

Driving the Europium Valence State in EuCo_2As_2 by External and Internal Impact

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Abstract The pressure effect on the europium valence state was investigated by means of X-ray absorption spectroscopy in the series of samples based on the EuCo_2As_2 compound. The pressure dependence of the europium valence was obtained in a wide range of applied and chemical pressures; the latter was reached by substituting Ca for Eu. The correlation between these two ways to impact the Eu valence was established. The data obtained allow estimating the pressure effect on the electronic structure of EuCo_2As_2 and other related properties such as the change in magnetic ordering.

Keywords Europium · Valence · XANES · High pressure · Pnictides · Magnetism

1 Introduction

RT_2X_2 pnictides (R = rare-earth or alkaline-earth metal, T = transition metal, X = pnictogen) crystallize in the tetragonal ThCr_2Si_2 -type structure famous for a variety of remarkable physical phenomena such as unconventional superconductivity, heavy fermion state, valence fluctuations, quantum criticality, multiple magnetic transitions, etc. [1–11]. The RT_2X_2 compounds are quite sensitive to the peculiarities of electronic band structure near the Fermi level, which can be altered in different ways including external stimuli (pressure, temperature) or chemical substitution. The study of charge instabilities in these materials is thence important and can shed more light on other interesting properties. For example, the famous EuFe_2As_2 ferropnictide compound shows an interesting spin and charge dynamics which in certain conditions results in coexistence of superconductivity and magnetism [5, 6].

Recently, we showed that the application of pressure can induce ferromagnetism in initially antiferromagnetic compound EuCo_2As_2 ($T_N = 47$ K) [7]. The redistribution of electronic density of states under compression probably causes the fulfillment of Stoner criterion for the cobalt states, which results in ferromagnetism. We also showed that the change of magnetic ordering correlates with the stabilization of mixed valence state of europium [7]. The similar interplay between valence and magnetism was previously observed in the isostructural EuCo_2P_2 -based phosphides [4]. In this work, we report the series of additional high pressure experiments, which we performed in order to obtain the comprehensive picture of europium valence behavior under different impact to better understand the magnetic states in EuCo_2As_2 -based systems.

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2 Experimental

The series of samples $\text{Ca}_{1-x}\text{Eu}_x\text{Co}_2\text{As}_2$ ($x = 0.1 - 1$) were prepared to induce the chemical compression in the Eu site due to the difference in the radii of calcium and europium ions. The synthesis procedure was similar to that described in [7].

The Eu valence was investigated by means of hard X-ray absorption near edge structure (XANES) spectroscopy at the Eu $L_{2,3}$ absorption edges. First successful experiment of XANES using for study of intermediate valence in rare earth elements was demonstrated by Bianconi for TmSe [12] and CePd_3 , $\gamma\text{-Ce}$, CeCu_2Si_2 [13] compounds. See [14] for recent review on the XANES experiments probing mixed valence state in oxides and high temperature superconductors.

Experiments at ambient pressure on $\text{Ca}_{1-x}\text{Eu}_x\text{Co}_2\text{As}_2$ ($x = 0.1 - 1$) series were carried out at the beamline mySpot of BESSY-II storage ring (HZB, Berlin, Germany) and the beamline i811 of MAX-lab (Lund, Sweden). The measurements were performed in transmission geometry using setup with continuous scan mode at Eu L_3 edge.

High-pressure XANES experiment was carried out at the ODE beamline of SOLEIL synchrotron (L'Orme des Merisiers, Saint-Aubin, France) [15]. The spectra of the sample $\text{Ca}_{0.5}\text{Eu}_{0.5}\text{Co}_2\text{As}_2$ ($x = 0.5$) under external pressure were measured using an energy dispersive scheme. The fine powder sample was subjected to pressures up to 40 GPa in a diamond anvil cell (DAC) with a rhenium gasket and alcohol as a pressure-transmitting medium. The pressure inside the DAC was controlled by the shift of a laser-excited ruby fluorescence line. The low temperature in the cell was maintained with a continuous helium flow cryostat. The XANES measurements were performed at the Eu L_2 absorption edge (7617 eV) with energy higher than L_3 edge (6977 eV), which allows a better acquisition of the spectrum due to the reduction of absorption in the diamond.

The maximum of the Eu L_2 edge is sensitive to the Eu valence in a way similar to that observed for the Eu L_3 line. The high pressure XANES data of the pure EuCo_2As_2 ($x = 1$) have been previously measured at the 4-ID-D beamline of APS (Argonne National Laboratory, US) and is addressed in detail in [7].

