Final-State Effects in the Eu L_{III}-Edge Spectrum of $\mathrm{EuPd_2P_2}$

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The Eu L_{III}-edge x-ray-absorption spectrum of $\mathrm{EuPd_2P_2}$ exhibits a double-peaked white-line structure typical for mixed-valent materials, while Mössbauer isomer-shift and other magnetic measurements prove the divalent ground state of this compound. This discrepancy clearly shows the possible presence of final-state configuration-interaction effects in the L_{III}-edge spectra of heavy-rare-earth systems, as well as a significant $4f$ covalent bonding, contrary to previous assumptions.

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One of the major issues in the field of valence fluctuation phenomena in rare-earth (RE) compounds is the precise determination of the mean valence, $\bar{v}$, of the RE ion. In this respect, L_{III}-edge x-ray-absorption (XA) spectroscopy—due to its universal applicability—is widely used.[1,2] The L_{III}-edge spectra of RE systems are characterized by intense "white line" at the edges, caused by $E1$ excitation of a $2p$-core electron into an empty $5d$ state at the Fermi level (E_{F}).[3] In mixed-valent systems, two white-line peaks, separated by 7–8 eV, are commonly observed, which are due to final states with different $4f$ occupation numbers.[4] A major assumption in deriving mean valences from such double-peaked L_{III}-edge profiles is the absence of final-state configuration-interaction effects in systems of the heavy RE's, despite the creation of a $2p$-core hole. Though this aspect has been discussed in connection with Ce and its compounds,[5,10] there is no consensus on this assumption.

In this paper, we report the first observation of such final-state effects in the L_{III}-edge spectrum of a heavy RE system, namely divalent $\mathrm{EuPd_2P_2}$ (with $\mathrm{ThCr_2Si_2}$ structure). While low-energy probes (Mössbauer isomer-shift, magnetic susceptibility, electron-spin resonance) as well as valence-band photoemission spectra clearly prove the divalent-$4f^7$ ground state of the Eu ion, the high-energy L_{III}-edge probe results in a hitherto unexpected double-peaked L_{III}-edge profile, with both $4f^7$ and $4f^6$ signatures in the final state. A comparative study of trivalent $\mathrm{GdPd_2P_2}$, on the other hand, leads to the expected single-peaked L_{III}-edge XA spectrum. It is suggested that the L_{III}-edge anomaly of $\mathrm{EuPd_2P_2}$ is the consequence of a considerable $4f$ participation in covalent bonding in this compound. The present results bear a strong significance for L_{III}-edge studies of mixed-valent RE compounds.

The studied samples were synthesized as described in the literature.[11] To avoid oxidation, the material was finely ground in a purified argon atmosphere and sandwiched in the form of a homogeneous absorber layer between Be sheets in a vacuum-tight, In-sealed metal capsule. The L_{III}-edge XA measurements were performed at the EXAFS-II beam line of HASYLAB/DESY, Hamburg, with a resolution of $\cong 2$ eV full width at half maximum at 7 keV, as well as with a laboratory XA spectrometer.[12] To check for $\mathrm{Eu^{3+}}$ contamination, ^{151}Eu-Mössbauer measurements were done after the L_{III}-edge studies on the same absorbers at various temperatures, with a $^{151}\mathrm{SmF_3}$ single-line source. An opposed-anvil device (sintered $\mathrm{B_4C}$ anvils) was employed for high-pressure Mössbauer studies at room-temperature (40 kbar) and at liquid-He temperature (80 kbar).[13]

Typical L_{III}-edge XA spectra obtained for $\mathrm{EuPd_2P_2}$ and $\mathrm{GdPd_2P_2}$ are displayed in Fig. 1. A single "white-line" peak, due to the optical excitation of a $2p$-core electron into an empty $5d$ state with a high density of states at E_{F}, is observed for trivalent $\mathrm{GdPd_2P_2}$.[3] In the

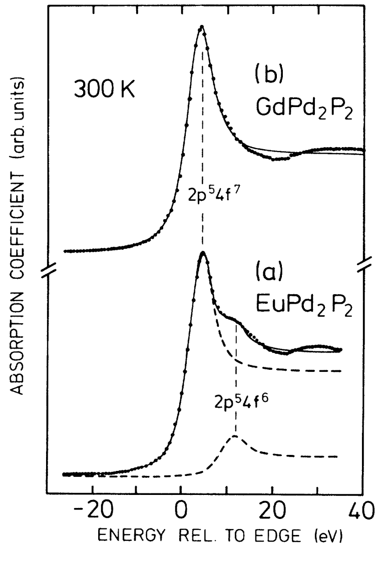

FIG. 1. RE L_{III}-edge XA spectra of $\mathrm{EuPd_2P_2}$ and $\mathrm{GdPd_2P_2}$, with the solid lines representing least-squares fit results. The subspectra due to the two different final states in the case of $\mathrm{EuPd_2P_2}$ are indicated by dashed lines. Zero on the energy scale represents the L_{III}-edge positions (6958.5 eV for $\mathrm{EuPd_2P_2}$ and 7227.4 eV for $\mathrm{GdPd_2P_2}$).

