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Electronic States of Cobalt Ions in $\text{EuBaCo}_2\text{O}_{5+\delta}$ Layered Cobaltites

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The oxygen K -edge X-ray absorption spectra in $\text{EuBaCo}_2\text{O}_{5.52 \pm 0.02}$ and $\text{EuBaCo}_2\text{O}_{5.24 \pm 0.02}$ cobaltites are measured at temperatures of 300 and 440 K, which are below and above the metal–insulator transition temperature, respectively. According to these spectra, the substitution of Co^{2+} ions for some Co^{3+} ions with a decrease in the oxygen content in the chemical formula of a cobaltite and, hence, an increase in the relative fraction of CoO_5 pyramids with respect to the number of CoO_6 octahedra leads to an increase in the band gap by about 0.3 eV. The band structure of $\text{EuBaCo}_2\text{O}_{5.5}$ is calculated using the method of linearized muffin-tin orbitals in the local density approximation taking into account the local Coulomb interaction. It is found that the low-spin state of Co^{3+} ions occurs in CoO_6 octahedra in $\text{EuBaCo}_2\text{O}_{5.5}$, whereas the high-spin state of Co^{3+} ions is typical of cobalt ions in pyramids.

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$\text{LnBaCo}_2\text{O}_{5+\delta}$ cobaltites (where Ln is a rare earth element and $0 \leq \delta \leq 1$) are characterized by magnetic and structural phase transitions and metal–insulator transitions and exhibit the magnetoresistance effect [1–3]. In cobalt oxides, cobalt ions can exhibit various charge and spin states depending on the temperature, oxygen nonstoichiometry, doping, etc. Oxidation states (charge states) and spin states of transition metal ions determine the physical, including magnetic, properties of these materials [4].

The low-spin (LS, $t_{2g}^3 t_{2g}^3 e_g^0$), intermediate-spin (IS, $t_{2g}^3 t_{2g}^2 e_g^1$), and high-spin (HS, $t_{2g}^3 t_{2g}^1 e_g^2$) configurations are possible for trivalent cobalt ions in the octahedral ligand field. The spin-state transition (crossover) temperature correlates with the metal–insulator transition temperature.

In layered $\text{LnBaCo}_2\text{O}_{5.5}$ cobaltites, Co^{3+} ions are located both in CoO_6 octahedra and in CoO_5 pyramids. With a decrease in the oxygen content ($\text{LnBaCo}_2\text{O}_{5.0}$ cobaltites), pyramids with Co^{2+} and Co^{3+} ions remain the only structural elements. The problem of spin states of trivalent cobalt ions in octahedra and pyramids of cobaltites above and below the metal–insulator transition temperature is actively discussed. The results of the studies on spin states are reviewed in our works [5, 6]. The main contradiction concerns the spin states of Co^{3+} ions in pyramids. An

almost unambiguous conclusion about the intermediate-spin character of Co^{3+} ions in the pyramids appearing in layered cobaltites is based on the magnetic measurements. However, the measurements of X-ray absorption spectra in $\text{GdBaCo}_2\text{O}_{5.5}$ suggest the high-spin character of Co^{3+} ions in pyramids [7].

In this work, we focus on the measurements of the oxygen K -edge X-ray absorption spectra for two cobaltites, $\text{EuBaCo}_2\text{O}_{5.52 \pm 0.02}$ and $\text{EuBaCo}_2\text{O}_{5.24 \pm 0.02}$, denoted as S1 and S2, respectively. The measurements were performed at temperatures of 300 and 440 K, which are below and above the metal–insulator transition temperature of 360 K for $\text{EuBaCo}_2\text{O}_{5.5}$ [8, 1]. Note that the spin crossover occurs in a certain temperature range. It is impossible to fix the exact temperature of the change in the spin state, but we can only speak about the change in the number of electrons in cobalt ions having the spin state different from the initial one.

