Coexistence of strong 3d antiferromagnetism and mixed-valent Kondo regime transition in Ce(Mn\(_x\)Cr\(_{1-x}\))\(_2\)Si\(_2\)

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Structural, thermal, magnetic, transport, and Ce \(L_3\)-edge spectroscopic measurements on the Ce(Mn\(_{1-x}\)Cr\(_x\))\(_2\)Si\(_2\) series are presented. These results all indicate that Cr substitution drives this system from a mixed-valent Ce state at \(x = 1.0\) to a Kondo or heavy-fermion state with increasing \(x\).

The reflection of the Ce valence-state variation (from \(L_3\) measurements) in the electronic specific heat coefficient and lattice parameters is discussed. The magnetic and transport measurements indicate that the Ce spin-flip scattering processes (i.e., the Kondo effect) apparently thrive within the Mn-moment antiferromagnetically ordered phase of these compounds.

I. INTRODUCTION

Recently, the ThCr\(_2\)Si\(_2\)-structure compounds CeT\(_2\)Si\(_2\) have been shown to exhibit an evolution from a Kondo regime for \(T = \text{Cu}\) to a mixed-valent (MV) regime for \(T = \text{Ni}, \text{Co}, \text{Fe}, \) and Mn followed by a reentrance into a Kondo regime between \(T = \text{Mn} \) and Cr.\(^1\) It is important to note that the Mn atoms in CeMn\(_x\)Si\(_2\) exhibit antiferromagnetic order at \(T_N = 376\) K in CeMn\(_x\)Si\(_2\), despite the MV state for Ce in this compound.\(^2\) Thus the Ce(Mn\(_{1-x}\)Cr\(_x\))\(_2\)Si\(_2\) system offers the opportunity to study the Ce MV to Kondo regime passage in a host where strong 3d magnetism could interplay with this passage. Specifically, internal or external magnetic fields with energy scales much larger than the Ce spin-fluctuation temperature might be expected to quench the nonmagnetic MV or Kondo behavior. As we shall see, however, in many respects, the Ce MV and Kondo effects appear to coexist (indeed to thrive) between the antiferromagnetically ordered Mn sublattices in this material.

A second important point which should be noted while reading this paper is the continuous way in which the Kondo regime evolves out of the MV regime. This is consistent with the idea that the MV and Kondo regimes (for Ce at least) are, respectively, the high-energy scale spin-fluctuation and low-energy scale spin-fluctuation regimes of the same problem. Indeed the thermal Ce \(L_3\) valence variations observed here appear consistent with recent Anderson model treatments by Schlottmann\(^3\) and Bickers et al.\(^4\) and Rice et al.\(^5\)

II. EXPERIMENT

The polycrystalline sample preparation and resistivity measurement methods have been discussed previously.\(^1\) The susceptibility and resistivity samples were (in almost all cases) taken from the same master samples. The much more massive specific heat samples were prepared separately. The specific heat and \(L_3\) measurement and analysis methods have been described elsewhere.\(^6\) The susceptibility measurements were made with a Faraday magnetometer in a magnetic field \((H)\) of 6.3 kOe. Ferromagnetic impurity contributions have been corrected via separate magnetization \(M\) versus \(H\) isotherms at several temperatures.

The x-ray diffraction data were taken at room temperature on an automated diffractometer. The lattice parameters were obtained by the least-squares-fitting method in the range of \(20^\circ \leq 2\theta \leq 80^\circ\). X-ray diffraction indicated that all of the samples were single phase with ThCr\(_2\)Si\(_2\) crystal structure except two specific heat, samples with \(x = 0.8\) and 0.7, which showed a weak second CeSi\(_x\) \((x = 1.7 - 2.0)\) phase presumably due to the Mn mass loss.

