La substitution effect on the magnetic phase transition of SmTi$_2$Al$_{20}$

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Abstract. Powder X-ray and specific heat measurements were performed on (Sm$_x$La$_{1-x}$)Ti$_2$Al$_{20}$ ($x = 0.2–1$) single crystals grown by the Al self-flux method. All samples crystallize in the CeCr$_2$Al$_{20}$-type structure with $Fd\bar{3}m$ symmetry and the lattice parameter changes almost linearly with respect to the Sm concentration. From a $\lambda$-type peak appearing in the specific heat, it was found that the antiferromagnetic phase transition occurring at 6.5 K for $x = 1$ remains in the large Sm-concentration range. The transition temperature decreases almost linearly depending on the Sm concentration and goes to zero at the finite Sm concentration value of $\sim 0.1$, indicating the possible existence of a quantum critical point. The robustness of the phase boundary against the magnetic field remains even in the La-substituted system. This behavior is in marked contrast to the field-sensitive behavior observed in Ce-based heavy fermion compounds.

1. Introduction
Sm compounds with cage structure have attracted considerable attention as a result of their unique properties, which are attributed to strong $c$-$f$ hybridization and fluctuations of high-rank multipoles and the rare-earth ion valence. Among the cage-structured compounds containing Sm, Sm$_2$X$_{20}$ ($Tr =$ transition metal, $X =$ Zn, Al, Cd), which crystallize in the cubic CeCr$_2$Al$_{20}$-type structure with $Fd\bar{3}m$ ($#227$) have been investigated intensively. This is because unusual field ($H$)-insensitive phase transitions and heavy fermion (HF) behaviors in the ordered state have been discovered in Sm$_2$Al$_{20}$ ($Tr =$ Ti, V, Cr, and Ta$)$[1, 2, 3].

The resistivity of these compounds exhibits a $- \log T$ dependence below 50 K, indicating the occurrence of the Kondo effect, and exhibits $H$-insensitive phase transitions at $T_x =$ 6.5, 2.9, 1.8, and 2.0 K for Sm$_2$Ti$_2$Al$_{20}$ ($Tr =$ Ti, V, Cr, and Ta), respectively. Below $T_x$, these compounds show unusual $H$-insensitive HF behaviors with $\gamma$ values of 0.15, 0.72, 1.0, and 3.2 J/(K$^2$ mol-Sm) for Sm$_2$V$_2$Al$_{20}$ ($Tr =$ Ti, V, Cr, and Ta), respectively[1, 2, 3]. The magnetic susceptibilities of these compounds exhibit weak $T$ dependences, which are evidently different from those for both free Sm$^{2+}$ and Sm$^{3+}$ ions. In addition, the X-ray absorption spectra for all $Tr$ show that the Sm ions are in a mixed-valence state, with an average Sm-ion valence of $2.87 \pm 0.02$ and no significant $T$ dependence down to 3 K[5, 6]. These results suggest the possibility that valence fluctuation plays a role in the field-insensitive nature.

From the specific heat $C$ data, a crystalline-electric-field (CEF) $\Gamma_8$ quartet state of the $J =$
5/2 multiplet is expected to be the ground state of these compounds[1, 2, 3]. The ordered Sm dipole moments estimated from the upturn in the nuclear specific heat below $T_x$ are $m_{Sm} = 0.51$, 0.28, and 0.22 $\mu_B$/Sm for SmTi$_2$Al$_20$ ($T_r$ = Ti, Cr, and Ta), respectively, which are significantly suppressed from 0.65 $\mu_B$/Sm expected for a $\Gamma_8$ quartet state and 0.84 $\mu_B$/Sm expected for a free Sm$^{3+}$ ion[1, 2]. The suppressed ordered moment has also been estimated from a neutron magnetic structural analysis using a $^{154}$SmTi$_2$Al$_20$ single crystal[4]. As a $\Gamma_8$ quartet includes octupolar degrees of freedom, octupole contribution to the ordering has been suggested.

Although plural degrees of freedom (charge and higher-rank multipoles) are expected to contribute to the unconventional $H$-insensitive HF formation judging from various experimental results, the origin of this behavior has not yet been clarified. For further investigation, it is important to study the effect of nonmagnetic La ion substitution for the Sm ion on the physical properties of the resultant material and to compare these results with those reported for typical Ce-based HF compounds. In this work, we perform powder X-ray and C measurements using ($Sm_{x}La_{1-x}$)Ti$_2$Al$_20$ single crystals.

