Mixed valence states in \((\text{Sm}_{x}\text{La}_{1-x})\text{Tr}_2\text{Al}_{20}\) (\(\text{Tr} = \text{Ti}\) and Ta) studied using X-ray absorption spectroscopy

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Abstract. X-ray absorption spectra of \((\text{Sm}_{x}\text{La}_{1-x})\text{Tr}_2\text{Al}_{20}\) (\(\text{Tr} = \text{Ti}\) and Ta), which exhibit unusual magnetic-field-insensitive physical properties, have been measured at the Sm \(L_3\)-edge at selected temperatures between 2.5 and 300 K. The spectra show that the Sm ions are in a mixed valence state and that their average valence is approximately +2.85, with almost no significant temperature and \(x\) dependences. For \(\text{SmTi}_2\text{Al}_{20}\), the average valence of the Sm ions does not display any change associated with the magnetic ordering below 6.5 K.

1. Introduction

In recent years, compounds with the general chemical formula \(R\text{Tr}_2X_{20}\) (\(R = \text{rare earth}, \text{Tr} = \text{transition metal}, X = \text{Al, Zn, and Cd}\)) crystallizing in the cubic \(\text{CeCr}_2\text{Al}_{20}\)-type structure have attracted considerable interest, as various strongly correlated electronic properties caused by the strong \(c-f\) hybridization have been found. Remarkable phenomena found among the \(R\text{Tr}_2X_{20}\) family include heavy fermion (HF) behavior with a large Sommerfeld coefficient \(\gamma\) of \(\approx 8\) J/mol K\(^2\) in \(\text{YbCo}_2\text{Zn}_{20}\) and superconductivity in the quadrupolar ordered state in \(\text{PrTi}_2\text{Al}_{20}\) [1, 2].

In the case of \(R = \text{Sm}\), unusually field-insensitive phase transitions at \(T_x = 6.5, 2.9, 1.8, \) and 2.0 K for \(\text{SmTr}_2\text{Al}_{20}\) (\(\text{Tr} = \text{Ti}, \text{V}, \text{Cr}, \) and Ta, respectively) and field-insensitive HF behavior in the ordered states have been discovered [3, 4, 5]. The resistivity \(\rho\) of these compounds exhibits a \(- \log T\) dependence, which is unusually insensitive to the magnetic field [3, 4, 5, 6]. Recent electronic transport measurements on \(\text{SmTa}_2\text{Al}_{20}\) have revealed that the transverse magnetoresistance (MR) is always positive, with a \(H^2\) dependence in a wide temperature \(T\) region between 2 and 300 K. Therefore, the magnitude of the expected negative MR due to the suppression of Kondo scattering by the magnetic field is significantly smaller than that of the ordinary MR due to the cyclotron motion of the conduction electrons [6]. These electronic transport measurements have also revealed a strongly enhanced deviation from Kohler’s rule in MR, which indicates development of the wave-vector \(k\) dependence of the conduction electron scattering due to \(4f\) electrons with decreasing \(T\) [6]. In the ordered state below \(T_x\), these compounds exhibit unusually field-insensitive HF behaviors with large Sommerfeld coefficients of \(\gamma = 0.15, 0.72, 1.0, \) and 3.2 J/mol K\(^2\) for \(\text{SmTr}_2\text{Al}_{20}\) (\(\text{Tr} = \text{Ti}, \text{V}, \text{Cr}, \) and Ta, respectively).
For SmTi$_2$Al$_20$, the quasiparticle mass enhancement has also been confirmed via a de Haas-van Alphen experiment [7]. The field-insensitive Kondo behavior mentioned above differs considerably from that of typical Ce-based HF compounds such as CeCu$_6$ [8], suggesting the occurrence of the Kondo effect with an unconventional mechanism in the SmTr$_2$Al$_20$ family.

The crystalline electric field (CEF) ground state of these Sm compounds is expected to be a $\Gamma_8$ quartet of the $J = 5/2$ multiplet [3, 4, 5]. The magnitudes of the ordered moments estimated from the nuclear specific heat in zero magnetic field, $m_{Sm} = 0.51$ (Ti), 0.28 (Cr), and 0.22 $\mu_B$/Sm (Ta), are suppressed from the value of 0.65 $\mu_B$/Sm expected for a $\Gamma_8$ quartet state. This suppression can be ascribed to the c-f hybridization or the involvement of higher-rank multipolar degrees of freedom belonging to the $\Gamma_8$ state [3, 5]. The magnetic susceptibilities exhibit weak temperature dependences, which are evidently different from those for both free Sm$^{2+}$ and Sm$^{3+}$ ions [3, 4, 5]. X-ray absorption spectroscopy (XAS) at the Sm $L_3$-edge [8], suggesting the occurrence of the Kondo effect with an unconventional mechanism in the SmTr$_2$Al$_20$ family.