III. RESULTS AND DISCUSSION

A. Lattice-parameter results

The lattice parameters and cell volume (as determined by x-ray diffraction studies) for the Ce(Mn\(_x\)Cr\(_{1-x}\))\(_2\)Si\(_2\) series are plotted versus \(x\) in Fig. 1(a). The first points we wish to note are that both the \(a\)-parameter and cell-volume \((V)\) data exhibit a nearly linear \(x\) dependence (i.e., Vegard's-law behavior) for \(0.2 \leq x \leq 0.7\), and that both \(a\) and \(V\) show a strong compressive deviation from this linear behavior onsetting and growing continuously between \(x = 0.7\) and \(x = 1.0\). The \(c\)-axis parameter remains much closer to a Vegard's-law-type behavior with a small compressive effect (similar to the \(a\) and \(V\) results) occurring for \(x > 0.7\).

Association of these \(a\) and \(V\) compressions with an anomalously low Ce-atom radius contraction (at 300 K) be-
between $x=0.7$ and $x=1.0$ is supported by two things. First is the observation that the $a$ and $V$ parameters of the 1:2:2 compound series typically respond to the lanthanide contraction but the $c$ parameter typically does not. Second is the observation that the $a$ and $V$ parameters of EuPd$_2$Si$_2$ respond directly to the nonlinear Eu valence (atomic radius) change but the $c$ parameter does not.$^8,^9$

B. $L_3$ x-ray absorption spectroscopy: general remarks

$L_3$-edge x-ray absorption spectroscopy (XAS) has been proved to be a very valuable tool in determining the valence in the mixed-valence field.$^7,^{10-13}$ The large number of unoccupied 5$d$ orbitals in rare-earth atoms produces (via $2p \rightarrow 5d$ transition) a prominent peak (the so-called $L_3$ white line) just above the $L_3$ absorption edge. In addition, an arctangent-type step-function feature, due to $2p_{3/2} \rightarrow$ continuum transitions, occurs at the $L_3$ edge. In rare-earth materials, the removal of an electron from the 4$f$ shell (e.g., $Ce^{3+}, 4f^1 \rightarrow Ce^{4+}, 4f^0$) reduces the screening of the $2p$ orbital thereby shifting the $2p_{3/2}$ energy level down by approximately 7–10 eV. A mixed-valent atom executes a quantum tunneling between two 4$f$ level occupation states (valence states) on a time scale ($\sim 10^{-13}$ sec) which is slow compared to the $L_3$ XAS time scale ($10^{-17}$ sec). Thus the $L_3$ edge of a MV atom consists of a superposition of two integral valent edges separated by 7–10 eV. The weight of each valence state in the MV state is evaluated by determining the spectral weight of the two integral valent edge features required to model the spectrum.

In Fig. 2 (top) we illustrate these ideas by showing the separate Ce$^{3+}$ and Ce$^{4+}$ components used to model the

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**FIG. 1.** Ce(Mn$_x$Cr$_{1-x}$)$_2$Si$_2$ series results as a function of $x$ for (a) the $a$ and $c$ parameters and unit-cell volume $V$; (b) the Ce $L_3$ valence $\nu_3$ at $T=300$ and 10 K; (c) the “high-temperature” ($T \sim 10$ K) linear coefficient of the specific heat $\gamma_h$. The solid and dashed lines in (a) and (b) guide the eye, respectively, through the linear and nonlinear data variations. The arrows are included to emphasize the close agreement of the room-temperature lattice and $L_3$ results and of the 10 K $\gamma_h$ and $L_3$ results. Finally in (c) the dashed curves represent the relation $\gamma = \gamma_0/(\nu - 3)$ with $\gamma_0 = 9$ mJ/mol K$^2$. Here the two dashed curves were generated from our 10 K $L_3$ results ($\nu_3$). The values of the valence $\nu$ substituted into this formula were $\nu_3 \pm 0.01$ thereby generating the two dashed curves reflecting the role of experimental uncertainty in the specific heat $\gamma$ prediction from the $L_3$ valence data.