2. Experimental

![Figure 1.](image_url)

Figure 1. (a) X-ray powder diffraction pattern for crushed ($Sm_{0.2}La_{0.8}$)Ti$_2$Al$_20$ single crystals obtained using Cu-K$_{\alpha 1}$ radiation. The Miller indices of the cubic symmetry $Fd\bar{3}m$ for the main peaks are shown. (Inset) Normalized X-ray powder diffraction patterns of (8 8 0) peak for ($Sm_{x}La_{1-x}$)Ti$_2$Al$_20$ ($x$ = 0.2, 0.4, 0.6, 0.8, and 1). (b) Lattice parameter $a$ as function of nominal Sm concentration $x$ along with that of LaTi$_2$Al$_20$[7]. The solid line represents Vegard’s law.

($Sm_{x}La_{1-x}$)Ti$_2$Al$_20$ ($x$ = 0.2, 0.4, 0.6, 0.8, and 1) single crystals were grown by the Al self-flux method under vacuum. The starting component atomic ratio was 3N (99.9% pure) Sm:3N La:5N Ti:4N Al = $x$:1-$x$:2:90. X-ray powder-diffraction experiments were carried out using a Rigaku SmartLab powder diffractometer equipped with a Cu-Ko1 monochromator. A silicon standard was used for accurate determination of the lattice parameter $a$. It was confirmed that all of the ($Sm_{x}La_{1-x}$)Ti$_2$Al$_20$ samples crystallize in the CeCr$_2$Al$_20$-type structure with $Fd\bar{3}m$ symmetry (figure 1(a)). The inset of figure 1(a) shows the normalized X-ray powder diffraction pattern of the (8 8 0) peak for various nominal Sm concentration values $x$. The peak position shifts to smaller 2$\theta$ with decreasing $x$. The determined $a$ increases almost linearly with decreasing $x$, as
shown in figure 1(b). As the single crystals were grown by the Al self-flux method, it is possible that the actual Sm concentration of each grown single crystal differs from the nominal \(x\) value given in the starting atomic ratio. Therefore, on the basis of Vegard’s law, we determined the value of the corrected Sm concentration \(x^*\) for each crystal using:

\[
(a^*) = a(1) + (1 - x^*)a(0),
\]

where \(a(1)\) and \(a(0)\) represent the lattice parameters of \(\text{SmTi}_2\text{Al}_2\) and \(\text{LaTi}_2\text{Al}_2\), respectively.

We use \(x^*\) in the following discussion.

3. Results and discussion

Figure 2. (a) Temperature \(T\) dependence of specific heat \(C/T\) of \((\text{Sm}_{x^*}\text{La}_{1-x^*})\text{Ti}_2\text{Al}_2\) in zero field along with that of \(\text{LaTi}_2\text{Al}_2\). (b) Corrected Sm concentration \(x^*\) dependence of \(T_{\text{peak}}\) in \(C/T\). The broken line is a guide to the eye.

Figure 2(a) shows the \(T\) dependence of \(C/T\) of \((\text{Sm}_{x^*}\text{La}_{1-x^*})\text{Ti}_2\text{Al}_2\) in zero field down to 2 K. In the high-\(T\) region above 30 K, there is no significant difference in the \(C/T\) behavior for all Sm concentrations, which indicates that the phonon contribution to \(C\) is not significantly affected by the La substitution. For \(x^* = 1\), a clear \(\lambda\)-type peak appears at 6.5 K, indicating the existence of a second-order phase transition. Our recent neutron scattering experiment suggests that this is a magnetic ordering with a \(q = 0\) antiferro (AF)-type magnetic structure[4]. The peak temperature \(T_{\text{peak}}\) shifts to lower values with decreasing \(x^*\). For \(x^* = 0.18\), \(C/T\) exhibits an increase below 6 K, which is attributable to the Kondo effect and/or a short-range ordering associated with the phase transition possibly shifted to a temperature below 2 K. The Sm concentration dependence of \(T_{\text{peak}}\) is shown in figure 2(b). In this figure, \(T_{\text{peak}}\) varies almost linearly depending on \(x^*\) (as shown by the broken line in figure 2(b)) and goes to zero at \(x^* \sim 0.1\). This indicates that a quantum critical point induced by La substitution may exist at \(x^* \sim 0.1\).

As regards the crystal structure of \(\text{SmTrAl}_2\), the Sm ions form a diamond lattice, which has a site percolation threshold of \(x_c = 0.43[8, 9, 10]\). Therefore, if the magnetic interaction among the Sm ions were dominated by a nearest-neighbor bond type, \(T_{\text{peak}}\) would exhibit a significant decrease as \(x\) approached \(x_c\). Further, no ordering would appear for \(x < x_c\). The observed linear
dependence of $T_{\text{peak}}$ over the entire Sm concentration range and the clear $\lambda$-type (mean-field type) $C$ anomaly associated with the phase transition indicate that the magnetic interaction among the Sm ions is of long-range type, most likely in line with the strong $c$-$f$ hybridization.

