Local electronic and crystal structure of rare-earth cobalt phosphides RCo_2P_2 studied by XAFS spectroscopy

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Abstract. The valence state of Ce and Eu was investigated by X-ray absorption near-edge structure (XANES) spectroscopy above L_3 -Ce and L_3 -Eu absorption edges in series of RCo_2P_2 ($\text{R} = \text{La, Ce, Pr, Eu}$) magnetic intermetallics. At the same time under similar conditions the rearrangement of Co and Pr local environment vs. temperature was studied by extended X-ray absorption fine structure (EXAFS) spectroscopy above K -Co and L_3 -Pr absorption edges.

Introduction

Magnetic ordering in RCo_2P_2 ($\text{R} = \text{La, Ce, Pr, Eu}$) 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 non-isoelectronic substitution in the rare-earth sublattice. In the series $\text{La}_{1-x}\text{R}_x\text{Co}_2\text{P}_2$, the Ce-substituted phases studied herein behave quite differently from the Pr- and Nd-substituted ones [2]. Another studied compound, $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$, is unexpectedly ferromagnetic ($T_C = 282\text{ K}$), while the pure PrCo_2P_2 and EuCo_2P_2 are antiferromagnets. This might be due to Ce and Eu intermediate valence states which are explored in this work by means of X-ray absorption fine structure (XAFS) spectroscopy along with such parameters of local crystalline structure as interatomic distances.

Experimental

All the studied samples were synthesized according to the standard reported procedures [2]. The phase purity of bulk products obtained was confirmed by powder X-ray diffraction. Energy-dispersive X-ray (EDX) analysis and single-crystal X-ray diffraction revealed that the composition of obtained materials is close to the nominal one. The X-ray absorption spectra of $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$ and $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{P}_2$ ($x = 0.3; 0.6; 0.9$) compounds were collected at C beamline of HASYLAB (DESY, Hamburg, Germany) in transmission mode above the L_3 -Eu (6977 eV), L_3 -Pr (5964 eV), L_3 -Ce (5723 eV) and K -Co (7709 eV) absorption edges. Energy resolution of the double-crystal Si (111) monochromator (detuned to reject 50% of the incident signal in order to minimize harmonic contamination) with a 0.3 mm slit at 7 keV was about 1.2 eV. Low-temperature measurements were carried out using a liquid helium continuous flow cryostat with a temperature control of $\pm 1\text{ K}$ at 300 K and $\pm 0.1\text{ K}$ at 5 K. The fitting of EXAFS-oscillation functions $\chi(k)$ and determination of local crystalline structure parameters were performed with VIPER software pack [3].

Fig. 1: L_3 -Eu XANES spectra of $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$; the fitting of spectrum at 8 K

Fig. 2: L_3 -Ce XANES spectra of $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{P}_2$ samples at different temperatures

Fig. 3: Temperature dependence of Eu valence in $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$

Fig. 4: Temperature dependence of Ce valence in $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{P}_2$ samples

Results and discussion

The normalized experimental L_3 -Eu and L_3 -Ce XANES spectra at all investigated temperatures are shown in Figs. 1 and 2. The absorption peaks, so-called “white lines”, are split due to the intermediate valence state of rare-earth ions. Two maxima corresponding to different valence contributions are resolved clearly in case of Eu and partially in case of Ce because of the predominant Ce^{3+} contribution, which is typical for Ce-containing intermetallics [4]. The amplitudes of Eu^{2+} and Ce^{3+} peaks increase with rising temperature while the Eu^{3+} and Ce^{4+} components become weaker.

The extraction of Eu valence from the the L_3 -Eu XANES spectra of $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$ was performed using the conventional fitting of complicated “white lines” with combinations of Lorentzian and arctangent curves of constrained widths and energy positions [5]. The example of the absorption peak decomposition into the Eu^{2+} and Eu^{3+} components for the spectrum at 8 K is shown in Fig. 1. This approach, however, does not work properly with L_3 -Ce XANES spectra of $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{P}_2$ (Fig. 2). The closeness of cerium valence state to 3+ makes the weak

Fig. 5: Temperature dependences of Co-Co interatomic distance in $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{P}_2$ samples

Fig. 6: Temperature dependences of Co-Ce interatomic distance in $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{P}_2$ samples

Ce^{4+} component negligible against the broad Ce^{3+} background. Nevertheless, it was found that the line shape in the spectrum of $\text{La}_{0.7}\text{Ce}_{0.3}\text{Co}_2\text{P}_2$ at 300 K does not exhibit any Ce^{4+} contribution. Therefore, this spectrum was assumed to correspond to the integer-valence standard, which already contains the necessary broadening and other characteristic features of the $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{P}_2$ system. Consequently, all the L_3 -Ce XANES spectra were fitted with the combination of two such standards corresponding to each valence contribution.