**FIG. 2.** Ce $L_3$ spectra, all normalized to the Ce$^{3+}$ peak, at $T=10$ K (dotted curves) and room temperature (solid curves) for three selected Ce(Mn$_x$Cr$_{1-x}$)$_2$Si$_2$ compounds. At the top of the figure, the separated Ce$^{3+}$ and Ce$^{4+}$ contributions to the Ce $L_3$ edge of CeMn$_2$Si$_2$, at $T=10$ K ($\nu_3 = 3.16$), as determined by our fitting procedure, are shown.
Ce $L_3$ spectrum of CeMn$_2$Si$_2$ ($T=10$ K) (pictured in the same figure). The details of the fitting procedure have been discussed elsewhere. The derived $L_3$ valence value ($v_3$) for this material is $v_3=3.16$. Whether the $L_3$ valence is in fact the absolute valence for Ce compounds is at present an unanswered question. However, in many Ce systems a one-to-one correspondence has been established between the Ce-volume collapse (associated with Ce valence mixing) and the Ce $L_3$ valence change. The spirit in which we use the $L_3$-valence values therefore is to identify changes in the Ce valence state.

We display the experimental Ce $L_3$ spectra superimposed and normalized to the first (Ce$^{4+}$ related) peak. With this normalization and superposition procedure, a spectrum with a higher $v_3$ value will lie naturally above a spectrum with a lower $v_3$ value in the energy range of the second (Ce$^{4+}$ related) peak. In this way a fitting-procedure-independent picture of the spectral evolution evidencing a Ce valence change can be seen.

C. $L_3$ results at room temperature

Our $L_3$ XAS results motivate a number of conclusions. See Fig. 1(b) for the $v_3$ variation versus $x$ and Figs. 3 for the spectra. First, the Ce $L_3$ valence ($v_3$) at $x=1.0$ is 3.12, typical of a mixed-valent material like CePd$_3$, and with Cr substitution $v_3$ is decreased continuously to $3.04$ (at $x=0.2$), typical of a Kondo regime material like CeCu$_2$Si$_2$. Second, the anomalous compressions in the $a$- and $V$-parameter results, noted above, track the $v_3$ results quite closely. That is, there appears to be a much more rapid change in $v_3$ between $x=0.8$ and 1.0 which is reflected in a one-to-one way by the lattice-parameter results.

In previous work, we have nominally associated $v_3$ values in the 3.07–3.10 range (at room temperature) as indicating the borderline between MV regime behavior (for larger $v_3$ values) and Kondo regime behavior (for smaller $v_3$ values). Here the lower end of this borderline occurs near $x=0.8$, above which $v_3$ and the lattice parameters manifest stronger $x$ variations. The resistivity results presented later also appear to support the passage into the Kondo regime (i.e., lower-energy scale spin fluctuations) somewhere in this same range. However, it should be noted that some variation in $v_3$ persists for $x \leq 0.8$ in the Kondo regime. This is in line with theoretical Anderson model results in which spin-fluctuation energy scale and small Ce valence variations go hand in hand. The low-temperature $v_3$ values discussed below further underscore the continuity of the physics underlying the MV to Kondo regime passage.

D. $L_3$ results at 10 K

Mixed-valent materials typically show valence variations below room temperature. In Fig. 1(b) we show the $v_3$ values for the Ce(Mn$_x$Cr$_{1-x}$)$_2$Si$_2$ series at 10 K (see Fig. 2 for illustrative spectra). These data exhibit the following features: (1) Ce $L_3$ valence increases in general with decreasing temperature; (2) the Ce $L_3$ valence shows little temperature-induced change for the nearly trivalent compounds ($x < 0.4$); and (3) for $x > 0.4$ the thermal valence variation grows continuously to a rather substantial value at $x=1.0$.

The observed thermal variation of the $v_3$ (and therefore the $4f$ occupation number $n_f$) is consistent with the degenerate Anderson model calculations by Schottmann and the recent self-consistent large-$N$-expansion calculations by Bickers et al. Their work showed thermal $n_f$ decreases (i.e., valence increases) on the same order as the $v_3$ variations we observe [i.e., $\Delta v_3 = v_3(10 \text{ K}) - v_3(300 \text{ K}) \leq 0.08$.]