Figure 3(a) shows $T$ dependence of $C/T$ for $x^* = 0.47$ under various magnetic fields up to 9 T near $T_{\text{peak}}$. This sample shows the robustness of $T_x$ against the field as observed for $x^* = 1$[1]. The shift of $T_{\text{peak}}$ between 0 and 9 T is smaller than 0.05 K. In figure 3(b), we summarize the $H$-$T$ phase diagram for $(\text{Sm}_{x^*}\text{La}_{1-x^*})\text{Ti}_2\text{Al}_{20}$. For all samples, $T_x$ exhibits almost no $H$ dependence up to 9 T.

The rare-earth element concentration dependence on strongly correlated electronic properties has been investigated for several Ce-based HF compounds, such as CeCu$_6$[11, 12], CeB$_6$[13, 14, 15, 16] and CeRu$_2$Si$_2$[17]. Among those compounds, systems with 100% Ce concentration exhibit the Kondo lattice (coherent) regime in their transport properties at low temperatures. As the Ce concentration decreases, this low-temperature regime continuously changes to the Kondo impurity (incoherent) regime. In the case of Sm compounds, we recently found that the resistivity exhibits a $-\log T$ even for $x = 0.01$ in $(\text{Sm}_{x}\text{La}_{1-x})\text{Ti}_2\text{Al}_{20}$. The coherence temperature, at which the resistivity exhibits a maximum, shifts to lower values with decreasing $x$ and is not apparent for $x = 0.01$[18]. This fact indicates that the system changes from the Kondo lattice to Kondo impurity regime in a similar manner to typical Ce-based HF compounds. However, strong robustness against $H$ is observed in all $x$ region, which is in marked contrast to the field-sensitive behavior in Ce-based HF compounds.

In Ce-based HF compounds, the ground state changes with decreasing Ce concentration. For example, the ground state of $(\text{Ce}_{x}\text{La}_{1-x})\text{B}_6$ with $x = 1$ is an antiferromagnetic (AFM) state coexisting with a quadrupolar ordering. With decreasing Ce concentration, the ground
state changes to an octupolar ordered phase at $x \sim 0.75$ and becomes a paramagnetic (PM) state at approximately $x = 0.6$ [13, 14, 15, 16]. The existence of these different ordered phases indicates competition among the magnetic-dipole, electric-quadrupole, and magnetic-octupole interactions in (Ce$_{2-x}$La$_{1-x}$)B$_6$. On the contrary, in (Sm$_{2-x}$La$_{1-x}$)Ti$_2$Al$_{20}$, $T_{\text{peak}}$ varies linearly depending on $x^*$. This feature suggests that a single type of Sm ion interaction, which leads to a $q = 0$ AFM ordering for $x^* = 1$, dominates the entire $x^*$ region.

In contrast to the $H$-dependent ground state in Ce-based HF compounds, the $H$-$T$ phase diagram of (Sm$_{2-x}$La$_{1-x}$)Ti$_2$Al$_{20}$ exhibits almost no $H$ dependence in the phase boundary between the PM phase and the ordered phase for a wide range of $x^*$ values ($0.47 < x^* < 1$), as shown in figure 3(b). This feature indicates that, in the La-substituted Sm 1-2-20 system, the nonmagnetic degrees of freedom possibly play an important role in the robustness of the ordered state against $H$, in contrast with the Ce-based HF compounds. In order to further investigate the detailed $x$ dependence of physical properties including the possibility of quantum criticality at $x^* \sim 0.1$ induced by the La substitution, we need to perform $C$ and resistivity experiments at lower temperatures.

4. Summary

We succeeded in growing (Sm$_{2-x}$La$_{1-x}$)Ti$_2$Al$_{20}$ ($x = 0.2, 0.4, 0.6, 0.8$, and 1) single crystals and performed powder X-ray and specific heat measurements. We confirmed that all of the (Sm$_{2-x}$La$_{1-x}$)Ti$_2$Al$_{20}$ samples crystallize in the CeCr$_2$Al$_{20}$-type structure and the lattice parameter $a$ increases almost linearly with decreasing $x$. Using the corrected value of the Sm concentration $x^*$ based on Vegard’s law, we found that the transition temperature changes almost linearly as a function of $x^*$ and goes to zero at $x^* \sim 0.1$, indicating the possible existence of a quantum critical point. Similar to Sm$T_2$Al$_{20}$, the robustness of the transition temperature against an applied magnetic field holds even in the La-substituted system. This behavior is in contrast to the field-sensitive behavior observed in Ce-based HF compounds.

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