The analysis showed that the average valence of Eu in $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$ increases from +2.35 at 300 K to +2.43 at 8 K (Fig. 3). The Ce valence in $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{P}_2$ samples increases from +3.00 in $x = 0.3$ sample at 300 K to +3.19 in $x = 0.9$ sample at 8 K (Fig. 4). The change can be explained by a gradual lattice contraction upon cooling and corresponding rise of the chemical pressure, which favors the smaller in volume Eu^{3+} and Ce^{4+} states. Besides, in $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{P}_2$ the substitution of Ce for La also increases the chemical pressure in the lattice so that the Ce valence increases.

L_3 -Pr EXAFS spectra of $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$ were collected in the range of $2.1 - 10.9 \text{ \AA}^{-1}$ limited only by the L_2 -Pr edge. The interatomic distances obtained from the fitting are $R(\text{Pr-P}) \sim 3.01 \text{ \AA}$ and $R(\text{Pr-Co}) \sim 3.09 \text{ \AA}$ and do not change much with temperature. The Pr-Pr and Pr-Eu distances were also estimated as $R(\text{Pr-Pr}) \sim 3.87 \text{ \AA}$ and $R(\text{Pr-Eu}) \sim 3.97 \text{ \AA}$, the difference being $\sim 0.1 \text{ \AA}$. Since the RE-RE interatomic distance nominally equals to the unit cell parameter a , the discrepancy between the Pr-Pr and Pr-Eu bond lengths shown above characterizes the local disorder in the structure.

The temperature dependences of four local distances between Co and other atoms were extracted from the K -Co EXAFS spectra of $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{P}_2$ collected in a broad range of $4.0 - 15.2 \text{ \AA}^{-1}$. The shortest interatomic Co-P distance differs in three samples because of different lattice parameters, but remains almost unchanged with temperature. The temperature dependence of the Co-Co bond length in three samples is more significant (Fig. 5). But the most intriguing result is the clear correlation between the Co-Co distance and the Ce valence state (Fig. 4). The Co-Co distance is proportional to the unit cell parameter a . When more electrons are transferred from cerium $4f$ levels to the cobalt $3d$ subband, the antibonding states of cobalt become more populated [2], which weakens the Co-Co bonds. So, upon cooling the Ce valence increases, leading to the higher $4f$ to $3d$ electron transfer and slightly longer Co-Co distances. This correlation is observed even better when comparing samples with different values of x . For the higher Ce content, both the Ce valence and the Co-Co distance notably increase (Figs. 4, 5).

The Co-Ce interatomic distance increases with the Ce concentration and upon heating (Fig. 6). In intermediate valence rare-earth and transition metal compounds this distance characterizes the $4f - 3d$ hybridization which affects the rare-earth valence state [2, 6]. Indeed, the Co-Ce bond length behavior in $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{P}_2$ correlates well with the Ce valence (Fig. 4): the smaller distance corresponds to the larger valence. The Co-La distance in various samples has different temperature dependence. Probably it should be treated along with the temperature behavior of lattice parameters. In all samples the Co-La distance exceeds the Co-Ce distance.

The EXAFS analysis of K -Co absorption spectra of $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$ was also performed. The estimated Co-Eu distance ($\sim 3.23 \text{ \AA}$) is longer than the Co-Pr distance ($\sim 3.09 \text{ \AA}$), which is consistent with the larger ionic radius of Eu^{2+} ion. Thus, in both $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{P}_2$ and $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$ a split of rare-earth coordination shell around Co atom is found which can strongly affect the interaction between the rare-earth $4f$ states and Co $3d$ states. Such an effect can be sufficiently large to alter the band structure at the Fermi level and, correspondingly, the magnetic properties of the materials.

Indeed, we have already reported the dramatic modification of the magnetic behavior of PrCo_2P_2 upon partial substitution of Eu for Pr [6]. In contrast to PrCo_2P_2 and EuCo_2P_2 , both of which exhibit antiferromagnetic ordering, $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$ orders ferromagnetically at 282 K. Our preliminary investigation of $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{P}_2$ indicates a strong change in the magnetic properties upon increasing x . The sample with $x = 0.3$ behaves similarly to $\text{La}_{1-x}\text{Pr}_x\text{Co}_2\text{P}_2$, exhibiting two consecutive magnetic transitions well separated in temperature. This similarity to the Pr-substituted samples is in accord with the +3.00 valence of Ce at $x = 0.3$. In contrast, for the sample with $x = 0.6$ these two transitions occur in a very narrow temperature interval, while they are not observed at all for $x = 0.9$. More detailed studies of magnetic behavior are currently in progress.

Summary

The temperature and concentration dependences of rare-earth valence states, local R-Co and Co-Co distances in $\text{La}_{1-x}\text{Ce}_x\text{Co}_2\text{P}_2$ and $\text{Pr}_{0.8}\text{Eu}_{0.2}\text{Co}_2\text{P}_2$ indicate a fast fluctuation of an electron between localized $4f$ and delocalized $3d$ levels which impacts the electronic band structure and drastically alters the magnetic properties.

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