] Low-temperature transport (and high-pressure transport), magnetic, and specific-heat measurements, along with Ce valence-state determination via L_3 x-ray absorption spectroscopy, will all be shown to support this conclusion.

Perhaps the most expeditious method of identifying valence mixing in a rare-earth material is through L_3 x-ray absorption spectroscopy. The Ce L_3 edge spectrum for $CePd_3$ is shown in Fig. 1. By fitting this L_3 spectra with a superposition of Ce^{3+} and Ce^{4+} edges (shown separately in the top of Fig. 1) one obtains an L_3 valence for $CePd_3$ of $v = 3.15$. This L_3 valence is squarely in the MV range lying intermediate between the L_3 valence of $CeRh_3$ ($v \simeq 3.27$) and of $Ce(Pd_{1-x}Ag_x)_3$, $x = 0.13$ ($v \simeq 3.06$). These extreme values of v represent roughly the highest and lowest Ce L_3 valence observed in $CePd_3$-based alloys. To emphasize this point empirically, we have overlayed the L_3 spectra of $CeRh_3$ and $Ce(Ag,Pd)_3$ (i.e., the

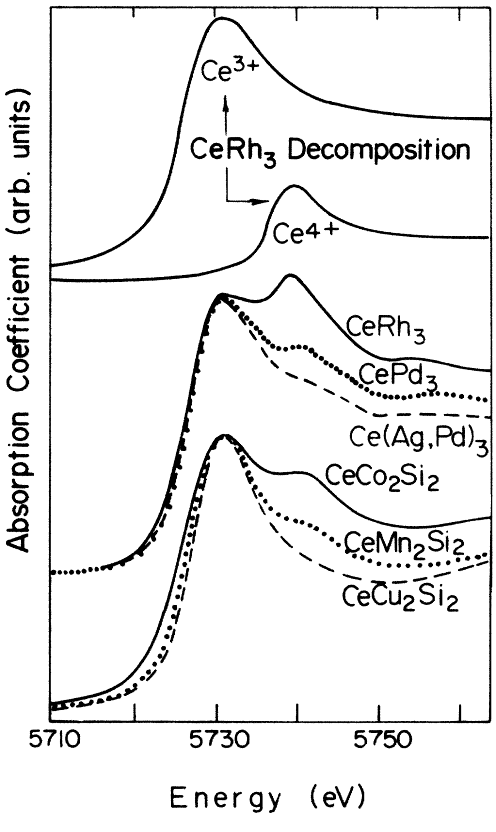

FIG. 1. The Ce L_3 spectra for a number of Ce compounds illustrating the changes with changing Ce valence in the CeT_3 series. $T = Ag_{0.13}Pd_{0.87}$ is a Kondo regime material ($v = 3.06$), $T = Rh$ is highest Ce metallic valence material ($v \approx 3.27$), and $T = Pd$ is a mixed-valent material. At the top of the figure, the separate Ce^{3+} and Ce^{4+} contributions to the Ce L_3 edge of $CeRh_3$, as determined by our modeling/fitting procedure, are shown. In the Ce T_2Si_2 series $T = Cu$ is a Kondo regime material ($v = 3.05$), $T = Co$ is a high-valent ($v = 3.16$) material, and $T = Mn$ is a mixed-valent material.

$x = 0.13$ alloy noted above) on that of $CePd_3$ in Fig. 1 with all spectra normalized to the first (Ce^{3+}) spectra peak. Using such a normalization-and-superposition technique, lower-valent spectra lie below higher-valent spectra in the region of the second (Ce^{4+}) peak. The intermediate-valence (or mixed-valent) state of Ce in $CePd_3$ is thus empirically underscored by the intermediate position of its L_3 spectra in Fig. 1.

It should be noted that the Ce $4f$ hybridization with band states is much stronger for Ce than for the other unstable rare earths. This fact complicates both the notion of valence and its determination via L_3 measurements for Ce compounds. Nevertheless, in a large number of studies,[7-11] it has been show that ground-state MV properties, such as the Ce volume magnetic response, and also the Fermi-liquid parameters in compounds, are correlated in a one-to-one way with the Ce L_3 valence. The CeT_3 system results presented here for $T = $Rh, Pd, and (Pd,Ag) illustrate the established signature of the Ce MV state in L_3 spectroscopy. Thus, while we do not assert that the Ce L_3 valence is in fact the absolute Ce valence, we do assert that the Ce L_3 valence provide an excellent empirical indicator of the degree of Ce valence mixing.

