Kondo effect in 3d-host ferromagnetic Sm$_{1-x}$Ce$_x$Mn$_2$Ge$_2$

G. Liang $^a$, Q. Yao $^a$, H. Xi $^a$, K. Mochizuki $^b$, J.T. Markert $^b$, M. Croft $^c$

$^a$ Department of Physics, Sam Houston State University, Huntsville, TX 77341, USA
$^b$ Department of Physics, University of Texas at Austin, Austin, TX 78712, USA
$^c$ Department of Physics, Rutgers University, Piscataway, NJ 08855, USA

Received 16 June 2005; accepted 29 June 2005
Available online 25 August 2005

Abstract

Lattice, Ce L$_3$-edge, magnetic susceptibility, and electrical resistivity results on polycrystalline Sm$_{1-x}$Ce$_x$Mn$_2$Ge$_2$ ($0 \leq x \leq 1$) compound series are presented. The lattice parameters $a$ and $c$ increase almost linearly with the increase of Ce concentration $x$. The Ce-L$_3$ X-ray absorption spectra indicate that the Ce in this series is nearly trivalent, and Ce valence decreases slightly with the increase of Ce concentration $x$. Magnetic susceptibility results indicate that the antiferromagnetic (AF) phase in the re-entrant ferromagnetic compound, SmMn$_2$Ge$_2$, is completely destroyed by merely 1.1% Ce for Sm substitution. For $x > 0.011$, only ferromagnetic (FM) phases exist below room temperature. It is found that in these materials Ce Kondo scattering coexists with the 3d-host FM fields and is also effectively weakened by such fields.

Keywords: Rare-earth compounds; Magnetically ordered materials; Kondo effect; Electrical transport; Magnetic measurements

1. Introduction

In the last two decades, a great deal of effort has been made in understanding the origin of heavy-fermion behavior [1–8]. Some experimental and theoretical work has attributed the origin of heavy-fermion behavior, observed in many Ce compounds, to the Kondo-type Ce-spin fluctuation process [2,9]. It is expected that Kondo-heavy-fermion behavior can be effectively affected by different types of magnetic fields. Although many studies have been carried out on Ce-based Kondo-heavy-fermion materials in which the Ce ions are in non-magnetic host environments [7,10,11], very little work has been done on materials in which the Ce Kondo sites are embedded in robust internal host magnetic fields, such as the fields generated by the Mn-sublattice in the RMn$_2$X$_2$ (R = rare-earth elements and X = Si, Ge) type materials [12–20].

Our motivations for studying Sm$_{1-x}$Ce$_x$Mn$_2$Ge$_2$ are the following. SmMn$_2$Ge$_2$ exhibits unique re-entrant ferromagnetism [21–26]. This peculiar magnetic property makes it a potential magnetic host for examining Kondo effect in different ferromagnetic (FM) or antiferromagnetic (AF) 3d-host fields. We already know that CeMn$_2$(Si$_{1-x}$Ge$_x$)$_2$ is a Kondo/mixed valence (MV) series with Ce nearly trivalent for the end compound CeMn$_2$Ge$_2$ (with $x = 1$). It is expected that the substitution of the Ce atoms in CeMn$_2$Ge$_2$ by smaller size Sm atoms could also drive the Ce valence higher. Thus, we would like to carry out X-ray diffraction (XRD), Ce-L$_3$ X-ray absorption spectroscopy (XAS), magnetic susceptibility, and electrical resistivity measurements on Sm$_{1-x}$Ce$_x$Mn$_2$Ge$_2$ intermetallics to: (1) better understand the lattice, Ce-valence instability, magnetic and transport properties of this series, and (2) provide more experimental results on the interplay between Ce Kondo scattering and Mn 3d-host magnetism.

2. Experimental detail

Polycrystalline Sm$_{1-x}$Ce$_x$Mn$_2$Ge$_2$ ($0 \leq x \leq 1.0$) samples with $x = 0$, 0.011, 0.2, 0.4, 0.5, 0.6, 0.8, and 1.0 were prepared by melting constituent elements in an Ar atmo-
sphere by standard arc furnace technique. The purity levels of the elements were 99.95% for Ce, 99.9% for Sm, 99.99% for Mn, and 99.9999% for Ge. For all samples, a 2% excess Mn over the stoichiometric amount was added before the arc melting to compensate for the mass loss of Mn during melting. After arc melting, the mass of each sample was checked, and it was found that the mass loss for all the samples is in the range from 1.6 to 3.0%. All of the samples were confirmed to be single phase by X-ray diffraction measurements using a Rigaku 2005 X-ray diffractometer. Lattice parameters were obtained by the least-square-fitting method in the range of \(20^\circ \leq 2\theta \leq 80^\circ\). The temperature-dependent resistivity was measured by a standard four-probe dc technique in a temperature range of 1–300 K. Magnetic susceptibility measurements were made with a superconducting quantum interference device (SQUID) magnetometer in a magnetic field of 1000 Oe and over a temperature range of 4.2–400 K. Ce L3-edge X-ray absorption spectroscopy (XAS) data were taken at room temperature at the National Synchrotron Light Source and the Ce L3 valence determination method used in this study has been described elsewhere [17,27].