Polycrystalline $\text{EuBaCo}_2\text{O}_{5+\delta}$, $\text{Sr}_2\text{CoO}_3\text{Cl}$, and EuCoO_3 samples were synthesized using the solid-phase reaction method. The initial components for the synthesis of $\text{EuBaCo}_2\text{O}_{5+\delta}$ were Eu_2O_3 , BaCO_3 , and Co_3O_4 . The samples were subjected to a stepwise annealing in the temperature range of 900–1150°C with the intermediate grinding. Upon finalizing the synthesis, the samples were slowly cooled in a furnace (at a rate of 1 K/min). The absolute oxygen content

was determined by reducing the samples in the hydrogen atmosphere to the initial oxides Eu_2O_3 , BaO, and metallic cobalt. The phase composition and crystal structure of the samples were determined using X-ray diffraction (DRON-2 diffractometer, Cr $K\alpha$ radiation) at room temperature. The oxygen index of the $\text{EuBaCo}_2\text{O}_{5.52 \pm 0.02}$ sample cooled simultaneously with the furnace was 5.52 ± 0.02 ($\text{EuBaCo}_2\text{O}_{5.52 \pm 0.02}$). To prepare the $\text{EuBaCo}_2\text{O}_{5.24 \pm 0.02}$ sample, the initial $\text{EuBaCo}_2\text{O}_{5.52 \pm 0.02}$ powder was annealed at a temperature of 530°C for 6 h and then quenched in air.

According to the X-ray diffraction data, the synthesized $\text{EuBaCo}_2\text{O}_{5.52 \pm 0.02}$ sample has the orthorhombic structure (space group $Pmmm$, no. 47); the lattice parameters of this compound are $a = 3.880(1) \text{ \AA}$, $b = 7.824(1) \text{ \AA}$, and $c = 7.539(7) \text{ \AA}$. The $\text{EuBaCo}_2\text{O}_{5.24 \pm 0.02}$ sample has the tetragonal structure (space group P_4/mmm , no. 123) and the lattice parameters $a = 3.902(6) \text{ \AA}$ and $c = 7.536(7) \text{ \AA}$.

The $\text{Sr}_2\text{CoO}_3\text{Cl}$ sample was prepared using SrCO_3 , Co_3O_4 , and SrCl_2 precursors at 830°C . According to the data of [9], $\text{Sr}_2\text{CoO}_3\text{Cl}$ has the tetragonal structure (space group P_4/nmm , no. 129) with the lattice parameters $a = 3.901(2) \text{ \AA}$ and $c = 14.341(3) \text{ \AA}$.

The EuCoO_3 sample was synthesized employing the Eu_2O_3 and Co_3O_4 compounds by the stepwise annealing in the range of $900\text{--}1140^\circ\text{C}$. The prepared sample has the orthorhombic structure (space group $Pnma$, no. 62), with the lattice parameters $a = 5.372(1) \text{ \AA}$, $b = 7.488(4) \text{ \AA}$, and $c = 5.259(6) \text{ \AA}$.

The oxygen K -edge X-ray absorption spectra were measured at the Russian–German beamline of the BESSY-II storage ring in the total photoelectron yield mode at room temperature and at a temperature of 440 K. The spectral intensities were normalized to the electron beam current in the storage ring. To eliminate the influence of contamination of the parts of the spectrometer with oxygen-containing substances, the O K -edge spectra of the samples under study were normalized with respect to the oxygen spectrum obtained from a gold foil measured in the same energy range.

The band structure of $\text{EuBaCo}_2\text{O}_{5.5}$ was calculated by the linearized muffin-tin orbital method [10] using the local density approximation taking into account the local Coulomb interaction (LSDA + U) [11]. A similar calculation for $\text{GdBaCo}_2\text{O}_{5.5}$ was performed in [12]. The integration over the Brillouin zone was carried out using a 48-point mesh in the irreducible part of the zone. The set of basis functions included the following electronic states: Co ($4s$, $4p$, $3d$), O ($2s$, $2p$, $3d$), Ba ($6s$, $6p$, $5d$), and Eu ($6s$, $6p$, $5d$, $4f$). The atomic positions for $\text{EuBaCo}_2\text{O}_{5.5}$ were taken from [13]. The local energy U of the Coulomb repulsion and the energy of the Hund's rule intra-atomic exchange J_H were the same as in [12], i.e., 7.00 and 0.99 eV, respectively.

