Lattice, Ce-\(L_3\) valence, transport, and magnetic results on mixed-valent/Kondo system Ce\(_{1-x}\)La\(_x\)Mn\(_2\)Si\(_2\)

G. Liang, H. Xi, E. Roberts, and T. Binford
Department of Physics, Sam Houston State University, Huntsville, Texas 77341

K. Mochizuki and J. T. Markert
Department of Physics, University of Texas at Austin, Austin, Texas 78712

M. Croft
Department of Physics, Rutgers University, Piscataway, New Jersey 08855

Lattice, Ce-\(L_3\) edge, resistivity, and magnetic susceptibility measurements have been carried out on the polycrystalline Ce\(_{1-x}\)La\(_x\)Mn\(_2\)Si\(_2\) system \((0 \leq x \leq 1)\) to study the interplay between Mn 3\(d\)-host magnetism and Kondo-type Ce-spin fluctuations. As \(x\) increases, the system varies gradually from a Ce mixed-valent system with 3\(d\)-host antiferromagnetism (at \(x = 0\)) to a nearly trivalent system with strong 3\(d\)-host ferromagnetism (near \(x = 1\)). In the antiferromagnetic (AF) phase region \((0 \leq x \leq 0.5)\), the Neel temperature \(T_N\) decreases with the increase of \(x\), manifesting the weakening of the host AF field. Impurity Kondo behavior is observed at \(x = 0.05\), indicating that the low-temperature coherence state in CeMn\(_2\)Si\(_2\) can be destroyed by ‘‘Kondo holes’’ which are created by very small substitution of La for Ce. The susceptibility and resistivity results suggest that the impurity Kondo effect in the 0.1 \(\leq x \leq 0.5\) samples is partially suppressed by a nonvanishing ferromagnetic (FM) field component; whereas the phononlike behavior of the resistivity curves in the Mn-host FM-phase region \((0.5 < x \leq 1.0)\) supports our previous proposal that the Kondo-type Ce-spin fluctuations can be effectively quenched by a strong 3\(d\)-host FM field. © 1997 American Institute of Physics. [S0021-8979(97)33208-3]

INTRODUCTION

The interplay of magnetism, the Kondo effect, and superconductivity in a very narrow band has stimulated a great deal of effort in Kondo/heavy-fermion (HF) systems.\(^1\) Our previous studies clearly showed that CeMn\(_2\)Si\(_2\) is a mixed-valent (MV) compound very similar to CePd\(_3\), but with the Mn-host antiferromagnetically ordered below 376 K.\(^2\)-\(^4\) They indicated that the energy scale of the 4\(f\)-moment quenching is dramatically lowered by substitutions of Cr for Mn and Ge for Si in CeMn\(_2\)Si\(_2\).\(^3\),\(^4\) These studies also provided supportive evidence that the Kondo scattering is effectively quenched by strong Mn-host ferromagnetic (FM) fields, but it thrives within an antiferromagnetic (AF) host phase.\(^2\)-\(^6\) In this article, we study the Ce\(_{1-x}\)La\(_x\)Mn\(_2\)Si\(_2\) series to see how a system evolves from a concentrated Kondo system to a dilute Kondo system in the presence of strong AF or FM Mn-host fields. We also want to compare this series with the ‘‘Kondo hole’’ compounds Ce\(_{1-x}\)La\(_x\)Pd\(_3\).\(^7\)-\(^9\)

EXPERIMENT

Ce\(_{1-x}\)La\(_x\)Mn\(_2\)Si\(_2\) \((0 \leq x \leq 1)\) polycrystalline samples were prepared by standard arc furnace technique. The resistivity rods in the range of \(0 \leq x \leq 0.4\) were annealed in quartz tubes at 800 °C for 5 days. All samples were confirmed to be single phase by x-ray diffraction measurements. The Ce \(L_3\)-edge spectra (not shown here) were taken at National Synchrotron Light Source. The electrical resistivity measurements were made using standard four-probe dc technique. The magnetic susceptibility measurements were performed using a SQUID magnetometer.