Turning now to the L_3 spectrum of $CeMn_2Si_2$ (shown in Fig. 1) we see the characteristic MV dual peak structure. The Ce L_3 valence for this material is again in the MV range ($v \simeq 3.12$). We also show the overlayed L_3 spectra of $CeCo_2Si_2$ ($v \simeq 3.16$) which manifests the highest (room-temperature) Ce L_3 valence in this crystal structure and $CeCu_2Si_2$ a famous heavy-fermion system with very little valence mixing ($v \simeq 3.05$). The intermediate position of $CeMn_2Si_2$ when compared to these other two spectra underscores its mixed-valent character in a manner analogous to the $CePd_3$ discussion presented above. Recent reports by our group have indicated that the thermal variation of the Ce valence in $CeMn_2Si_2$ is more appreciable ($v = 3.16$ at $T = 11$ K) than in the $CePd_3$ case.[12,13] (Ammarguellat, Godart, Haen, and Krill[13] observe a similar effect.) Such temperature dependencies in the valence of MV systems are in fact common.

In MV materials a large density of states arises near the Fermi energy due to the strong $4f$ conduction-band interaction. The resulting low-temperature Fermi-liquid ground state displays an enhanced electronic contribution to the specific heat (e.g., $\gamma \approx 40$ mJ/mole K^2 for $CePd_3$) and an enhanced Pauli susceptibility [e.g., $\chi(0) = 1.3 \times 10^{-3}$ cm^3/mole for $CePd_3$]. The energy scales for the onset of MV ground-state behavior can be discerned in the thermal variations of the magnetic susceptibility (χ) and the electrical resistivity. In the case of χ the crossover from a high-temperature Curie-Weiss to the low-temperature Pauli susceptibility is marked by a maximum in χ occurring for $CePd_3$ near 150 K. The typical resistivity of a MV Ce system will be discussed below.

The low-temperature (T) specific heat (C_p) of $CeMn_2Si_2$ is displayed in Fig. 2 in the form of C_p/T vs T. The solid line through the data represents a fit to a $C_p = \gamma T + \beta T^3$ with $\gamma = 47$ mJ/mole K^2 and $\beta = 0.26$ mJ/mole K^4. The presences of magnetic oxide impurities can also be seen by the phase transition anomaly near 6.4 K. The γ value for $CeMn_2Si_2$ is quite typical of a MV material as indicated above for $CePd_3$. Indeed, the $CePd_3$ C_p/T results also shown for comparison in Fig. 2 are very similar to the $CeMn_2Si_2$ results right down to the oxide impurities. It should be noted that spin-wave contributions to the specific heat are dominated by the conduction-electron specific heat even in normal metals hence the Mn ordered-state spin waves should not appreciably influence the high γ value here.[14]

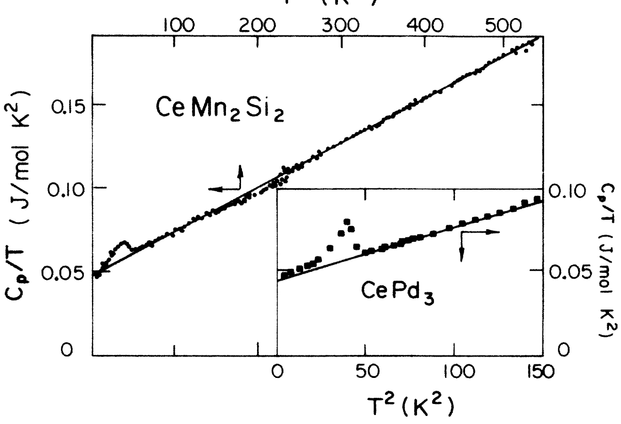

FIG. 2. The thermal variation of the low-temperature (T) specific heat (C_p) of $CeMn_2Si_2$ plotted as C_p/T vs T^2. The solid line is the fitted form $C_p = \gamma T + \beta T^3$ with $\gamma = 47$ mJ/mole K^2 and $\beta = 0.26$ mJ/mole K^4. The inset illustrates the similar T^2 behavior for $CePd_3$ with $\gamma \approx 40$ mJ/mole K^2 (Refs. 4–6 and 15).