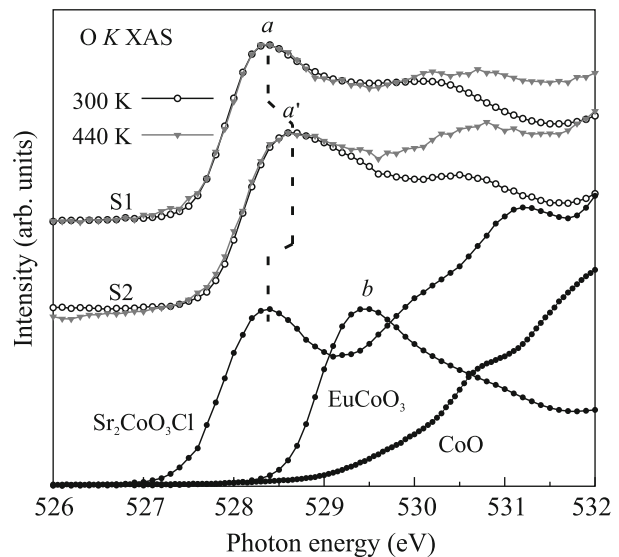


Fig. 1. O K -edge X-ray absorption spectra in (S1) $\text{EuBaCo}_2\text{O}_{5.52 \pm 0.02}$ and (S2) $\text{EuBaCo}_2\text{O}_{5.24 \pm 0.02}$ measured at room temperature and at about 440 K. For comparison, we present the spectra of the reference compounds $\text{Sr}_2\text{CoO}_3\text{Cl}$ (high-spin Co^{3+} ions in pyramids), EuCoO_3 (low-spin Co^{3+} ions in octahedra), and CoO (high-spin Co^{2+} ions in octahedra).

In Fig. 1, we show the oxygen K -edge X-ray absorption spectra of $\text{EuBaCo}_2\text{O}_{5.52 \pm 0.02}$ (sample S1) and $\text{EuBaCo}_2\text{O}_{5.24 \pm 0.02}$ (sample S2) cobaltite samples measured at room temperature and at 440 K, which far exceeds the metal–insulator transition temperature of 360 K for $\text{EuBaCo}_2\text{O}_{5.5}$ [1]. For comparison, we show the spectra of reference $\text{Sr}_2\text{CoO}_3\text{Cl}$, EuCoO_3 , and CoO compounds. The O K -edge X-ray absorption spectra are related to the O $1s \rightarrow 2p$ electronic transition. Owing to the hybridization of $3d$ states of the transition element and $2p$ states of oxygen, the vacant $3d$ states of cobalt manifest themselves in the O K -edge absorption spectrum.

The $\text{Sr}_2\text{CoO}_3\text{Cl}$ compound has the Ruddlesden–Popper structure [14]. The distorted CoO_5Cl octahedra, because of relatively large Co–Cl distances (as compared to the Co–O distance), can be attributed to the CoO_5 square pyramids [14]. The high-spin character of Co^{3+} ions in the $\text{Sr}_2\text{CoO}_3\text{Cl}$ pyramids was revealed from the Co $L_{2,3}$ -edge and O K -edge X-ray absorption spectra [15, 16, 7]. Consequently, the structure of the O K -edge spectrum in the range from 528 to 533 eV is due to the transition of electrons from the inner O $1s$ orbitals to the O $2p$ orbitals, and the low energy peak a in the spectrum of $\text{Sr}_2\text{CoO}_3\text{Cl}$ should be attributed to Co $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$ orbitals, which appear in the O K -edge spectra owing to their hybridization with O $2p$ orbitals. According to [15], Co^{3+} ions in octahedra in EuCoO_3 cobaltite exhibit the low-spin

state. Therefore, the first peak *b* in the O *K*-edge absorption spectrum should be related to unoccupied e_g states ($3d_{x^2-y^2}, 3d_{3z^2-r^2}$) [15, 16, 7]. The CoO spectrum, which exhibits the high-spin states of Co^{2+} ions in octahedra, occupies the photon energy range which is located rather high relative to that of the O *K*-edge absorption in cobaltites.

