X-Ray Absorption Co L Spectra for the Determination of the Charge and Spin States of Cobalt Ions in LnBaCo$_2$O$_5$ + $\delta$ Cobaltites (Ln = Eu, Gd, Tb)

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Co L X-ray absorption spectra were used to determine the charge and spin states of ions in LnBaCo$_2$O$_5$ + $\delta$ cobaltites (Ln = Tb, Eu and Gd, 0.08 $\leq$ $\delta$ $\leq$ 0.55). It is shown that with a decrease in the oxygen content in cobaltites (with a decrease in the average charge state of cobalt ions), the Co L$_3$ maximum shifts linearly towards low photon energies. It was found using Co L$_3$ X-ray spectra that the mechanical action on GdBa-Co$_2$O$_5$.5 (uniaxial compression and torsion under pressure) leads to the appearance of divalent cobalt ions, i.e., the CoO phase. The CoO phase appears in the sample under pressure even in the absence of shear deformations. Based on the measurements of X-ray absorption spectra at different temperatures, it was found that at 440 K, which is above the metal—insulator transition point, some of the low-spin Co$^{3+}$ ions in EuBa-Co$_2$O$_5$.52 cobaltite octahedra pass into the high-spin state. No change of the spin state of Co ions in EuBa-Co$_2$O$_5$.24 with temperature was found.

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Layered rare-earth cobaltites LnBaCo$_2$O$_5$ + $\delta$ (Ln is a rare earth element, 0 $\leq$ $\delta$ $\leq$ 1) are advanced materials for new cathodes of solid oxide fuel cells due to the high level of both electronic and oxygen-ion conductivity [1], as well as due to the high activity of the oxygen reaction in many energy storage and conversion processes [2]. Therefore, it is necessary to know the resistance of these materials to external influences.

These materials are also of interest for studying the spin states of cobalt ions. Firstly, LnBaCo$_2$O$_5$ + $\delta$ compounds have two types of structural complexes (CoO$_6$ octahedra with Co$^{3+}$ ions and Co$_2$O$_5$ pyramids in which Co$^{3+}$ and Co$^{2+}$ ions coexist at $\delta$ $<$ 0.5). Secondly, there is a metal—insulator transition in these cobaltites. Thirdly, the spin transition associated with the metal—insulator transition occurs at rather easily attainable temperatures (e.g., 360 K for EuBaCo$_2$O$_5$.5 [3, 4]).

For Co$^{3+}$ ions in a ligand field, the following spin configurations are possible: high spin (HS, $S$ = 2), low spin (LS, $S$ = 0), intermediate spin (IS, $S$ = 1). The transition from one spin state to another is achieved by changing the temperature, pressure, or photoexcitation. The realization of a particular spin state depends on the magnitude and symmetry of the crystal field.

The spin state of cobalt ions in octahedra and pyramids of cobaltites above and below the metal—insulator transition point is the subject of intense discussion. Literature data on the study of the spin states of Co$^{3+}$ ions in cobaltites are presented in our works [5, 6]. The main contradiction concerns the problem of spin states of Co$^{3+}$ ions in pyramids. The conclusion about the intermediate-spin character of Co$^{3+}$ ions in pyramids follows from magnetic studies [3, 7–9]. However, measurements of X-ray absorption and magnetic dichroism spectra indicate the high-spin character of Co$^{3+}$ ions in pyramids [10–12].

Co L$_{2,3}$ and O K X-ray absorption spectra in the temperature range of 70–500 K were measured in [10, 12, 13]. Previously, we measured oxygen K spectra of cobaltites at room temperature and at 440 K, but we did not find any changes of the spin state of cobalt ions with temperature [14]. It should be noted that the spin crossover occurs smoothly in a certain temperature range. Therefore, it is impossible to fix the exact temperature of spin transitions, and we can only talk about a change in the number of electrons on cobalt ions with a spin state different from the initial one.

In this paper, we consider the following questions: (1) how does the energy position of the X-ray absorption Co L$_3$ line depend on the average charge state (average valence) of cobalt ions; (2) how does the...
decomposition of cobaltites occur due to mechanical action (during torsion deformation under pressure); (3) how the spectra of cobaltites change with temperature (whether spin crossover occurs).

Polycrystalline samples of cobaltites were synthesized using the solid-phase method. The synthesis technology is described in detail in our paper [14]. The phase composition and crystal structure of the samples were determined by X-ray diffraction at room temperature. The absolute oxygen content was estimated by reducing the samples in a hydrogen atmosphere to the initial oxides (Eu₂O₃, Tb₂O₃, Gd₂O₃, and BaO) and metallic cobalt. The error in determining the oxygen content in prepared cobaltites was ±0.02 (e.g., for europium cobaltite, in accordance with the chemical formula, EuBaCo₂O₅.52 ± 0.02).