3. Results and discussion

Lattice parameters \(a\) and \(c\) for the Sm\(1-x\)Ce\(x\)Mn\(_2\)Ge\(_2\) \((0.0 \leq x \leq 1.0)\) series are shown in Fig. 1. Both parameters \(a\) and \(c\) increase almost linearly with increasing \(x\). The parameter \(a\) for \(x = 0\) sample, SmMn\(_2\)Ge\(_2\), is 4.061 Å, corresponding to an intralayer Mn–Mn distance \(R_{\text{Mn-Mn}}\) of 0.2871 nm. Since it is typical that parameter \(a\) deviates from Vergard’s law for mixed valence CeT\(_2\)X\(_2\)-based compound series \([15,17,28]\), the linear relationship between the lattice parameter \(a\) and Ce concentration \(x\) suggests that the Ce-valence state in this compound series should be trivalent or nearly so. Similar Vergard’s law behavior has been also observed for compound series Sm\(_{1-x}\)R\(_x\)Mn\(_2\)Ge\(_2\) with R as trivalent rare-earth ions Gd, Y, and Nd \([29–31]\). Fig. 2 shows the Ce L3-edge spectra for three Sm\(_{1-x}\)Ce\(_x\)Mn\(_2\)Ge\(_2\) samples with \(x = 0.2, 0.5,\) and 1.0. Since the feature change in the spectra of the entire series is very small, we only show the spectra of three samples here. All the spectra in Fig. 2 are background subtracted and normalized to the value at the low-energy (Ce\(^{3+}\)) peak. A weak high-energy (Ce\(^{4+}\)) feature at about 9 eV above the low-energy peak is observed for the \(x = 0.2\) spectrum but disappears for \(x = 0.5\) and 1.0. This result indicates that the Ce-valence state in this series is basically trivalent, but there is a small Ce\(^{4+}\) mixing for the \(x = 0.2\) sample. The values of the Ce L3 valence, \(v_{3}\), determined by our curve fitting method described elsewhere \([17]\), are 3.00 and 3.04 for the \(x = 1.0\) and \(x = 0.2\) samples, respectively. We previously proposed that a rough division between mixed valence regime and Kondo-local-moment (KLM) regime exists in the range \(3.07 \leq v_{3} \leq 3.10\) (at room temperature) for the CeT\(_2\)X\(_2\) (or 1:2:2) type compounds \([32]\). This division is within the range of our specific Ce-valence analysis method and was seen in previous studies spanning most known Ce-transition metal intermetallic compounds. Thus, according to this criterion, the range of the \(v_{3}\) values \((v_{3} \leq 3.04)\) clearly places Ce in the KLM regime for
the entire Sm$_{1-x}$Ce$_x$Mn$_2$Ge$_2$ series is shown in Fig. 4. All of the Sm$_{1-x}$Ce$_x$Mn$_2$Ge$_2$ samples, our lattice parameter results show that the lattice parameter $c$ decreases almost linearly with $x$, and $T_2$ decreases about seven times faster than $T_1$ (see Table 1). We find in Table 1 that the decreasing rates for $T_1$ and $T_2$ are, respectively, $\Delta T_1/\Delta x = 22$ K and $\Delta T_2/\Delta x = 155$ K. These observations can be explained within the following framework. Since Ce is non-magnetic down to 1.6 K [18, 35, 36] whereas Sm is ferromagnetically coupled with Mn-sublattice at temperatures below $T_1$ [21], the magnetic coupling is much stronger between Sm and Mn than between Ce and Mn. Thus, Ce for Sm substitution creates spin disorder on the ferromagnetically polarized Mn layers by diluting the Sm sublattice. It also can weaken the overall ferromagnetic coupling between the rare-earth (Sm, Ce) layers and the Mn layers, resulting in a rapid decrease of $T_1$. On the other hand, the decrease of $T_2$ due to the substitution of the smaller size Ce can be attributed to the weakening of the coupling between adjacent Mn layers (along the c-axis direction) rather than between (Sm, Ce) and Mn layers. For Sm$_{1-x}$Ce$_x$Mn$_2$Ge$_2$ samples, our lattice parameter result shows that the lattice parameter $c$ increases almost linearly with the Ce substitution level $x$. Thus, the interlayer Mn–Mn distance $R_{\text{Mn-Mn}}$ also increases almost linearly with $x$. This increase of $R_{\text{Mn-Mn}}$ can weaken the out-of-plane ferromagnetic coupling between adjacent Mn layers and thus reduce $T_1$.