3 Discussion

The experimental XANES spectra show the double peak structure corresponding to the contributions from Eu^{2+} and Eu^{3+} states (Fig. 1a). The separation of the spectral components arising from different europium valence states was done in a conventional way by fitting the experimental spectra, corrected for a polynomial background, with a combination of Lorentzian (representing the absorption resonance) and arctangent (describing the transitions to the continuum) curves of constrained widths and energy positions. In this approach, the input of each Eu valence state is assumed to be proportional to the area under the corresponding Lorentzian curve or, equivalently, to its weight in the fitting formula.

The europium oxidation state in EuCo_2As_2 under ambient conditions is close to +2, which corresponds to the $4f^7$ ($J = 3/2$) magnetic state. In $\text{Ca}_{1-x}\text{Eu}_x\text{Co}_2\text{As}_2$ the Eu valence slightly increases with decreasing Eu concentration from +2.05 for $x = 1$ to +2.18 for $x = 0.1$ (Fig. 1b). This behavior is expected and can be explained in simple terms of the difference between Eu^{2+} and Eu^{3+} ionic radii—1.25 and 1.07 Å, respectively. Increasing the concentration of Ca^{2+} ions (radius 1.12 Å) induces the rise of chemical pressure thus favoring the Eu^{3+} electronic configuration and causing the increase in the average Eu valence. This increase can be considered in terms of $4f-3d$ hybridization [4, 7–11]. The pressure enhances the electronic transfer between localized f states of europium and

Fig. 1 **a** XANES spectra at L_3 Eu absorption edge for $\text{Ca}_{1-x}\text{Eu}_x\text{Co}_2\text{As}_2$ compounds with different Eu concentration (x) at ambient pressure. **b** the europium valence in $\text{Ca}_{1-x}\text{Eu}_x\text{Co}_2\text{As}_2$ series vs. x

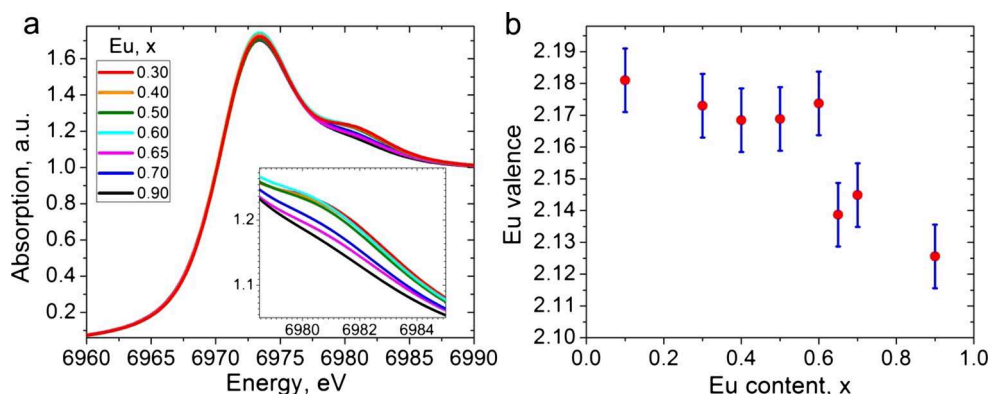
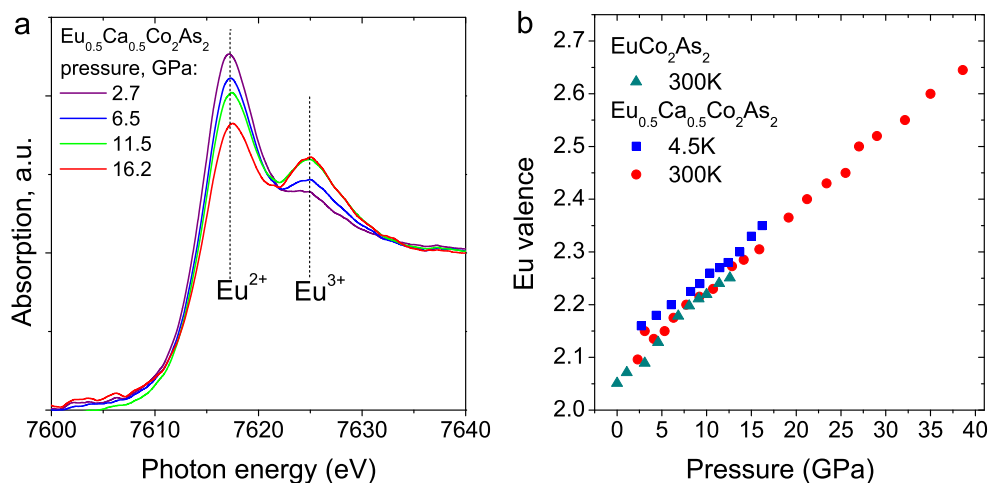