E. Specific heat results

We now turn to the low-temperature specific heat result on the Ce(Mn$_x$Cr$_{1-x}$)$_2$Si$_2$ series. The values of the linear coefficient of the specific heat, $\gamma$, were obtained from the data by fitting to the relation $C/T = \gamma + BT^2$ in the range of $T$ from 10 to 25 K. We observed a small bump at $T = 6$ K for the entire series, similar to that attributed in the MV compound CePd$_3$ to Ce$_2$O$_3$ impurities. The estimated entropy due to this bump is about 25 mJ/molK corresponding to about 0.4% of the Ce atoms in our compounds if we attribute it to the magnetic phase transition of the Ce$_2$O$_3$ impurities. We also observed a second small bump for $x=0.2$–0.5 at $T \sim 7.4$–9.9 K. This bump is due to the very weak CeSi$_{1.7}$ ($y < 2.0$) phase. The CeSi$_{1.7}$ impurities constitute less than 5% of the Ce atoms by entropy estimate for $x=0.2$ and 0.3, and less than 1% for $x=0.4$ and 0.5.

Heavy-fermion systems typically show a very strong increase in their $\gamma$ values below 10 K and in some cases below 1 K. For CeCu$_2$Si$_2$ at roughly 10, 4, and 1 K the $\gamma$ values are, respectively, $\sim 110$, 180, and 1050.

FIG. 3. Ce $L_3$ absorption spectra of Ce(Mn$_x$Cr$_{1-x}$)$_2$Si$_2$ compounds superimposed to compare intensity in the Ce peak region, all normalized to the Ce$^{4+}$ peak.
mJ/mol K², respectively. Since we are using the γ values from fitting data in the 10–25-K range we will refer to our results as γₜ₉ for “higher-temperature” linear specific coefficient. In mixed-valent materials where γ typically has little thermal variation below 10 K no distinction between the T=0 and high-temperature γ values need be made.

The γₜ₉ value is 47 mJ/mol K² for CeMn₂Si₂, analogous to that of typical MV compounds (e.g., for CePd₃, γ ~ 38 mJ/mol K²). The γₜ₉ values increase dramatically as one moves towards the nearly trivalent Kondo regime until at x=0.2, γₜ₉ = 184.7 mJ/mol K² [see Fig. 1(c)]. Such a value of γₜ₉ is typical of a Kondo regime or heavy-fermion system. By comparison the γₜ₉ values for the heavy-fermion system CeCu₂Si₂ and the Kondo system Ce(Pd₀.₈₇Ag₀.₁₃)₂ are both well under 200 mJ/mol K². As will be noted in the next section, the enhancement of γ in Kondo-MV systems is associated with the increase in the f-quasiparticle density of states at ε_F which has a width proportional to T_SF (the spin-fluctuation or Kondo temperature) and a height proportional to 1/T_SF. Thus the γ enhancement is associated with a decrease in T_SF.

F. γₜ₉–v₃ correlation

It is important to note that the γₜ₉ values versus x data correlate very closely with the 10-K L₃ valence variation data [Fig. 1(b)]. That is, the γₜ₉ values become independent of x where the thermal variation of v₃ nearly disappears (i.e., for x ≤ 0.4); and the γₜ₉ and v₃ data both show strong variations with x between x=0.4 and x=1.0. We would like to underscore that the L₃ valence at 10 K is thus supported by the ground-state measurements (specific heat) as the 300-K L₃ valence variation was supported by the ground-state lattice-parameter measurements. As noted earlier, this supports our claim that L₃ valence variations (i.e., Δv₃) faithfully reflect (but are not necessarily equal to) the absolute valence variations (i.e., Δv). Although the scaling between Δv₃ and Δv may be nonlinear in the absence of evidence to the contrary we would propose Δv₃ ~ Δv.