Peak *a* in the spectrum of sample S1 coincides in energy with the corresponding peak in the spectrum of $\text{Sr}_2\text{CoO}_3\text{Cl}$. A decrease in the oxygen content in cobaltites (an increase in the relative fraction of CoO_5 pyramids with respect to the CoO_6 octahedra) manifests itself in the X-ray spectra: peak *a'* in the spectrum of sample S2 is shifted toward high energies by about 0.3 eV relative to that in the spectrum of sample S1. A similar shift of the peak in the O *K*-edge spectrum toward the higher energies with a decrease in the oxygen content in cobaltites was found for the $\text{PrBaCo}_2\text{O}_{5+\delta}$ system. According to [17], it occurs with the change in δ from 0.74 to 0.5 and, according to [18], with the change from $\delta = 0.802$ to $\delta = 0.432$. It was explained by a change in the degree of hybridization of the Co–O states [17].

We can suppose that the shift of the peak in the O *K*-edge absorption spectrum with a decrease in the relative oxygen content (appearance of Co^{2+} ions and an increase in the relative fraction of CoO_5 structural fragments) is related to the change in the position of the bottom of the conduction band of cobaltites. A band gap of 0.05 eV was found from the optical experiments for $\text{EuBaCo}_2\text{O}_{5.5}$ cobaltite [19]. For related $\text{PrBaCo}_2\text{O}_{5.5}$ and $\text{GdBaCo}_2\text{O}_{5.5}$ cobaltites, the optical experiments give the gap values of 0.26 eV [12]. The authors of [12] suppose that the difference in the gap values is due to the different qualities of the single crystals used in the experiment. Taking into account the band gap $E_{\text{gap}} \approx 0.05$ eV and the shift of the peak *a'* in the O *K*-edge absorption spectrum of $\text{EuBaCo}_2\text{O}_{5.24 \pm 0.02}$ relative to the peak in the spectrum of $\text{EuBaCo}_2\text{O}_{5.52 \pm 0.02}$ by 0.30 eV, we can expect the band gap in oxygen-deficient cobaltites to increase: $E_{\text{gap}} \approx 0.35 \pm 0.05$ eV for $\text{EuBaCo}_2\text{O}_{5.25}$.

Let us now turn to the temperature effects in absorption spectra. It was found in [7] that the oxygen *K*-edge absorption spectrum in $\text{GdBaCo}_2\text{O}_{5.5}$ is only slightly shifted toward low energies by about 0.1 eV with increasing temperature from 300 to 400 K. In our experiments, the temperature changes in the spectra of samples S1 and S2 are absent, as follows from Fig. 1. This means that, in fact, there are no changes in the spin states of cobalt ions. This is not surprising, since only a small fraction of Co^{3+} ions are involved in the spin-state transition in this temperature range, and the changes in the spin states of the ions are too small to be detected in the measured spectra. Note that there is also a difference in the spin states of cobalt ions in