The temperature-dependent resistivity, $\rho(T)$, for the Sm$_{1-x}$Ce$_x$Mn$_2$Ge$_2$ series is shown in Fig. 4. All of the $\rho(T)$ curves are normalized to the resistivity values at 273 K. The $\rho(T)$ curve for Sm$_{1-x}$Mn$_2$Ge$_2$ ($x=0$) exhibits a phonon behavior similar to that for LaMn$_2$S$_2$ [19] or LaMn$_2$Ge$_2$ [37]. The slight drop of the resistivity in the AF phase region, which

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**Table 1**

<table>
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<th>$T_2$ (K)</th>
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<tr>
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<td>0</td>
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**Fig. 3** Temperature dependence of magnetic susceptibility $\chi$ for Sm$_{1-x}$Ce$_x$Mn$_2$Ge$_2$ measured at 1000 Oe.

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The magnetic susceptibility $\chi(T)$ data for seven Sm$_{1-x}$Ce$_x$Mn$_2$Ge$_2$ samples with Ce concentrations at $x=0.0$, 0.011, 0.2, 0.4, 0.5, 0.8, and 1.0 are shown in Fig. 3. For the $x=0$ sample, SmMn$_2$Ge$_2$, the $\chi(T)$ curve shows an AF phase transition at $T_1 = 341$ K, an AF phase transition at $T_2 \approx 155$ K.

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The magnetic susceptibility $\chi(T)$ of the notations of the magnetic ordering of Mn and rare-earth atoms in these other groups [21–24]. In one of our previous paper [25], samples with the entire Sm$_{1-x}$Ce$_x$Mn$_2$Ge$_2$ series is shown in Fig. 4. All of the $\chi(T)$ curves are normalized to the resistivity values at 273 K. The $\chi(T)$ curve for Sm$_{1-x}$Mn$_2$Ge$_2$ ($x=0$) exhibits a phonon behavior similar to that for LaMn$_2$S$_2$ [19] or LaMn$_2$Ge$_2$ [37]. The slight drop of the resistivity in the AF phase region, which
Fig. 4. Temperature-dependent electrical resistivity $\rho(T)$ curves for the $\text{Sm}_{1-x}\text{Ce}_x\text{Mn}_2\text{Ge}_2$ ($0 \leq x \leq 1$) series, all normalized to the $\rho(T)$ values at 270 K. For the purpose of separating the curves from each other, each curve is offset by 0.5 of a normalized unit.

was reported by van Dover et al. [38] and Sampathkumaran et al. [37], is not observed in the $\rho(T)$ curve for the $x = 0$ sample.

The $\rho(T)$ curves for the $x \geq 0.2$ samples display a wide bump in the temperature range from 20 to 150 K, very similar to the $\rho(T)$ curves found in the Kondo system $\text{CeMn}_2(\text{Si}_{1-y}\text{Ge}_y)_2$ (with $0.6 \leq y \leq 1.0$) system. Thus, we can discuss the resistivity result for the $\text{Sm}_{1-x}\text{Ce}_x\text{Mn}_2\text{Ge}_2$ in comparison with the Kondo system $\text{CeMn}_2(\text{Si}_{1-y}\text{Ge}_y)_2$.

If the phonon background could be subtracted from these $\rho(T)$ curves, then a Kondo-like upturn would be expected to present in the difference resistivity curves. To see the Kondo spin-flip scattering due to the Ce moments, as the first approximation, we can use the phonon-like $\rho(T)$ curve of the un-substituted SmMn$_2$Ge$_2$ as the phonon background. In Fig. 5, we display the difference resistivity $\Delta \rho(T)$ curves for the $\text{Sm}_{1-x}\text{Ce}_x\text{Mn}_2\text{Ge}_2$ series. These $\Delta \rho(T)$ curves are obtained by subtracting the $x = 0$ $\rho(T)$ curve from the $x \neq 0$ $\rho(T)$ curves shown in Fig. 4. The negative temperature coefficient of resistivity (TCR) of these difference resistivity curves indeed indicates that the Kondo-type Ce-spin fluctuations due to the Ce moments exist in these materials.