case of $EuPd_2P_2$, a system undoubtedly divalent in the ground state (see below),[14] however, a double-peaked L_{III}-edge structure, typical for mixed-valent RE systems, is clearly observed.[5] We have carefully investigated three different batches of $EuPd_2P_2$ samples, as well as absorbers with largely different thickness, with practically identical results. In addition, each absorber was checked by ^{151}Eu-Mössbauer measurements, performed *after* the L_{III}-edge studies, for Eu^{3+} contamination; in no case was the Eu^{3+} fraction found to exceed 1% (see below).

We have least-squares fitted the sum of a Lorentzian line and an arctanlike edge feature, convoluted by a Gaussian spectrometer function, to the experimental spectrum of $GdPd_2P_2$. In the case of $EuPd_2P_2$, a superposition of two such subspectra, shifted by 7.7 eV against each other (dashed lines in Fig. 1), describes the data well. The low-energy peak, as well as the single peak in $GdPd_2P_2$, is assigned to a $2p^54f^7$ final-core state, while the peak at higher excitation energy is assumed to be due to a $2p^54f^6$ final-core state. Its fractional intensity is found to be $(15 \pm 5)\%$. Even though the exact lineshapes of L_{III}-edge spectra are not well known, the fractional intensity of the high-energy peak in $EuPd_2P_2$ is rather independent of different spectral shapes used in the analysis (e.g., Fano line shape), and possible systematic errors are included in the quoted error bar. The given assignment of the high-energy peak as due to a $2p^54f^6$ final-core state is strongly supported by the observed energy separation, typical for Eu systems representing[15] the difference in Coulomb energies of the $2p$-core hole in the two final states.[4] An anomalous near-edge structure can also be excluded as the possible origin of this peak, since such a structure seems to be totally absent in isostructural trivalent $GdPd_2P_2$ [see Fig. 1(b)].

We will now briefly describe our careful ^{151}Eu-Mössbauer spectroscopic work to characterize the divalent ground state of $EuPd_2P_2$, and check each L_{III}-edge absorber for possible Eu^{3+} contamination. The 21.6-keV Mössbauer resonance of ^{151}Eu is uniquely suitable for such an undertaking, since the isomer shift S is known to be a very sensitive measure of the Eu valence.[16] Typical results of such Mössbauer experiments are shown in Fig. 2 for different absorber temperatures, along with a spectrum taken at 4.2 K and an external pressure of 80 kbar. A heterogeneous mixed-valent situation can be clearly excluded as the origin of the high-energy L_{III}-edge peak in $EuPd_2P_2$, since no trivalent-Eu signal, expected around zero Doppler velocity, is observed at all temperatures studied. An anomalously low Debye-Waller factor of such an Eu^{3+} phase can also be excluded on the basis of the low-temperature spectra. We conclude that a possible Eu^{3+} content in the studied absorbers is definitely below 1% in all cases.

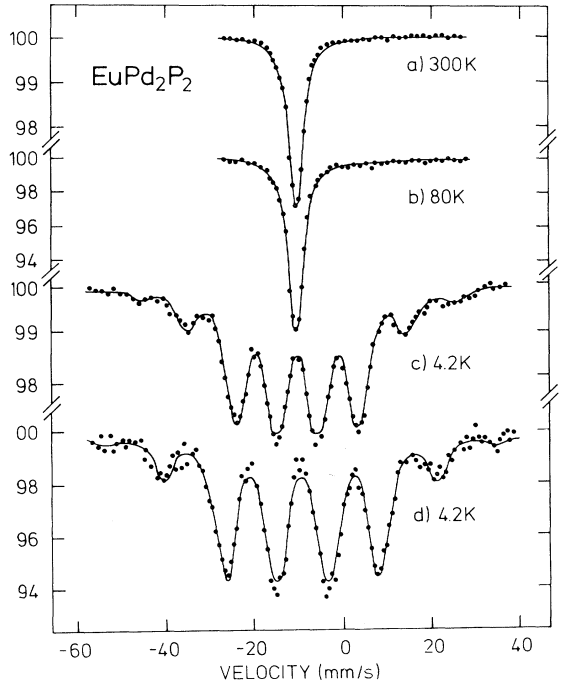

FIG. 2. (a)–(c) ^{151}Eu-Mössbauer spectra at various temperatures at ambient pressure, taken after the L_{III}-edge measurements on the identical absorber. (d) The spectrum at 4.2 K at a high pressure (80 kbar).