In the temperature dependence of the resistivity one can discern two characteristic energy scales: one for the onset of single-impurity MV ground-state behavior; and the other, a coherency energy scale for correlations between MV sites. The above-noted high density of states near the Fermi energy in MV materials is the source of a large (roughly 200 $\mu\Omega$ cm) incoherent scattering. This incoherent scattering displays a negative temperature coefficient of resistivity (TCR) and is always present in MV Ce systems at high temperatures. As coherence between MV scattering centers sets in at lower temperatures, in a well ordered lattice, the resistivity passes through a maximum and falls rapidly with decreasing temperature by an amount on the order of 100 to 200 $\mu\Omega$ cm.[15] In $CePd_3$ this resistivity maximum occurs at a temperature just over 100 K (see Fig. 3).[6] The low-temperature coherence in the narrow, hybridized f-d band can often be disrupted by the introduction of only moderate levels of defects or chemical substitutes.[15] Upon such a disruption (as in the case for $CePd_3$ disordered by excess Pd addition, Ce sublattice substitution, or altered annealing procedures) the low-temperature resistivity shows a negative TCR over a larger temperature range (see Fig. 3, inset).[6] This single-impurity-type resistivity is reminiscent of the Kondo effect. Rough estimates of the single-impurity energy scale can be made by choosing the temperature where the negative TCR is largest. For $CePd_3$ this temperature is on the order of 150 K.

The temperature-dependent resistivity of two polycrystalline samples of $CeMn_2Si_2$ (one annealed and the other

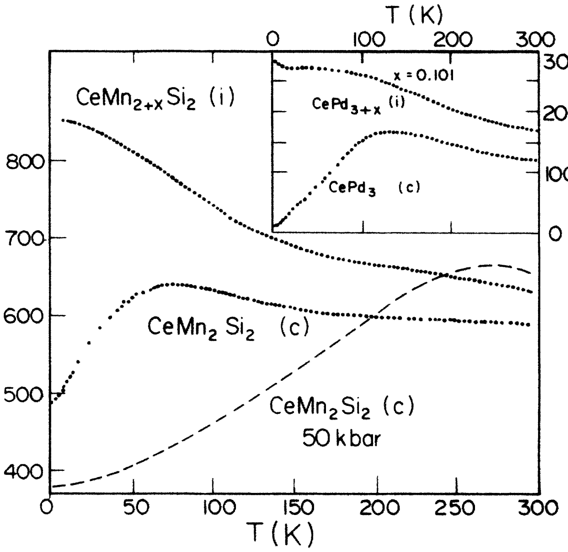

FIG. 3. The resistivity of $CeMn_2Si_2$ compounds. The $CeMn_2Si_2$ (*c*) sample was annealed stoichiometric, and displays a low-temperature "coherency"-related drop in the resistivity. The $CeMn_2Si_2$ (*i*) was unannealed, has excess Mn, and exhibits a single-particle-like "incoherent" behavior in the resistivity. The dashed line is the resistivity of $CeMn_2Si_2$ at a pressure of 50 kbar. The inset illustrates the analogous coherent (*c*) and incoherent (*i*) behavior of the resistivity of the prototypic mixed-valent Ce system $CePd_3$ (Ref. 6).

unannealed with a Mn excess) is shown in Fig. 4. Both annealed and unannealed samples showed the proper crystal structure; however, our resistivity results place the former in the coherent lattice and the latter in the single-impurity low-temperature regimes. The well ordered (annealed) sample displays the high-*T* negative TCR along with the rapid low-*T* resistivity drop accompanying the onset of coherent narrow-band behavior. The 70 K temperature of the resistivity maximum would indicate a lower coherency temperature than in $CePd_3$. In the unannealed sample intersite coherence is essentially quenched and a single-impurity-type resistivity is seen. The characteristic energy scale for the single-impurity resistivity (roughly 90 K) is again smaller than in the $CePd_3$ case. Summarizing, we find a close analogy between the $CeMn_2Si_2$ and $CePd_3$ resistivities along with indications that the ground-state *f-d* hybridized bandwidth energy scales are smaller in the ternary compound.

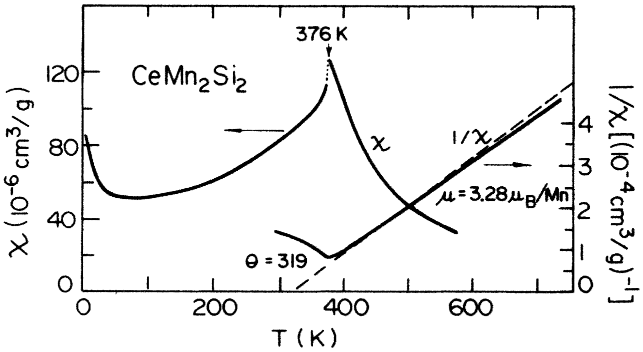

FIG. 4. The thermal variation of the magnetic susceptibility (χ) and its inverse (1/χ) of $CeMn_2Si_2$. Note the sharp peak in the susceptibility (at 376 K) near the antiferromagnetic ordering temperature.