A sample of GdBaCo₂O₅.5 cobaltite was subjected to severe plastic deformation under uniaxial compression up to a pressure of 7 GPa, as well as torsion under pressure with rotation of the anvils between which the sample is clamped, up to 180°. A press with a force of 100 tons and anvils made of VK-6 alloy were used. X-ray absorption spectra for GdBaCo₂O₅.5 subjected to torsion under pressure by 360° were previously published in [15]. In this study, the emphasis will be on the analysis of the spectrum of cobaltite subjected only to pressure without torsional deformation under pressure.

The cobalt L₂,₃ X-ray absorption spectra were measured at the Russian–German beamline of the BESSY-II storage ring in the total photoelectron yield mode. The spectral intensities were normalized to the electron beam current in the storage ring. The spectra of EuBaCo₂O₅,52 and EuBaCo₂O₅,24 were measured both at room temperature and at 440 K.

One of the key problems in the study of cobaltites is the determination of the oxygen content in them, on which the charge state (valence) of cobalt ions depends. Although the method of reducing samples in hydrogen involves determining the error of oxygen in the chemical formula of cobaltites ±0.02, nevertheless, there is a possibility that oxygen forms new phases on the surface of crystallites with barium and carbon. In addition, the ratio of other elements (rare earths, cobalt and barium) in cobaltite may also differ from what is expected from the chemical formula. Let us consider how a change in the mean valence affects the cobalt L spectra.

Figure 1 shows Co L₃ X-ray absorption spectra of some LnBaCo₂O₅,5 + δ cobaltites. Co L₃ X-ray absorption spectra arise due to the electronic transition 2p⁰⁶3dⁿ → 2p⁵3dⁿ⁺¹. These spectra are determined by the Coulomb and exchange interactions between the Co 2p hole and the Co 3d electrons, and also depend on the magnitude of the crystal field. Intense peak at 784.5 eV is the barium L₃ lines. The Ba M₄,₅ spectra are due to the process 3d¹⁰4f⁰ → 3d⁹4f¹. The Co L₂,₃ and Ba M₄,₅ spectra are close to each other in energy, but do not overlap. In contrast to the cobalt line, the energy position of the barium line practically does not change. Thus, the barium line can be used as an internal energy standard. According to the deviation of the maximum of the Co L₃ spectrum from the expected position for the supposed valence of cobalt ions, one can judge whether the actual composition of cobaltite corresponds to the declared chemical formula.

LnBaCo₂O₅,5 + δ cobaltites differ of oxygen content and, consequently, of average charge states (average valences) of cobalt ions. The position of the Co L₃ maximum correlated with the valence of cobalt ions is shown by a sloping line. The presence of Co²⁺ ions in cobaltite (the decrease in the average valence of cobalt ions) leads to a shift of the spectral maxima towards low energies, since the binding energy of the Co 2p electrons involved in the spectral process decreases with a decrease in the valence.
Deviations of the positions of the spectral maxima from a straight line can be explained by the difference in the elemental composition of cobaltite from that assumed by the chemical formula. It is possible that some oxygen ions are not included in the composition of the compound, but form barium-based impurities. The presented dependence of the position of the spectral maxima on the average charge state of cobalt ions can be used to reveal the deviation of the actual composition of cobaltite from its chemical formula. In particular, the difference between the position of the maximum of the spectrum and the expected one is observed for Tb$_{0.95}$Ba$_{1.05}$Co$_{1.9}$O$_{5.21}$, in which the cobalt valence should be somewhat higher, than follows from the chemical formula. Thus, with a decrease in the oxygen content in cobaltites (with a decrease in the average charge state of cobalt ions), the Co $L_3$ maximum shifts linearly towards low photon energies.

A change of the charge state of cobalt ions is also accompanied by a change in the shape of the spectra. In the Co $L_3$ spectra, the $A$ feature is formed by Co$^{2+}$ ions, which appear in cobaltite due to a slight oxygen deficiency or due to the reduction of trivalent cobalt ions on the surface [10]. The $B$ feature is formed by the contributions of HS-Co$^{3+}_{\text{oct}}$, HS-Co$^{3+}_{\text{pyr}}$, and HS-Co$^{2+}_{\text{oct}}$. This part of the spectrum will be used to reveal 2+ ions in cobaltites subjected to mechanical action, and to confirm the change of the spin states of trivalent ions in cobaltites subjected to mechanical action, and to confirm the change of the spin states of trivalent ions in octahedra under the influence of temperature.