RESULTS AND DISCUSSION

Shown in Fig. 1 (top) is the Ce \(L_3\) valence, \(v_3\), obtained by fitting the Ce-\(L_3\) spectra by our fitting procedure.\(^2\) With the substitution of La for Ce, \(v_3\) continuously decreases from 3.12 at \(x = 0\), to about 3.03 at \(x = 0.8\), driving the system from a MV to a nearly trivalent system. The \(a\) and \(c\) lattice parameters of this series are also plotted in Fig. 1 (bottom and middle). It can be seen that both parameters, \(a\) and \(c\), deviate from Vegard’s law and track the \(v_3\) variation closely. It is typical that the \(a\) parameter in a Ce\(_T\)Si\(_2\)-based compound series responds sensitively to rare-earth radius change.\(^3\),\(^4\),\(^10\),\(^11\)

The thermal dependence of the magnetic susceptibility \(\chi(T)\) for five samples of the Ce\(_{1-x}\)La\(_x\)Mn\(_2\)Si\(_2\) series is shown in Fig. 2. For the samples with \(x = 0.0, 0.2\), and 0.4, the Mn atoms exhibit antiferromagnetic (AF) order and thus a sharp peak at the Neel temperature \((T_N)\) is evident in the \(\chi(T)\) curves in Fig. 2 (top). The field-dependent magnetization \(M(H)\) data shown in the inset of Fig. 2 (top) for the \(x = 0.2\) sample has extremely small field response and thus is consistent with AF ordering.\(^4\) The \(M(H)\) data indicate that the magnetization at 55 kOe is 1.6 kemu/mole (or 0.2 \(\mu_B/\text{Mn}\)), or about 8% of the saturation magnetization \(\mu_{sat} = 2.4 (\mu_B/\text{Mn})\) for CeMn\(_2\)Si\(_2\).\(^3\) With the increase of La concentration \(x\), \(T_N\) decreases from 376 K at \(x = 0.0\) to 354 K
at $x=0.2$, and then to 322 K at $x=0.4$. This drop of the AF ordering energy scale reflects the weakening of the strength of the Mn-host AF field. Since LaMn$_2$Si$_2$ is an FM system ordered at 308 K, it is possible that by substitution of La for Ce, the collinear AF structure in CeMn$_2$Si$_2$ could be modified in a certain way and a nonvanishing ferromagnetic field component could be produced. The increase of $x$ with increasing $x$ below 300 K manifests the strengthening of the FM field component. Also, the wide-bump feature, evidenced in the $x=0.2$ and 0.4 curves below 300 K, could be attributed to this FM field component.

Figure 2 (bottom) shows that for $x=0.8$ and 1.0, the Mn atoms are FM ordered at ferromagnetic transition temperatures $T_c=306$ K and 308 K, respectively. The effective moment ($\mu_{\text{eff}}$) value for $x=0.8$ sample is 4.0 $\mu_B$ per formula unit (or 2.84 $\mu_B$/Mn), which is obtained by fitting the $\chi^{-1}(T)$ data from 320 to 400 K to the Curie–Weiss law $\chi=C/(T-\Theta p)$ with $C=2.0$ emuK/mole and $\Theta p=312$ K. The $\mu_{\text{eff}}$ value estimated here is very close to the value 4.3 $\mu_B$ reported by Szytula et al. These results are consistent with the following division made by Szytula et al.: the compound series is in AF phase for $x<0.5$, FM phase for $x>0.7$, and both AF and FM phases (with $T_N<T_c$) for $x=0.6$.

The valence state of Mn in this series has not been well studied. In a previous study, we found that the effective moment of Mn in CeMn$_2$Si$_2$ is $\mu_{\text{eff}}=3.28$ $\mu_B$/Mn. This value is consistent with a combination of 50% Mn$^{3+}$($3d^44s^2$) and 50% Mn$^{3+}$($3d^44s^2$) with two paired electrons in the 3d shell (as proposed by Szytula et al.). This formal valence value of Mn roughly satisfy the charge balance requirement if the Si is in a Si$^{4-}$ state and Ce is nearly Ce$^{3+}$ (here Ce is Ce$^{3+}$ by our Ce $L_3$ measurement). Further study by other methods such as Mn $K$-edge absorption is needed to confirm the above Mn valence values. At present, the reasons for the reduction of the $\mu_{\text{eff}}$ from the $x=0.0$ to $x=0.8$ sample are not clear.