From a theoretical viewpoint, the similar x variations of γₜ₉ and v₃ appear to be reasonable. Increasing Cr substitution should be acting to decrease the spin-fluctuation or Kondo temperature (T_SF). (This will be supported by our transport results discussed below.) The notion that the f-related quasiparticle density of states at the Fermi energy scales with 1/T_SF or that γ ~ 1/T_SF is a longstanding one in the mixed-valent-heavy-fermion field. Rice et al. have recently pointed out that one also expects the effective mass m_e ~ T_SF ~ γ(1−n_f)⁻¹ where n_f is the Ce 4f occupation number. Thus, since the absolute valence v = 4−n_f, one would in general expect variations in n_f to lead to variations in both γ and v₃.

If one makes the assumption that the L₃ valence (v₃) actually yields the absolute valence one can be somewhat more quantitative. (Recall that we have indicated that we regard this as a trial ansatz only.) With this assumption, one can use n_f = 4−v₃ to extract n_f values from our v₃ data and γ = γ₀(1−n_f)⁻¹ to derive the corresponding specific heat values from our v₃ results. The dashed lines in Fig. 1(c) represent the results of this procedure with γ₀ = 9 mJ/mol K² and an optimistic uncertainty in v₃ of ±0.01. This quantitative agreement is interesting, however we only wish to use it (at present) to stress the natural correlation between the v₃ (10 K) and the specific heat γₜ₉ results.

G. Magnetic susceptibility and magnetism

Shown in Fig. 4 is the thermal dependence of the magnetic susceptibility χ(T) for four samples in the Ce(Mn₉,Crₙ)₂Si₂ system. All of the samples, except for x = 0.2, evidence antiferromagnetic ordering at Néel temperatures (T_N) which (together with the paramagnetic Curie-Weiss temperature Θ, effective moment μₑff and the saturation moment μₛ) are listed in Table I. For the x = 0.2 sample, paramagnetic behavior was found in the entire temperature range. The Θ and μₑff values were obtained by fitting the data to a Curie-Weiss law χ = C/(T − Θ) + X₀ on the high-temperature (paramagnetic) side of the χ(T) peaks. The antiferromagnetic nature of the ordering in all samples was supported by the precursors of the so-called “spin-flop” transition observed in high-field magnetization measurements at several temperatures below T_N (the M-versus-H plots are not shown here). No evidence for Ce magnetic ordering was detected in this series. We are currently pursuing low-field and ac magnetic measurements to probe for possible short-range order or spin-glass effects in samples with low Mn content.

It has been previously reported that no magnetic moments are detected on the Ce atoms in CeMn₂Si₂ by neutron scattering, which is consistent with the observation that CeMn₂Si₂ is a MW system. The upturn of the χ(T) below 50 K (see Fig. 4) could contain contributions from both the standard paramagnetic impurities and possibly the low T_SF impurity sites for the Ce atoms. It would ap-

![FIG. 4. Temperature dependence of the magnetic susceptibility χ(T) of the Ce(Mn₉,Crₙ)₂Si₂ series. Note the sharp peaks in the susceptibility (except for x=0.2 sample) near the antiferromagnetic ordering temperatures T_N. Note also the decrease of T_N with decreasing x.](image-url)
TABLE I. Magnetic susceptibility data for Ce(Mn, Cr$_{1-x}$)$_2$Si$_2$ compounds determined from $\chi$-vs-$T$ measurements.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$T_N$ (K)</th>
<th>$\Theta$ (K)</th>
<th>$\mu_{\text{eff}}$ (units of $\mu_B$)</th>
<th>$\mu_{\text{sat}}$ (units of $\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeMn$_2$Si$_2$</td>
<td>376</td>
<td>319</td>
<td>3.28</td>
<td>2.42</td>
</tr>
<tr>
<td>Ce(Mn$<em>{0.75}$Cr$</em>{0.25}$)$_2$Si$_2$</td>
<td>177</td>
<td>165</td>
<td>3.38</td>
<td>2.52</td>
</tr>
<tr>
<td>Ce(Mn$<em>{0.5}$Cr$</em>{0.5}$)$_2$Si$_2$</td>
<td>124</td>
<td>145</td>
<td>2.92</td>
<td>2.09</td>
</tr>
<tr>
<td>Ce(Mn$<em>{0.25}$Cr$</em>{0.75}$)$_2$Si$_2$</td>
<td>-66</td>
<td></td>
<td>3.73</td>
<td>2.86</td>
</tr>
</tbody>
</table>