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In the case of another field-insensitive HF compound SmOs$_4$Sb$_{12}$, it is believed that the $T$-dependent behavior of the Sm-ion valence is key to understanding the field-insensitive HF state in SmOs$_3$Sb$_{12}$ [10]. Recent XAS experiments on (Sm$_x$La$_{1-x}$)Os$_4$Sb$_{12}$ with $x = 0.2–1$ indicate that the Sm-ion valence exhibits log $T$-dependent behavior [11]. The $T$-dependent variation of the Sm-ion valence is attributed to an unconventional Kondo effect associated with charge degrees of freedom [12]. In the present study, we investigate the $T$ and $x$ dependences of the Sm-ion valence in (Sm$_x$La$_{1-x}$)Tr$_2$Al$_{20}$ ($Tr = Ti$ and Ta) using XAS measurements.

### 2. Experimental

(Sm$_x$La$_{1-x}$)Ti$_2$Al$_{20}$ ($x = 0.01$, 0.05, 0.25, and 1) and (Sm$_x$La$_{1-x}$)Ti$_2$Al$_{20}$ ($x = 0.1$, 0.2, 0.4, 0.6, and 1) single crystals were grown by the Al self-flux method. For this purpose, mixtures with atomic ratios of Sm(3N):La(3N):Ta(3N5):Al(4N) = $x$:1-$x$:2:150 and Sm(3N):La(3N):Ti(5N):Al(4N) = $x$:1-$x$:2:90 (the purity is shown in parentheses) were used.

X-ray powder diffraction patterns collected using a Rigaku SmartLab powder diffractometer equipped with a Cu K$_{\alpha 1}$ monochromator indicated that all samples crystallized in the CeCr$_2$Al$_{20}$-type cubic structure with space group $Fd\bar{3}m$. XAS spectra at the Sm $L_3$-edge were measured for (Sm$_x$La$_{1-x}$)Tr$_2$Al$_{20}$ ($Tr = Ti$ and Ta) at BL01B1 of SPring-8 in Japan. This beam line features a double-crystal monochromator equipped with a Si 111 crystal and a Si mirror for eliminating the higher harmonics [13]. The XAS spectra for (Sm$_x$La$_{1-x}$)Ti$_2$Al$_{20}$ ($x = 0.1$, 0.2, 0.4, 0.6, and 1) and (Sm$_x$La$_{1-x}$)Ta$_2$Al$_{20}$ ($x = 0.25$ and 1) were recorded in the transmission mode using ionization chambers at various $T$ between 3 and 300 K. For the Sm-dilute compounds (Sm$_x$La$_{1-x}$)Ta$_2$Al$_{20}$ ($x = 0.01$, 0.05, and 0.25), the fluorescence mode was employed using a 19-element Ge solid-state detector. The energy resolution was approximately 1 eV around the Sm $L_3$-edge. The incident photon energy was calibrated using the Sm $L_3$-edge XAS spectrum of Sm$_2$O$_3$ at 300 K.

### 3. Results and discussion

The normalized XAS spectra for SmTi$_2$Al$_{20}$ and SmTa$_2$Al$_{20}$ are shown in figures 1(a) and (b), respectively. The spectra consist of two components; the lower and higher energy peaks at the photon energies $E = 6716$ and 6722 eV correspond to the divalent and trivalent components, respectively. The XAS spectra in the X-ray energy range of 6700–6730 eV was fit according to
as expressed by equation (1). The average valence of the Sm ions was determined from fitting curve reproduces the experimental data well, confirming the validity of the present model. The oscillatory structure appearing above 6730 eV, which is caused by the extended X-ray absorption fine structure (EXAFS) and which reflects the local crystal structure around the Sm ions. The fitting curve reproduces the experimental data well, confirming the validity of the present model as expressed by equation (1). The average valence of the Sm ions was determined from