The wide bump-like features for the $x \neq 0$ $\rho(T)$ curves in Fig. 4 or $\Delta \rho(T)$ curves in Fig. 5 can be explained theoretically by the Cornut–Coqblin model of the crystalline-electric field (CEF) Kondo effect [39]. Since the range of the $v_3$ values ($v_3 \leq 3.04$) clearly places the entire $\text{Sm}_{1-x}\text{Ce}_x\text{Mn}_2\text{Ge}_2$ series (with $x \neq 0$) in the Kondo-local-moment (KLM) regime with Ce nearly trivalent, it is expected that the Ce Kondo effect (or Kondo-type spin fluctuation) should prevail. Due to the same crystal structure and similar range in lattice parameters, the CEF structure of the $\text{Sm}_{1-x}\text{Ce}_x\text{Mn}_2\text{Ge}_2$ series can be assumed to be similar to that of $\text{CeCu}_2\text{Si}_2$. For $\text{CeCu}_2\text{Si}_2$, the first excited CEF level is at about 140 K and the second excited CEF level is near 360 K [40]. The Kondo scattering from the first excited CEF level and the ground state level of Ce should produce two Kondo resistivity minima, one at a higher temperature above 140 K (due to scattering from the first excited level) and one below 20 K (due to the ground state level). The part of the $\rho(T)$ curves between these two minima should be a prominent maximum, as observed for $\text{CeMn}_2(\text{Si}_{1-y}\text{Ge}_y)_2$ with $y = 0.3$ and 0.4 [17]. However, since all of the $\text{Sm}_{1-x}\text{Ce}_x\text{Mn}_2\text{Ge}_2$ samples with $x \geq 0.2$ are in one or two 3d ferromagnetic phases below room temperature (see Fig. 3), the Ce spins are actually acted on by a local 3d-host field generated by the ferromagnetically ordered Mn moments. In this case, the Ce Kondo spin-flip scattering (or Kondo-type spin fluctuation) could be effectively weakened by FM field. This weakening could reduce the wide maximum to a visible wide bump in the $\rho(T)$ curves, as shown in Fig. 4. To "free up" the suppressed Kondo spin-flip scattering, one needs to turn the Mn moments from the FM ordered phase into an AF ordered phase. In such an AF ordered phase, the resulting RKKY field could be much smaller at the Ce sites, which are symmetrically located between two oppositely aligned Mn-moment layers [17,27]. The AF phase can be achieved by applying high pressure on the samples to reduce their $R_{\text{Mn-Mn}}$ to certain values below 0.2871 nm [34]. Indeed, our
high-pressure resistivity measurement on CeMn$_2$Ge$_2$ clearly shows that high pressure can free up the quenched Ce Kondo spin-flip scattering [41].

To see the weakening effect on the Ce Kondo spin-flip scattering by the Mn-host FM fields more clearly, we plot in Fig. 6 some measured $\rho(T)$ curves for four CeT$_2X_2$-based compounds. All the $\rho(T)$ curves are normalized at $T=273$ K. The Ce L$_3$ valence values for these four compounds are all between 3.03 and 3.04, well within the nearly trivalent KLM regime. For CeCu$_2$Si$_2$ and CeNi$_2$Cu$_4$Si$_2$, the 3d transition metal host is non-magnetic, and thus, there is no suppression of the Kondo effect by any 3d-host magnetic fields, as evidenced by the negative temperature coefficient of resistivity (TCR) of the $\rho(T)$ curves. However, the negative TCR is not seen in the other two compounds, CeMn$_2$Si$_{0.8}$Ge$_{1.2}$ and Sm$_{0.8}$Ce$_{0.2}$Mn$_2$Ge$_2$, due to the suppression of the Ce Kondo effect by the magnetic fields generated by the FM ordered Mn-host.

4. Summary

We have studied the lattice, Ce L$_3$-edge, magnetic, and transport properties of intermetallic Sm$_{1-x}$Ce$_x$Mn$_2$Ge$_2$ ($0 \leq x \leq 1$) compounds. We have found that the lattice parameters $a$ and $c$ increase almost linearly with the increase of $x$. The Ce L$_3$ result shows that Ce is nearly trivalent in this series. The Ce valence measured by Ce-L$_3$ spectra decreases slightly with the increase of Ce concentration $x$. Magnetic susceptibility data indicate that the AF phase in the re-entrant ferromagnetic compound, SmMn$_2$Ge$_2$, is destroyed by a very small (about 1.1%) Ce for Sm substitution. It is found that for $x>0.01$, only ferromagnetic phases exist below room temperature. Our resistivity result supports the idea that, for all the Ce substituted compounds ($x>0$), Ce Kondo scattering coexists with the 3d-host FM fields and is also effectively weakened by such fields.

Acknowledgments

The work at Sam Houston State University (SHSU) was supported by Texas ARP/ATP/TD&T grants, Texas Excellence Fund, an award from Research Corporation, and SHSU Faculty Research Council. The work at University of Texas at Austin was supported by The Welch Foundation under Grant No. F1191.

References