In the very low temperature range one typically observes a Fermi-liquid $\rho = \rho_0 + AT^2$ type behavior in MV and Kondo Ce systems. Indeed, there is a close correlation[16] of A and the specific heat γ [through the empirical relation $A/\gamma^2 \approx 10^{-5}\ \mu\Omega\,\mathrm{cm}\ (\mathrm{mole\,K/mJ})^2$]. For $CePd_3$, $A/\gamma^2 \approx 6.07\times10^{-5}\ \mu\Omega\,\mathrm{cm}\ (\mathrm{mole\,K/mJ})^2$ consistent with this expression. For $CeMn_2Si_2$, $A/\gamma^2 \approx 6.6\times10^{-5}\ \mu\Omega\,\mathrm{cm}\ (\mathrm{mole\,K/mJ})^2$, which is also in agreement with these empirical arguments. Before proceeding the reader should be aware that the resistivity of these $ThCr_2Si_2$ structure materials should be anisotropic as was the case for $CeCu_2Si_2$.[17] Nevertheless, the reflection of the basic MV and Kondo mechanisms in the resistivity should persist just as it did in the $CeCu_2Si_2$ based systems.[10]

A final indicator of the MV character of $CeMn_2Si_2$ is the strong pressure sensitivity of the resistivity maximum. Increasing pressure increases the magnitude of both the spin-fluctuation and charge-fluctuation energy scales in all Ce systems. The stabilization of the nonmagnetic (and coherent) ground state to higher temperatures is reflected by a strong pressure enhancement of the resistivity maximum in the MV and Kondo Ce systems. In Fig. 3, we also show the temperature dependence of the resistivity of well ordered $CeMn_2Si_2$ at a pressure of 50 kbar. The dramatic enhancement of the resistivity maximum from 90 K at $P = 0$ to near room temperature at 50 kbar is clear from the data. Thus, the sensitivity of the resistivity to pressure further supports the MV character of $CeMn_2Si_2$.

To this point in our presentation one could argue that $CeMn_2Si_2$ was a MV system broadly similar to $CePd_3$. This situation abruptly changes upon considering our magnetic susceptibility results from $CeMn_2Si_2$ (see Fig. 4). The onset of the antiferromagnetism near $T_N = 376$ K is clearly seen by the sharp peak in the magnetic susceptibility. Neutron scattering measurements have confirmed that the Mn atoms order in ferromagnetic planes with successive planes antiferromagnetically aligned.[18] The ferromagnetic nature of the Mn-Mn in-plane interactions is further supported by the ferromagnetic Curie constant $\theta \approx 319$ K above T_N. The previous neutron scattering measurements detected no moment at the Ce sites, which is not surprising in view of the weak Pauli paramagnetism of the MV state. The strong magnetism of the Mn atoms at present does not allow the small MV Ce magnetic susceptibility contribution below T_N.

The single-impurity energy scale for Ce nonmagnetic behavior in this MV system ($CeMn_2Si_2$) is on the order of 100–200 K both from the "disordered" resistivity results and from the magnitude of the specific heat γ. The "coherent" resistivity results indicate coherent narrow-band behavior with an energy scale below 70 K. The novelty of the $CeMn_2Si_2$ system lies in the fact that low-energy-scale MV behavior persists in the presence of magnetic order. The internal fields of a magnetic material which orders at 376 K might reasonably be expected to substantially quench the MV effects in a way similar to the quenching of Kondo behavior in large magnetic fields.[19] The positioning of the Ce atoms symmetrically between antialigned ferromagnetic Mn planes should place the Ce atoms at nodes of the internal field. This is presumably at the root of the Ce MV state's indifference to the Mn magnetism in $CeMn_2Si_2$. It is as if the Ce atoms sit in a nonmagnetic eye of a magnetic hurricane. As one moves out of the Ce atom plane the internal field should of course depart from zero.

The potential existence of such a class of materials where low-energy-scale MV effects occur in a magnetic host opens a new class of questions regarding the coupling and competition between magnetic and MV phenomena. The first question that comes to mind is whether even lower-energy-scale nonmagnetic behavior (i.e., heavy-fermion behavior) can persist in such a magnetic host. Another question is whether an antiferromagnetic-to-ferromagnetic transition could be induced and whether a substantial Ce valence (and Ce magnetism) change would be coupled to it. Yet another question would address the interference effects of the Ce spin compensation cloud with the magnetically polarized conduction bands. On the theoretical-model side, the Anderson model (often used to model MV behavior) assumes $4f$ hybridization with a paramagnetic and everywhere unpolarized conduction band. This assumption will certainly have to be relaxed in $CeMn_2Si_2$-type materials. In general, many of the traditional basic assumptions in the MV Kondo field may have to be reconsidered in this new class of materials.

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