pear reasonable to propose that the magnetic structure in the Ce(Mn$_{1-x}$Cr$_x$)$_2$Si$_2$ series is similar to that of CeMn$_2$Si$_2$. That is, with ferromagnetically ordered Mn-Cr layers in the $a$ planes which are antiferromagnetically aligned along the $c$ axis and with the nonmagnetic Ce and Si layers lying in between. The ferromagneticlike $\Theta$ values for these ordered compounds (like in CeMn$_2$Si$_2$) support this proposal.

The $T_N$ values were found to decrease linearly with $x$ at a rate of $\Delta T_N/\Delta x \approx 6.0$ K/(at. % Mn) for the Ce(Mn$_{1-x}$Cr$_x$)$_2$Si$_2$ series. The fact that Obermeyer et al. have observed a very similar linear rate of depression of $T_N$ [i.e., 6.3 K/(at. % Mn)] in the Nd(Mn$_{1-x}$Cr$_x$)$_2$Si$_2$ system supports the notion that the rare-earth sublattice plays very little role in the high-temperature ordering in these alloys. In Fig. 5 we plot $T_N$ against $x$ along with literature results for the Ce(Fe$_{1-x}$Mn$_x$)$_2$Si$_2$ system. We attribute the sharp drop of $T_N$ to dilution and the breakup of percolation in the ferromagnetic Mn planes through the weakly magnetic Cr and Fe substitution. Thus, Figs. 4 and 5 show that there is an antiferromagnetic to paramagnetic evolution as $x$ is decreased from $x=1.0$ to $x=0.2$ in Ce(Mn$_{1-x}$Cr$_{1-x}$)$_2$Si$_2$.

The large 3$d$ interlayer distance (equal to $c/2 \approx 5.3$ Å) in the Ce(Mn$_{1-x}$Cr$_x$)$_2$Si$_2$ compounds and the Ce-Si-Mn(Cr)-Si-Ce layer structure suggest that indirect interaction is responsible for the interlayer 3$d$ antiferromagnetic ordering. Although some authors attribute the interlayer interactions to superexchange the metallic character of these compounds would suggest Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions mediated via the conduction electrons.

The effective moment of Mn in CeMn$_2$Si$_2$ is $\mu_{\text{eff}} = 3.28 \mu_B$, much smaller than the 5.9$\mu_B$ of the Mn$^{3+}$ (3$d^5$) ions. Within a formal Mn local moment interpretation these values correspond to a combination of 45% 3$d^7$ and 55% 3$d^6$ per Mn atom. Recently, Szytula et al. have proposed that the short Mn-Si distance (2.4 Å) in this compound makes it possible for the electronic charge to transfer from the 3$p$ shell of Si to the 3$d$ shell of Mn, thereby achieving the requisite $d$-orbital charge increase. Of course, interactions of the Mn 3$d$ states with itinerant band states could also lead to Mn moment reduction with smaller $d$-orbital occupation changes. The $\mu_{\text{eff}} = 3.73 \mu_B$ for Ce(Mn$_{0.75}$Cr$_{0.25}$)$_2$Si$_2$ is 0.45$\mu_B$ larger than that for CeMn$_2$Si$_2$. This could reflect the Ce moment formation (as might be expected) in the nearly trivalent Ce end of the Ce(Mn, Cr)$_2$Si$_2$ series.

H. Resistivity results

We show in Fig. 6 the resistivity $\rho(T)$ of the Ce(Mn$_{1-x}$Cr$_x$)$_2$Si$_2$ (the Ce series) from 1.7 K to room temperature after subtracting the $\rho(T)$ of Th(Mn$_{1-x}$Cr$_x$)$_2$Si$_2$ (the Th series). Here the Th-series $\rho(T)$ measurements were used to estimate both the Mn magnetic and phonon background scattering. We chose this Th series rather than the La(Mn$_{1-x}$Cr$_x$)$_2$Si$_2$ series to estimate the $\rho(T)$ background based on their magnetic structure. That is, ThMn$_2$Si$_2$ has the same antiferromagnetic structure (at $T_N = 483$ K) as CeMn$_2$Si$_2$, while LaMn$_2$Si$_2$ on the other hand, orders ferromagnetically at 303 K.

