Resonant inelastic X-ray scattering investigation of Ce and Eu valence state in RCo$_2$P$_2$

A.A. Yaroslavtsev, A.P. Menushenkov, R.V. Chernikov$^1$, W. Caliebe$^1$, I.A. Zaluzhnyy, K. Kovnir$^2$, M. Shtrak$^2$

NRNU “Moscow Engineering Physics Institute”, Kashirskoe sh. 31, 115409 Moscow, Russia

$^1$ HASYLAB at DESY, Notkestrasse 85, D-22603 Hamburg, Germany

$^2$ Department of Chemistry & Biochemistry, Florida State University, Tallahassee, FL 32306, USA

Magnetic ordering in RCo$_2$P$_2$ (R = La, Ce, Pr, Nd, Eu) itinerant magnets is dictated by peculiarities of electronic band structure at the Fermi level and can be affected by external perturbation, e.g. pressure [1]. The similar modification of electronic structure can be induced by chemical compression via nonisoelectronic substitution in the rare-earth sublattice [2]. Compound EuCo$_2$P$_2$ is antiferromagnetic with magnetic Eu sublattice at ambient pressure, but at pressure > 3.1 GPa it becomes antiferromagnetic with magnetic Co sublattice [1]. PrCo$_2$P$_2$ is also antiferromagnetic with magnetic Co sublattice, but upon Eu-substitution the resulting compound Pr$_{0.8}$Eu$_{0.2}$Co$_2$P$_2$ becomes ferromagnetic with magnetic Co sublattice. In LaCo$_2$P$_2$ (magnetic Co sublattice) the Ce-substituted phases studied herein behave quite differently from the Pr- and Nd-substituted ones [3]. The reason for such unusual changes of magnetic ordering type in RCo$_2$P$_2$ phosphides might be the intermediate valence states of Ce and Eu. In this work the features of Ce and Eu valence state were explored by means of RIXS and XANES spectroscopy in two series of RCo$_2$P$_2$ phosphides: (Pr,Nd)$_{1-x}$Eu$_x$Co$_2$P$_2$ and La$_{1-x}$Ce$_x$Co$_2$P$_2$.

(Pr,Nd)$_{1-x}$Eu$_x$Co$_2$P$_2$ (x = 0.2, 0.4, 1.0) and La$_{1-x}$Ce$_x$Co$_2$P$_2$ (x = 0.6) samples were prepared by standard procedures reported in [2, 3]. Resonant inelastic X-ray scattering spectra were collected at W1 beamline of DORIS-III storage ring (HASYLAB/DESY, Hamburg, Germany) above the L$_3$-Eu and L$_3$-Ce absorption edges at room temperature. The high-resolution X-ray spectrometer equipped with spherically bent Si(531) and Si(440) analyzer crystals was used to register the emission spectra. Europium RIXS maps were recorded by measuring the intensity of Eu L$\beta_{1,15}$ emission line (core-hole decay channel 2p$^5$4f$^0$$\epsilon d \rightarrow 4d^5$4f$^0$$\epsilon d$) with the maximum at 6843.2 eV while scanning the incident photon energy $h\nu_{in}$ with the 0.5 eV step around the L$_3$-Eu absorption edge. Cerium RIXS maps were recorded by measuring the intensity of Ce L$\alpha_1$ emission line (core-hole decay channel 2p$^7$4f$^0$$\epsilon d \rightarrow 3d^7$4f$^0$$\epsilon d$) with the maximum at 4839.2 eV while scanning the incident photon energy $h\nu_{in}$ with the 0.5 eV step around L$_3$-Ce absorption edge. XANES spectra of the same samples were collected at C and A1 beamlines above the L$_3$-Eu and L$_3$-Ce absorption edges in the transmission geometry.

In fig.1 RIXS maps of EuCo$_2$P$_2$, Nd$_{0.6}$Eu$_{0.4}$Co$_2$P$_2$ and La$_{0.4}$Ce$_{0.6}$Co$_2$P$_2$ compounds are plotted vs. incident photon energy $h\nu_{in}$ and transferred energy $h\nu_T = h\nu_{in} - h\nu_{out}$, i.e. the excitation energy that is transferred from the photon to the solid. The maximum of Eu L$\beta_{2,15}$ and Ce L$\alpha_1$ fluorescence intensity is marked with a diagonal line. Vertical line marks the emission spectrum at constant emission photon energy. In the intermediate valence compounds [4] the absorption peak at L$_3$ absorption edge is split due to the two-way electron excitation: 2p$^7$4f$^n$$\rightarrow 2p^6$4f$^{n-1}$5d$^1$ and 2p$^7$4f$^n$$\rightarrow 2p^6$4f$^{n-1}$5d$^2$. Consequently, in Eu RIXS maps resonances at energies ~6975.5 eV correspond to Eu$^{3+}$ and Eu$^{4+}$ contributions; in Ce RIXS maps resonances at energies ~5725.7 eV and ~5736.6 eV correspond to Ce$^{3+}$ and Ce$^{4+}$ contributions, i.e. Eu and Ce are in the intermediate valence state. Moreover, different valence contributions emit at the same emission energy in case of both Eu and Ce in all samples.

The high energy resolution fluorescence detected X-ray absorption spectra (HERFD XAS, see fig.2) extracted from RIXS maps were used for precise valence determination [5]. The broadening of HERFD XAS (2.75 eV for Eu and 3.1 eV for Ce) is less than broadening of XANES (3.63-4.08 eV for Eu and 4.2 eV for Ce) on the same compounds, providing a better resolution of valence contributions. The HERFD XAS spectra were fitted using both the combination of analytical functions [6] and combination of two integer valence standard spectra, calculated with FDMNES code [7]. In La$_{0.4}$Ce$_{0.6}$Co$_2$P$_2$ the valence of cerium (+3.032) exceeds the integer value +3 slightly.
The Eu valence in the Nd-containing sample (+2.336) is larger than in the Pr$_{1-x}$Eu$_x$Co$_2$P$_2$ (+2.298 for $x = 0.4$ and +2.341 for $x = 0.2$). This might be explained by the smaller ionic radius of Nd$^{3+}$ as compared to Pr$^{3+}$. Thus, Eu and Ce valence increases upon rise of chemical pressure caused by Pr/Nd and Ce substitution into EuCo$_2$P$_2$ and LaCo$_2$P$_2$ crystal structures. Besides, in the pure sample EuCo$_2$P$_2$ the europium valence is also found to be intermediate (+2.151), which is noteworthy because of the antiferromagnetic ordering of Eu sublattice in this compound.

In general, RIXS and XANES researches confirm Ce and Eu to be in the intermediate valence state in RCo$_2$P$_2$ compounds. This fact indicates the hybridization between the partially localized 4f-orbital of rare-earth and Co 3d-subband which impacts the electronic band structure and drastically alters the long-range magnetic order. RIXS provides advantage in accuracy of rare-earth valence determination over XANES due to better resolution of spectral contributions.

![Figure 1. RIXS maps of EuCo$_2$P$_2$, Nd$_{0.6}$Eu$_{0.4}$Co$_2$P$_2$ and La$_{0.4}$Ce$_{0.6}$Co$_2$P$_2$. The maximum of Eu L$\beta_{2,15}$ and Ce L$\alpha_1$ fluorescence intensity is marked with a diagonal line. Vertical line marks the emission spectrum at constant emission photon energy.](image1.png)

![Figure 2. HERFD XAS at the L$_3$-Ce absorption edge in comparison with the conventional transmission XANES-spectrum](image2.png)

References