Ce-$L_3$-XAS study of the temperature dependence of the $4f$ occupancy in the Kondo system Ce$_2$Rh$_3$Al$_9$

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Abstract

We have used temperature dependent x-ray absorption at the Ce-$L_3$ edge to investigate the recently discovered Kondo compound Ce$_2$Rh$_3$Al$_9$. The systematic changes of the spectral lineshape with decreasing temperature are analyzed and found to be related to a change in the $4f$ occupation number, $n_f$, as the system undergoes a transition into a Kondo state. The temperature dependence of $n_f$ indicates a characteristic temperature of 150 K, which is clearly related with the high temperature anomaly observed in the magnetic susceptibility of the same system. The further anomaly observed in the resistivity of this system at low temperature (ca. 20 K) has no effect on $n_f$ and is thus not of Kondo origin.

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The most successful description of Kondo systems is that of the Anderson impurity model (AIM). In this model the energy of the 4f levels and their hybridization with the conduction band states are taken into account to explain the low temperature behavior of the resistivity and the magnetic susceptibility. The coupling between 4f levels and band states leads to the formation of a non-magnetic, singlet ground state on a temperature scale characterized by \( T_K \), the Kondo temperature. The theory also provides two predictions: firstly the formation of the singlet state leads to the occurrence of the Abrikosov-Suhl peak at \( E_F \) in the density of states (the Kondo resonance). Secondly, the 4f occupation, \( n_f \), should show a characteristic temperature dependence as a function of \( T/T_K \).

RE-L\textsubscript{3} x-ray absorption (XAS) is very sensitive to the distribution of the valence electrons and has therefore often been used to study the change of \( n_f \) with temperature. The advantages of this technique are: 1) the clear signature of the 4f\textsuperscript{0} configuration on the high-energy side of the main line; 2) the negligible role played by multiplet effects; 3) the absence of surface related effects.

Recently we have applied this technique to the classical Kondo system CeSi\textsubscript{2}, and found that the extracted \( n_f \) shows a characteristic temperature dependence as expected by the AIM, whereby the strong change in \( n_f \) is centered at a value of \( T_K \) which is fully compatible with the Kondo temperature as determined by thermodynamic measurements.

In this work we report Ce-L\textsubscript{3} XAS results from the new Kondo system Ce\textsubscript{2}Rh\textsubscript{3}Al\textsubscript{9}, which crystallizes in a complicated orthorhombic (Cmcm) \( Y_2\text{Co}_3\text{Ga}_9 \)-structure, with only one Ce site. Neutron diffraction experiments of Ce\textsubscript{2}Rh\textsubscript{3}Al\textsubscript{9} show no magnetic ordering down to 1.8 K. The susceptibility data present a maximum at 150 K, while the transport data show the occurrence of two clear anomalies at 20 K and 150 K. Although a satisfactory explanation of the behavior of the 4f Ce states in this compound is still to be found, this unconventional situation might invoke the necessity of a description in terms of two different energy scales for the same 4f electrons. An alternative explanation in analogy with heavy fermion systems which have Kondo temperatures of about 20 K and crystal field excitations at around 150 K seems unlikely on the basis of magnetic susceptibility considerations.
Powder samples were synthesized by repeated argon arc melting of the constituent elements, followed by annealing in vacuum at high $T$ for 120 h. X-ray powder diffraction measurements taken immediately after melting showed that the samples were phase pure. The Ce-$L_3$ XAS experiments were performed at the A1 beamline in HASYLAB in the transmission geometry with the help of three ionization chambers in series for the sample and a reference. The overall resolution at the Ce-$L_3$ edge (5720 eV) was estimated to be about 1.5 eV. The measurements were recorded within a few days of the sample preparation, and concurrently we detected no appreciable change due to sample oxidation. We also prepared homogeneous absorbers of polycrystalline CeF$_3$ and CeO$_2$ as trivalent and tetravalent Ce reference compounds, respectively.

Fig. 1 shows the Ce-$L_3$ spectrum of Ce$_2$Rh$_3$Al$_9$ together with those of CeF$_3$, CeO$_2$ and CeSi$_2$, measured at room temperature. The spectrum of Ce$_2$Rh$_3$Al$_9$ shows clearly the characteristic signature of the $4f^0$ final state in the form of the shoulder seen at 5735 eV, which is well known from previous studies of mixed valent Ce compounds. The main line is due to the $4f^1$ final state, mixed with $4f^2$. Since the $4f$ states are characterized by a strong on-site $4f$ electron-electron repulsion $U_{ff}$ (about 10 eV), the contribution of $4f^2$ is small and the contribution from higher $4f$ occupancies is negligible. Ce$_2$Rh$_3$Al$_9$ shows a more pronounced high-energy shoulder than CeSi$_2$, indicating that the $4f^0$ configuration plays a more important role in the room temperature ground state of the former.