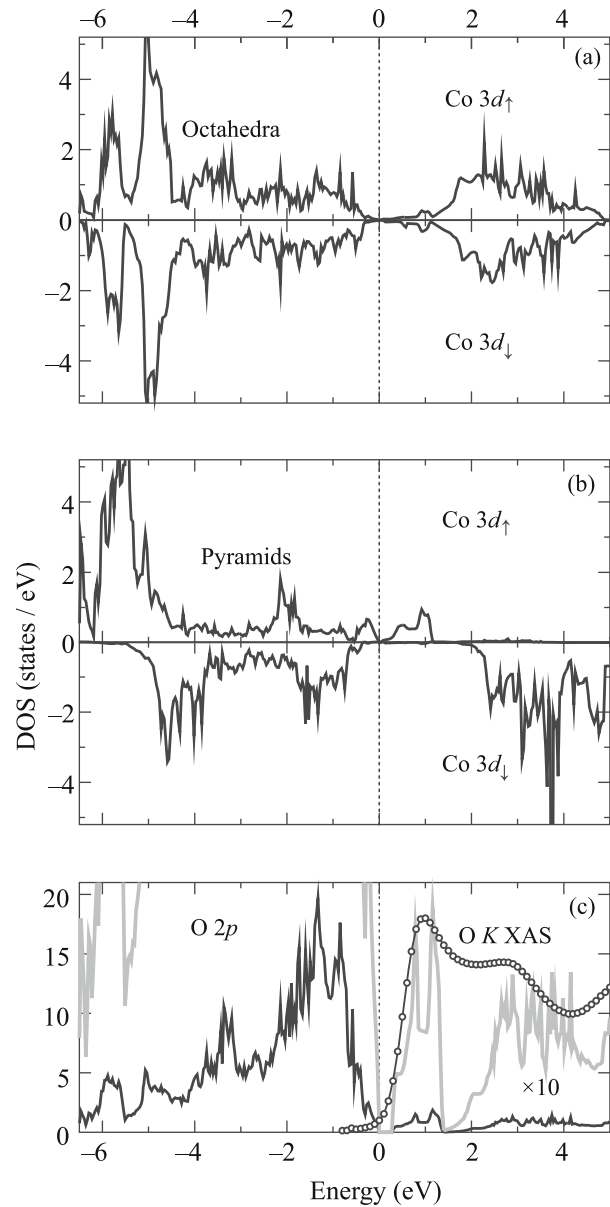


Fig. 2. Partial Co *3d* and O *2p* electron densities of states in $\text{EuBaCo}_2\text{O}_{5.5}$. Symbols $\text{Co}3d_{\uparrow}$ and $\text{Co}3d_{\downarrow}$ denote the densities of states for different spin orientations. These densities of states are shown for octahedra and pyramids. For comparison, we present the O *K*-edge X-ray absorption spectrum measured for $\text{EuBaCo}_2\text{O}_{5.52 \pm 0.02}$ at room temperature. The spectrum is plotted using the common energy scale after fitting the energies of spectral peaks and the density of states for vacant O *2p* states.

PrCoO_3 and EuCoO_3 , where Co^{3+} ions are located in CoO_6 oxygen octahedra. At room temperature, Co^{3+} ions in PrCoO_3 are in the high-spin state [20], while Co^{3+} ions in EuCoO_3 have the low-spin character [15].

To interpret the experimental results, we use the ab-initio calculations of the electron density of states. In Fig. 2, we show the partial electron densities of

states corresponding to Co $3d$ and O $2p$ for octahedra and pyramids in $\text{EuBaCo}_2\text{O}_{5.5}$. According to these calculations, the band gap is 0.04 eV. Note that the gap estimated in [12] for the related $\text{GdBaCo}_2\text{O}_{5.5}$ cobaltite using the LDA + U calculations is 0.24 eV. The main contribution near the bottom of the conduction band (unoccupied electron states) comes from hybridized O $2p$ –Co $3d$ states of the pyramids, whereas the contribution of the states corresponding to the octahedra is negligible. The spin magnetic moment of cobalt ions in the pyramids determined from the calculation of the density of states is $2.3\mu_B$, which is close to a value of $2.0\mu_B$ expected for the high-spin state of the system involving Co^{3+} ions. The magnetic moment in octahedra is zero, which is a signature of the low-spin state.

To summarize, the electron states of cobalt ions in $\text{EuBaCo}_2\text{O}_{5.52 \pm 0.02}$ and $\text{EuBaCo}_2\text{O}_{5.24 \pm 0.02}$ have been studied using oxygen K -edge X-ray absorption spectra measured at temperatures of 300 and 440 K, which are below and above the metal–insulator transition temperature, respectively. The substitution of Co^{2+} ions for some Co^{3+} ions with a decrease in the oxygen content in the chemical formula of cobaltite and, therefore, an increase in the relative fraction of CoO_5 pyramids with respect to the number of CoO_6 octahedra determined from the spectra is accompanied by an increase in the band gap by about 0.3 eV. There is nearly no effect of temperature on the spectra. The band structure of $\text{EuBaCo}_2\text{O}_{5.5}$ has been calculated by the linearized muffin-tin orbital method in the framework of the local density approximation taking into account the local Coulomb interaction. It has been found that the low-spin state of Co^{3+} ions arises in CoO_6 octahedra of $\text{EuBaCo}_2\text{O}_{5.5}$, while the high-spin state is characteristic of cobalt ions in the pyramids.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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