\[ f(E) = \sum_{i=2}^{3} \left[ \sum_{j=0}^{1} \left\{ \frac{A_j^i (\Gamma_i/2)}{(E - E_i - j \cdot \Delta)^2 + (\Gamma_i/2)^2} \right\} + \frac{(A_0^i + A_1^i) \Gamma_i}{(A_0^i + A_2^i) \Gamma_2 + (A_0^i + A_1^i) \Gamma_3} \left\{ \frac{1}{2} + \frac{1}{\pi} \arctan \frac{E - (E_i + \delta)}{\Gamma'_i/2} \right\} \right], \]

where \( A_j^i \), \( \Delta \), \( \Gamma_i \), \( \Gamma'_i \), and \( \delta \) are fitting parameters and the subscript \( i = 2 \) and 3 denotes the divalent and trivalent states, respectively. In the \( \text{Sm}^{3+} \) family, the peak structure attributed to the \( \text{Sm}^{3+} \) states exhibits a noticeably asymmetric shape compared with that of \( \text{Sm}_2\text{O}_3 \), indicating that the 5d empty states of Sm are split into two states by the CEF effect [9]. We introduced the superscript \( j = 0 \) and 1 to equation (1), representing a lower and higher state of the split 5d empty state, respectively. The energy gap \( \Delta \) and the intensity ratio \( A_0^i/A_1^i \) were assumed to be identical for \( \text{Sm}^{2+} \) and \( \text{Sm}^{3+} \). In the present analysis, we do not consider the oscillatory structure appearing above 6730 eV, which is caused by the extended X-ray absorption fine structure (EXAFS) and which reflects the local crystal structure around the Sm ions. The fitting curve reproduces the experimental data well, confirming the validity of the present model as expressed by equation (1). The average valence of the Sm ions was determined from

Figure 1. (a) Normalized X-ray Absorption Spectroscopy (XAS) spectra at Sm \( L_3 \)-edge of \( \text{Sm}_2\text{Al}_{20} \) measured at \( T = 2.5 \) K. (b) Normalized XAS spectra at Sm \( L_3 \)-edge of \( \text{Sm}_2\text{Al}_{20} \) measured at \( T = 3 \) K. The closed circles represent the measured spectra, and the broken, dotted, and solid lines indicate the \( \text{Sm}^{3+} \), \( \text{Sm}^{2+} \), and total components fitted to the experimental data, respectively. (c) \( T \)-dependence of the average Sm ion valence in \( \text{Sm}_2\text{Al}_{20} \) and \( \text{Sm}_2\text{Ta}_{20} \). The solid line is a guide for the eye. (d) \( T \)-dependence of resistivity for \( \text{Sm}_2\text{Al}_{20} \) and \( \text{Sm}_2\text{Al}_{20} \) (data taken from Ref. [3, 6]).
Figure 2. (a) Normalized XAS spectra at Sm L3-edge of (Sm_{x}La_{1-x})Ta_{2}Al_{20} recorded in transmission (open symbols) and fluorescence (solid symbols) modes, measured at $T = 3$ K. The small anomalies in the spectra appearing in the energy ranges of 6720.6–6722.6 eV and 6731.5–6733.5 eV for $x = 0.01$ are removed from the fitting. (b) $x$ dependence of the average valence measured in the fluorescence (transmission) mode, represented by solid (open) symbols. The solid line is a guide for the eye.

$$v = 2 + \frac{(A_0^0 + A_1^0)\Gamma_3}{(A_0^0 + A_1^0)\Gamma_2 + (A_3^0 + A_3^1)\Gamma_3},$$

using the relative intensities of the Sm$^{2+}$ and Sm$^{3+}$ components. The present result clearly demonstrates that the Sm ions are in a mixed valence state with an average valence of approximately $+2.85$ for both SmTi$_2$Al$_{20}$ and SmTa$_2$Al$_{20}$. This value is in agreement with the previous report [9]. The $T$ dependence of the average valence was investigated for both SmTi$_2$Al$_{20}$ and SmTa$_2$Al$_{20}$. As shown in figure 1(c), the Sm-ion valence in SmTr$_2$Al$_{20}$ ($Tr = Ti$ and $Ta$) displays no significant $T$ dependence between 3 and 300 K. Although $\rho$ exhibits a clear $-\log T$ dependence between 7 and 50 K (between 3 and 40 K) for $Tr = Ti$ ($Ta$) as shown in figure 1(d), no associated valence change is observed. In SmTi$_2$Al$_{20}$, no noticeable change appears in the Sm-ion valence below $T_x = 6.5$ K [3].