Fig. 2 shows the Ce-$L_3$ XAS spectra of Ce$_2$Rh$_3$Al$_9$ taken at temperatures between 6 and 240 K. From Fig. 2 one can clearly see a change of the relative intensity ratio of the shoulder structure compared to the main peak at 5726 eV as the temperature is altered. As mentioned above, although the main peak and shoulder are dominated by the $4f^1$ and $4f^0$ final state configurations, respectively, there is also a non-zero $4f^2$ admixture. Therefore the spectral weight of the high-energy shoulder alone does not represent an accurate measure of $n_f$ in the initial state. In order to take this into account, we analyse the data using a simplified version of the Anderson single-impurity Hamiltonian. In this analysis, each final state itself is represented by a Lorentzian function with an arctan-like step function.
describing the edge jump (for details see Refs. 4,6). To reduce the number of free parameters to a minimum, the energy separation between the Lorentzian and the arctan step function, as well as the ratio of the Lorentzian intensity to the arctan step height were kept equal for all final state components. Finally, the theory data were broadened using a Gaussian function of width 1.5 eV to account for the finite experimental energy resolution.

In Fig. 3 we plot the temperature dependence of the 4f occupation number, $n_f$, deduced using this procedure. We obtain a zero temperature extrapolation $n_f(T=0)$ of 0.806, which is smaller than the 0.9 obtained for CeSi$_2$, which is in keeping with the qualitative comparison the spectral profiles as discussed above. As the temperature increases, one can clearly see an increase in $n_f$. In the XAS spectra of Fig. 2, this is evident as a reduction of the 4f$^0$-related shoulder for $T > T_K$. This increase in $n_f$ is centered at $\sim 150$ K, which is consistent with the anomaly observed in the susceptibility data. This result indicates that the anomaly at 150 K is not due to a crystal field effect, but rather is related to a change in the 4f occupancy. The onset of this change in $n_f$ is at about 70 K, and no variation in $n_f$ could be detected for $T \ll 60$ K. Thus, the low temperature anomaly observed in this system in transport measurements is not connected to a change in the 4f occupancy. This implies that of the two energy scales shown by the system in transport and susceptibility measurements, only one (the higher energy one) is related to Kondo behavior.

In summary, we have used bulk sensitive Ce-$L_3$ XAS to measure a powdered single crystal of Ce$_2$Rh$_3$Al$_9$ and we have shown that the Ce 4f occupancy, $n_f$, shows a temperature dependent behavior which is in good agreement with expectations from the single Anderson impurity model with a Kondo temperature $T_K \sim 150$ K. This is the same temperature at which anomalies are seen in both susceptibility and transport measurements, thus putting beyond doubt the Kondo origin of these anomalies. However, no change in $n_f$ is found at temperatures near to the low temperature anomaly observed in transport data, which calls for further experimental and theoretical work aimed at understanding this intriguing observation.

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FIGURES

FIG. 1. Ce-$L_3$ x-ray absorption spectra of Ce$_2$Rh$_3$Al$_9$ recorded room temperature together
with those of CeSi$_2$ (from Ref. [8]) and the Ce(III) and Ce(IV) standards CeF$_3$ and CeO$_2$.

FIG. 2. Ce-$L_3$ x-ray absorption spectra of Ce$_2$Rh$_3$Al$_9$ at various temperatures. A fit of the
main line (labelled $|f^1\rangle$) and the edge-jump is also shown as a solid line. Comparison between
the data and the fit clearly shows the change in the intensity of the $2p ~ 4f^05d^r$-related final state
feature.

FIG. 3. Ce 4$f$ occupancy, $n_f$, extracted from the Ce-$L_3$ x-ray absorption data of Fig. 2 versus
$T$. The dotted vertical line indicates the center of the strong temperature dependence of $n_f$ at ca.
150K.
Grazioli et al. Fig. 1

Normalised absorption (arb. units)

CeF$_3$

Ce$_2$Rh$_3$Al$_9$

CeSi$_2$

CeO$_2$

Photon energy (eV)
Grazioli et al. Fig. 2

Normalised absorption (arb. units)

Photon energy (eV)

T(K)

240K

170K

60K

30K

11K

6K

$|f^1\rangle$

$|f^0\rangle$
$4f$ occupancy $n_f$ vs. Temperature (K)

Grazioli et al. Fig. 3