Fig. 2 **a** Eu L_2 XANES spectra of $\text{Ca}_{0.5}\text{Eu}_{0.5}\text{Co}_2\text{As}_2$ at 4.5 K and different pressures. **b** Eu valence in EuCo_2As_2 and $\text{Ca}_{0.5}\text{Eu}_{0.5}\text{Co}_2\text{As}_2$ vs. pressure and temperature



valence d states of cobalt and the subsequent rise of Eu valence.

External and chemical pressure have similar influence on the oxidation state of europium. The application of high hydrostatic pressure results in a significant change of XANES spectral shape and increase of the europium valence in the samples (Fig. 2). In $\text{Ca}_{0.5}\text{Eu}_{0.5}\text{Co}_2\text{As}_2$ the Eu valence increases almost linearly up to +2.65 in the pressure range from 2.3 to 38.6 GPa. It was also shown that with cooling from 300 to 4.5 K the valence slightly increases, probably, due to the lattice contraction.

The Eu valence dependences for compounds EuCo_2As_2 ($x = 1$) and $\text{Ca}_{0.5}\text{Eu}_{0.5}\text{Co}_2\text{As}_2$ ($x = 0.5$) are nearly linear and have similar slopes (Fig. 2b). This means that the chemical and external pressure use the same mechanism of the influence on the valence state in EuCo_2As_2 -based systems. The change of dopant concentration just shifts slightly the starting point of the linear dependence, but the general way of compound's sensitivity to the external impact apparently does not change.

Using the Eu valence data obtained, we made a quantitative comparison of the scales of chemical and external pressure impact. With the Ca content changing from 0.1 to 0.9, the increase of the Eu valence in $\text{Ca}_{1-x}\text{Eu}_x\text{Co}_2\text{As}_2$ series at ambient pressure approximately matches the valence increase in EuCo_2As_2 under the applied pressure changing from 4.5 to 7.0 GPa. Thus, the full range of Ca doping corresponds to the pressure range of only 2.5 GPa, which is obviously a relatively weak effect. Or, for instance, in the pure and the Ca-substituted ($x = 0.5$) compounds, the similar values of Eu valence, +2.25 and +2.27, are reached at quite close pressures of 12.6 and 12.8 GPa, respectively. From all these facts, we can conclude that the crystal structure of EuCo_2As_2 is rather soft. One probably needs to apply

a significant pressure to drive the europium valence in this compound to a sort of saturation (+3), while the effect of doping on the electronic structure is even much weaker.

We can also note that the maximum europium valence reached in our experiment in the sample with $x = 0.5$ at the pressure of 38.8 GPa is +2.65, while the isostructural and closely related compound EuCo_2P_2 undergoes the transition to an almost trivalent state at much smaller pressure [4, 7–11, 16]. This again confirms the softness of EuCo_2As_2 lattice, but also agrees with the more electronegative nature of the phosphorus atoms, which causes phosphides to favor higher oxidation states of Eu as compared to arsenides [17]. The larger As ion increases the lattice parameter c and the distance between different atomic layers in the structure in comparison with EuCo_2P_2 . It affects the Eu-Co interaction (both electronic and magnetic) and reduces the pressure sensitivity of material.

4 Conclusion

The external and chemical pressure dependences of europium oxidation state in pnictides $\text{Ca}_{1-x}\text{Eu}_x\text{Co}_2\text{As}_2$ were obtained from the XANES study. It was shown that europium valence increases with pressure and Ca concentration. Such behavior agrees well with the concept of $f-d$ hybridization as a main mechanism defining the electronic structure and in particular the valence states in rare-earth transition metal intermetallics. Under applied pressure the Eu valence changes almost linearly and does not reach saturation in the pressure range tested. In comparison with the external pressure, the chemical pressure exerts a rather weak on the Eu valence. This implies the softness of the EuCo_2As_2 crystal lattice. The demonstrated modification of

electronic structure will also influence the magnetic properties of these compounds. A more detailed investigation of $\text{Ca}_{1-x}\text{Eu}_x\text{Co}_2\text{As}_2$ series, including magnetic studies, is currently in progress and will be published in the near future.

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