Finally, in Fig. 3, we show the temperature-dependent resistivity $\rho(T)$ results for the Ce$_{1-x}$La$_x$Mn$_2$Si$_2$ alloys. In the following, we discuss the resistivity results in three regions.
Mixed-valent Mn-AF phase region: 0.0≤x<0.1. The ρ(T) curve of the x=0.0 compound CeMn2Si2 displays a low-temperature coherence drop below 73 K. The impurity Kondo behavior of the ρ(T) curve of the x=0.05 sample clearly shows that 5% La substitution for Ce can completely destroy the low temperature coherence behavior in CeMn2Si2. Since both the x=0 and x=0.05 samples were annealed, the defect disorder as a destructive factor to the coherence behavior can be ruled out here. The destruction of the low temperature coherence observed here is indeed very similar to that occurred in Ce1-xLa3Pd3 (x≤0.1)7–9 and thus can be attributed to the Kondo hole effect.7

KLM Mn-AF phase region: 0.1≤x<0.5. The Ce L3 valence, ν3, in this x range is between 3.04 and 3.11, which, as mentioned previously, should place the samples in this x range in the KLM regime.10 However, unexpectedly, the impurity Kondo-like negative temperature coefficient of resistivity (TCR), which was observed in both the Ce(Mn1−xCrx)2Si2 and CeMn2(Si1−xGe)x2 systems with the same Mn-AF phase and ν3 range, is not seen in the ρ(T) curves in Fig. 3. The absence of the negative TCR can be explained by the magnetic results discussed earlier. As x increases, the Mn-AF field is weakened, whereas the Mn-FM field component is strengthened. This FM field component could suppress the Kondo scattering (or Kondo-type Ce-spin fluctuation) to certain degrees, resulting in the observed negative curvature in the ρ(T) curves. This negative curvature can be found in many Kondo systems, such as CeRu2Si212 and Ce(Mn1−xCrx)2Si23 and can be interpreted in terms of a crystalline electric field modified Kondo effect as treated by Cornut and Coqblin.13 Sometimes, the Kondo-like negative TCR can be seen after the phonon contribution to the ρ(T) curve is removed. For the present series, however, the ρ(T) curve of the x=1.0 compound LaMn2Si2 cannot be used as the phonon background because the Mn-host FM field strength in this compound could be much stronger than in those x≠1.0 compounds.

Kondo-quenched Mn-FM region: 0.8≤x<1.0: In this region, Ce is substantially diluted and in a nearly trivalent state (with ν3<3.03). Mn moments are ferromagnetically (FM) ordered slightly above 300 K. The x=1.0 sample LaMn2Si2 shows the pure phonon behavior similar to LaPd3. This was expected because LaMn2Si2 does not contain 4f moments. The two ρ(T) curves for x=0.8 and 0.9 also exhibit the phononlike behavior without negative curvature, indicating that the Kondo scattering has been quenched in these two dilute Ce compounds. This is in sharp contrast with the trivalent Ce1−xLa3Pd3 compounds with x=0.8 and 0.9 which exhibit strong impurity Kondo behavior below Kondo minima 180 and 32 K,9 respectively. The disappearance of the impurity Kondo effect in the x=0.8 and 0.9 samples in the Ce1−xLa3Mn2Si2 series is in accord with our previous proposal that the low-energy-scale Kondo-type Ce-spin fluctuations can be effectively quenched by high-energy-scale (with Tc>300 K) Mn-host FM fields.

ACKNOWLEDGMENTS

The work was supported by Texas ARP, Research Corporation, SHSU, and The Welch Foundation under Grant No. F1191.