In order to investigate the $x$ dependence of the Sm-ion valence in the (Sm$_x$La$_{1-x}$)Tr$_2$Al$_{20}$ family, the XAS spectra at the Sm L3-edge were measured. The normalized spectra for (Sm$_x$La$_{1-x}$)Ta$_2$Al$_{20}$ ($x = 0.01$, 0.05, 0.25, and 1) measured at 3 K are shown in figure 2(a). As can be seen in figure 2(b), the average Sm-ion valence determined from these XAS spectra exhibits almost no $x$ dependence within the experimental uncertainty. In principle, the Sm-ion valence can shift in response to La substitution because of the following factors: 1) Considering the fact that the radius of a Sm$^{2+}$ ion is larger than that of a Sm$^{3+}$ ion, Sm$^{2+}$ ions become more stable via La substitution, because of the negative chemical pressure caused by the lattice expansion (the lattice parameters of SmTa$_2$Al$_{20}$ and LaTa$_2$Al$_{20}$ are 14.750 and 14.811 Å, respectively); 2) As La$^{3+}$ substitution increases the conduction electron density (i.e., the Fermi energy), if the phenomenon of the mixed Sm-ion valence is coupled with the conduction electrons in some ways, the Sm-ion valence may shift. For another field-insensitive HF compound (Sm$_x$La$_{1-x}$)Os$_4$Sb$_{12}$, a decrease in the Sm-ion valence by approximately 0.05 from $x = 1$ to $x = 0.2$ has been observed [11]. The present result indicates that these effects are below the detectable levels in the SmTr$_2$Al$_{20}$ family, even if they exist.

The $T$ dependence of the Sm-ion valence in (Sm$_x$La$_{1-x}$)Tr$_2$Al$_{20}$ ($Tr = Ti$ and $Ta$) was
The valences of the Sm ions in all of the compounds investigated in this study exhibit almost no dependence. In contrast, it has been reported that the Sm-ion valence displays a clear decrease in SmOs₄Sb₁₂ between 2.5 and 300 K, where no T-dependent change is observed. As summarized in Figure 3(f), the valences of the Sm ions in all of the compounds investigated in this study exhibit almost no T dependence. In contrast, it has been reported that the Sm-ion valence displays a clear decrease with decreasing T in SmOs₄Sb₁₂ [10] and the Kondo insulator SmB₆ [16]. In SmOs₄Sb₁₂, the Sm-ion valence shifts from ~2.83 at 300 K to ~2.76 at 10 K. This T dependence can be attributed to the unconventional Kondo effect associated with charge degrees of freedom with the associated Kondo temperature $T_K$ of 56 K [11, 12]. For SmB₆, the average valence shifts from ~2.6 at room temperature to 2.5 at 15 K, which is considered to be associated with the development of the Kondo insulating gap with decreasing T [14, 15, 16, 17]. At present, in the (SmₓLa₁₋ₓ)Tr₂Al₂₀ family (Tr = Ti and Ta), the physics of the mixed valence states of the Sm ions was also investigated. Figures 3(a)–(e) show the XAS spectra measured at selected $T$ between 2.5 and 300 K, where no $T$-dependent change is observed.
ions is unclear. Considering the fact that the XAS measurement timescale is $10^{-12} – 10^{-15}$ s, systematic studies of Sm-ion valence in Sm mixed-valence compounds are required, combined with complementary techniques for detecting slower dynamics, i.e., Mössbauer ($~10^{-8}$ s) and nuclear quadrupole resonance ($~10^{-7} – 10^{-6}$ s) experiments.

4. Summary
We have revealed that the Sm ions in the $(Sm_xLa_{1-x})Tr_2Al_{20}$ family ($Tr = Ti$ and Ta) are in a mixed valence state, using X-ray absorption spectroscopy measurements at the Sm $L_3$-edge. The average Sm-ion valence is approximately +2.85 and is almost independent of $x$ and temperature. Although the electrical resistivity exhibits a clear $-\log T$ dependence between 7 and 50 K (between 3 and 40 K) for $Tr = Ti$ (Ta), no corresponding valence change is observed. For SmTi$_2$Al$_{20}$, the average valence in the ordered state below $T_x = 6.5$ K is almost identical to that in the paramagnetic state.

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