The basic feature of the $\rho(T)$ curves of the Th(Mn$_{1-x}$Cr$_x$)$_2$Si$_2$ compounds (which are not shown here) is a phononlike behavior except for the $x=0.5$ and 0.6 samples which exhibited a wide but small amplitude bump at about 120 and 160 K, respectively. We illustrate
the Ce- and Th-system resistivities for the $x=0.8$ in the inset of Fig. 6. The absolute value of $\rho(T)$ for the Th series was always smaller than that of the corresponding Ce compounds.

It is clear in Fig. 6 that the temperature dependence of the resistivity of the background-subtracted Ce(Mn$_x$Cr$_{1-x}$)$_2$Si$_2$ series is very similar to the $\rho(T)$ plotted in Ref. 1 where no background was subtracted. That is, (1) the MV compound CeMn$_2$Si$_2$ displays a high-$T$ negative temperature coefficient of resistivity (TCR) along with a rapid low-$T$ resistivity drop from a maximum at $T=73$ K [this $\rho(T)$ feature is very similar to what was found in the prototypic MV system CePd$_3$, and is related to the onset of coherent scattering between different Ce sites]; (2) with $x$ moving down from $x=1$, this coherence effect is rapidly destroyed by the disorder of the Mn-Cr sublattice and almost disappears by $x=0.8$; and (3) the positions of the low-temperature minimum ($T_{\text{min}}$) are almost unchanged by the background subtraction. The $T_{\text{min}}$ values move down steadily with decreasing Mn content and, as will be emphasized below, are closely correlated with the onset of the antiferromagnetic ordering of the 3$d$ sublattice. Thus the anomalous increases in the $\rho(T)$ curves, with decreasing temperature, can be attributed to Ce scattering, presumably of Kondo-spin-flip type. The negative curvature of $\rho(T)$ which develops for $x \leq 0.5$ is very similar to that found in some Kondo systems such as CeAl$_3$, where they have been interpreted in terms of a Kondo-modified crystalline electrical field effect as treated by Cornut and Coqblin.

The Kondolike resistivities in this series occur at progressively lower temperature ranges and become weaker with increase in Cr content. This is consistent with the evolution from MV to Kondo regimes and decreasing spin-fluctuation temperatures evidenced in the earlier lattice parameters—$L\bar{3}$, specific heat, and magnetic susceptibility results.

I. Antiferromagnetic-order–Kondo-scattering correlation

We would now like to discuss the correlation of the Kondo minimum temperature $T_{\text{min}}$ to the 3$d$ antiferromagnetic ordering temperature $T_N$. We have observed that the $T_{\text{min}}$ values of the $\rho(T)$ curves are very close to the $T_N$ values for the Ce(Mn$_x$Cr$_{1-x}$)$_2$Si$_2$ series (see Fig. 5). The small deviation of $T_N$ from $T_{\text{min}}$ for $x=0.6$ can reasonably be considered within measurement and sample duplication errors. Recently, we have also observed this $T_N$ and $T_{\text{min}}$ correlation in the CeMn$_2$(Si$_2$Ge$_{1-x}$)$_2$ compounds.

**FIG. 6.** Electrical resistivity vs temperature results for the Ce(Mn$_x$Cr$_{1-x}$)$_2$Si$_2$ series after subtracting the Th(Mn$_x$Cr$_{1-x}$)$_2$Si$_2$ background, i.e., the Mn magnetic and phonon background scattering. The inset shows the resistivity for the $x=0.8$ compounds. Note the rapid quenching of the low-temperature coherence and the steady state decrease of the resistivity minimum temperature as $x$ moves down from $x=1.0$.