We can also rule out a dynamic or homogeneously mixed-valent state for the Eu ion in $EuPd_2P_2$ on the basis of the observed temperature and pressure dependence of S (see Fig. 2). The observed isomer shift, $S = -9.73 \pm 0.05$ mm/s (at 300 K; relative to the SmF_3 source), falls within the range known for divalent Eu compounds, and is only weakly temperature dependent due to thermal red shift.[16] In accordance with this observation, the pressure-induced variation of S is found to be weak, $dS/dP = +0.015$ (mm/s)/kbar, and in agreement with dS/dP values known for other divalent Eu compounds.[17] It should be recalled here that S is generally observed to vary appreciably with pressure and temperature in homogeneously mixed-valent Eu compounds.[13,18,19] Therefore, magnitude as well as temperature and pressure dependence of S prove the divalent ground state of the Eu ion in $EuPd_2P_2$. This is also borne out by the observed magnetic ordering of $EuPd_2P_2$ below $\cong 30$ K, leading to a magnetically split spectrum [see Fig. 2(c)], with a magnetic hyperfine field of $B_{hf} = 35.5 \pm 0.5$ T. Again, the observed pressure dependence, $d\ln B/dP = 1.10 \times 10^{-3}$ kbar^{-1}, is characteristic for divalent Eu compounds.[14]

Independent support for the above conclusion is given by the following experiments: (1) The effective magnetic moment derived from susceptibility measurements is $\mu_{\rm eff} = (8.0 \pm 0.1)\mu_{\rm B}$, which is in good agreement with the free-ion value for a $4f^7\,{}^8S_{7/2}$ ion.[14] (2) The electron spin resonance (ESR) signal from the Eu ions, with a g value of 2.00 ± 0.05, and a linewidth of 800 Oe at 77 K, typical for divalent Eu systems,[20] could be observed. In an intermediate valent (IV) compound, the fast relaxation between two valence states completely wipes out the ESR signal.[20] (3) We have performed[21] valence-band photoemission measurements on $\rm EuPd_2P_2$, using synchrotron radiation. We do not see any emission from the trivalent Eu ions in the region 5–10 eV below $E_{\rm F}$, even at the giant $4d \rightarrow 4f$ resonance. This observation is strictly against any kind of mixing between $4f^7$ and $4f^6$.

With $\rm EuPd_2P_2$ we are therefore faced with a situation that the $L_{\rm III}$-edges show mixed-valent features, while Mössbauer spectroscopy, magnetic susceptibility, ESR, and valence-band photoemission clearly prove the divalent ground state of the Eu ions. This finding represents the first conclusive evidence for possible discrepancies in valence determinations by $L_{\rm III}$-edge XA spectroscopy, even in compounds of the heavy RE's. We assign the observed discrepancy to core-hole induced final-state configuration-interaction effects. In the present case, this obviously leads to a 15% probability for a shakeup of a $4f$ electron to one of the ligand orbitals (Pd, P). In this connection, we point out that shakeup effects have also been reported in core-level x-ray photoemission spectra for (XPS) of a few integral-valent Eu compounds.[22] Very recently, the connection between such effects in core-level XPS and L-edge XA spectra has also been pointed out.[23]

The question one would like to answer is why such strong final-state effects are seen in the $L_{\rm III}$-edge spectra of $\rm EuPd_2P_2$, whereas in other compounds they seem to be small or absent.[15] The answer must lie in the degree of covalent mixing of the $4f$ electrons with ligand states, since the magnitude of final-state configuration-interaction effects is known to depend generally on this hybridization strength.[24] In this way, we come to the conclusion that the $4f$ electrons in $\rm EuPd_2P_2$ participate rather strongly in chemical bonding with the ligands, contrary to the present assumption for heavy RE systems. Our conclusion is supported by the unusual lattice-parameter anomaly reported previously for $\rm EuPd_2P_2$.[11,14] The crystal structure of $\rm EuPd_2P_2$ contains layers of identical atoms in the sequence Eu-P-Pd-P, stacked perpendicular to the **c** axis. The lattice parameter c of $\rm EuPd_2P_2$, when compared with those of the series of trivalent $\rm REPd_2P_2$ compounds, deviates considerably to a *smaller* value even though a constant or larger value would be expected from ionic-size arguments.[14] This c deviation of $\rm EuPd_2P_2$ is considerably larger than the observed c variation in the series of trivalent compounds from Ce to Tm. It indicates strong covalent bonding between Eu and the ligands in this compound, presumably involving the $4f$ electrons. In this connection, we would like to recall that the covalent bonding should not be confused with the mixed valence due to charge fluctuations ($4f^n \leftrightarrow 4f^{n-1}$), as pointed out by Wachter[25] for the case of $\rm CeO_2$.

Finally, we would like to point out that a related discrepancy between lattice properties and effective magnetic moments from susceptibility measurements has recently been reported for the semiconducting $\rm TmSe_{1-x}Te_x$ system.[26] It was interpreted as an indication of a strong hybridization which leads to a partial extension of $4f$ orbital radius, at the same time preserving the localized character of $4f$ electrons. These views could be applicable to the present case also.

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