**FIG. 7.** Electrical resistivity vs temperature results for two Ce(Fe$_{1-x}$Mn$_x$)$_2$Si$_2$ compounds after subtracting the corresponding background, i.e., the resistivity of Th(Fe$_{1-x}$Mn$_x$)$_2$Si$_2$. Note the resistivity minimum at temperature close to $T_N$ (see Fig. 5).
series.\textsuperscript{24} This closeness of $T_N$ and $T_{\text{min}}$ can potentially be explained by the effect of the 3$d$ magnetic field on the Ce atoms in the following picture. Above $T_N$ the Ce spins are actually acted on by a local temperature varying RKKY field (or conduction electron polarization field), produced by the Mn moments which are in the nearest-neighbor layers.\textsuperscript{25} In this case the Ce Kondo spin-flip process could be effectively quenched by this dynamic RKKY field. When the temperature falls below $T_N$, the interlayer 3$d$ antiferromagnetic ordering occurs giving rise to a static RKKY field. The resulting static RKKY field could be much smaller at the Ce sites which are symmetrically located between oppositely aligned ferromagnetic 3$d$ (Mn-Cr) layers. Thus, the Kondo spin-flip process could be freed up below $T_N$ and the Kondo-type negative TCR would arise at a temperature near $T_N$. If the 3$d$ sublattices were ferromagnetically ordered then the Ce Kondo spin-flip processes would presumably be further quenched by a large static RKKY field and thus no resistivity minimum would be expected.

Further evidence of the onset of Ce scattering in the antiferromagnetic phase of these types of compounds can be gleaned from the background-subtracted resistivity, $\rho(T)$, curves of the Ce(Fe\textsubscript{1-x}Mn\textsubscript{x})\textsubscript{2}Si\textsubscript{2} shown in Fig. 7. A resistivity minimum occurs at $\approx 2.52$ and 138 K for $x=0.6$ and 0.4, respectively, in this system. These values are very close to the $T_N$ value observed by Sztluma et al.\textsuperscript{20} (see Fig. 5). The Ce(Mn,Fe)\textsubscript{2}Si\textsubscript{2} samples are within the MV regime. However, the disordered MV materials (such as CePd\textsubscript{3} or CeMn\textsubscript{3}Si\textsubscript{2}) have been shown to exhibit a negative TCR reminiscent of the Kondo effect. Thus, in this system, also the Ce scattering appears quenched above $T_N$ but freed up below $T_N$.

\textbf{IV. SUMMARY}

In summary, we have found Ce(Mn\textsubscript{x}Cr\textsubscript{1-x})\textsubscript{2}Si\textsubscript{2}, with 0.2 $\leq x \leq$ 1.0, to be the first compound series in which the Ce undergoes an evolution from a coherent MV regime to a noncoherent nearly trivalent Kondo system despite the presence of strongly interacting 3$d$ moments. Indeed, the continuous nature of this evolution appears consistent with the philosophy of recent Anderson-model treatments\textsuperscript{3-5} in which the 4$f$ occupancy varies in the 1.0 $\geq n_f \geq$ 0.7 range. More specifically, some of the noteworthy points that have been brought out are listed below.

(1) Ce Kondo-type spin-fluctuation scattering apparently survives within the antiferromagnetically ordered phase of these materials.

(2) The paraagnetic state of these materials containing Mn moments appears hostile to the Ce spin-flip (i.e., Kondo scattering) process.

(3) The Ce $L_3$ valence variation and lattice parameter results at 300 K both support a Ce valence decrease with Cr substitution in these materials.

(4) The enhancement of the low-temperature specific heat with Cr substitution is consistent in magnitude with the observed Ce $L_3$ valence state variation (at 10 K) in the light of recent theoretical work.\textsuperscript{3-5}

Finally, our work should motivate generalizations of traditional Anderson-model treatments of MV-Kondo phenomena to magnetic host lattices. Specifically, the band states with which the 4$f$ states hybridize could be considered to be partially spin polarized in a static or dynamic way. Questions also arise of how the band electron RKKY field interacts spatially with the Ce 4$f$ moment screening cloud set up in the Kondo ground state.

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