It is known that at temperatures of 500–700°C in a CO$_2$–O$_2$ atmosphere, orthorhombic GdBaCo$_2$O$_{5.5}$ decays into tetragonal GdBaCo$_2$O$_{5.5}$, GdCoO$_3$, BaCO$_3$ and Co$_2$O$_4$ [16]. Mechanical impact can be similar to thermal. Severe plastic deformations lead to partial decomposition of cobaltite and to appearance of less oxidized phases in the Co–O system. In the case of torsion under pressure, the CoO phase appears and nanoparticles with a size of 50–70 nm are formed (according to X-ray diffraction analysis) [15]. During milling, due to a lower degree of deformation effect and the appearance of a competing process of oxidation of small particles over time, reduction occurs to the Co$_2$O$_4$ phase [17]. Reduction and oxidation processes of oxides during milling are considered in [18]. A nonmonotonic change of the unit-cell volume of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ manganite with increasing milling time also points to similar processes [19]. With a decrease in the oxygen content, the perovskite unit-cell parameter increases, with an increase in the oxygen content, the parameter decreases, respectively, which was shown in [19].

The following questions remained unanswered: (1) whether the second phase occurs if the sample is under pressure in the absence of rotation of the anvils; (2) how it is displayed on the spectra of cobaltites? It is the mechanical action on the samples that makes it possible to trace the response of the Co $L_3$ spectra to the appearance of Co$^{2+}$ ions. The Co $L_3$ spectra of the GdBaCo$_2$O$_{5.5}$ sample after deformation are shown in Fig. 2.

In the spectrum of the GdBaCo$_2$O$_{5.5}$ sample after deformation, which is characterized by an anvil rotation angle of 180°, signals from CoO appear clearly (marked by arrows). These features are less noticeable in the spectrum of the sample after pressure without rotation. To highlight the spectral signals from CoO, we subtracted the spectrum of the original sample from the spectra of the samples after deformation. Unfortunately, due to the lack of an internal standard (the Ba $M_4$ line retains its energy position, but changes in intensity from sample to sample due to uncontrolled release of barium on the ceramic surface), the subtrac-
tion was performed by selecting the coefficients by which the intensities of the spectra were multiplied. In Fig. 2, the intensities of the spectra are taken in accordance with the selected coefficients. This subtraction procedure allowed us to obtain difference spectra that were in good agreement with the spectrum of CoO, both for the sample under pressure after rotation of the anvils by 180° and in the absence of rotation. Thus, even with a small degree of deformation under pressure, only the CoO phase arose. No signs of Co3O4 are observed in the spectrum after such treatment of the samples.

Figure 3 shows the X-ray absorption spectra of EuBaCo2O5.52 and EuBaCo2O5.24 measured at room temperature and at 440 K. As noted above, the feature B of the spectrum of EuBaCo2O5.52 is determined by the contributions of Co3+ ions both in octahedra and in pyramids, as well as by Co2+ in pyramids. An increase in temperature leads to an increase in the intensity of the B feature in the spectra of EuBaCo2O5.52. To eliminate the contribution of Co2+ ions, we use the spectra of deformed cobaltites shown in Fig. 2. The A peak indicates the presence of Co2+ ions in the sample. The Co L3 spectrum of EuBaCo2O5.52 lacks the A feature. This means that this sample does not contain Co2+ ions. Divalent cobalt ions appear in EuBaCo2O5.24; the A feature appears in the spectrum. Thus, the feature B in the spectra of EuBaCo2O5.52 is determined exclusively by the contributions of Co3+ ions. Using the band structure calculations, we found that at room temperature, the Co3+ ions in the CoO6 octahedra of EuBaCo2O5.52 are in the low-spin state, while in the pyramids, the Co3+ ions are in the high-spin state [14]. The concentration of pyramids in EuBaCo2O5.5 cobaltites does not change with increasing temperature, therefore, the increase in the B spectral intensity with increasing temperature should be attributed to the appearance of high-spin Co3+ ions.

On the other hand, the spectra of EuBaCo2O5.24 cobaltites do not change with temperature. It is known that LnBaCo2O5+δ cobaltites at δ < 0.45 are in the insulator state and do not undergo the metal–insulator transition [20]. Since the transition with a change of spin correlates with the metal–insulator transition, the absence of a change in the spin in this compound with an increase in temperature in our experiment confirms this statement. Thus, we can assume that at high temperatures (440 K), some of the low-spin Co3+ ions in EuBaCo2O5.52 octahedra transform into high-spin ions. No change in the spin at this temperature was found in EuBaCo2O5.24.

To summarize, in this paper, Co L3 spectroscopy is used to study the charge and spin states of ions in cobaltites LnBaCo2O5+δ (Ln = Tb, Eu, and Gd). It is shown that with a decrease in the oxygen content in cobaltites (with a decrease in the average charge state of cobalt ions), the Co L maximum shifts linearly towards low photon energies. Using X-ray spectra, phase analysis of GdBaCo2O5.5 cobaltite subjected to mechanical action in the form of uniaxial compression and torsion under pressure, was carried out. It is shown that, under this treatment, divalent cobalt ions (the CoO phase) appear in GdBaCo2O5.5. The CoO phase appears in the sample under pressure even in the absence of shear deformations. It was found that at a temperature above the metal–insulator transition point, some low-spin Co3+ ions in EuBaCo2O5.52 octahedra transform into high-spin ions. In cobaltite with a lower oxygen content (EuBaCo2O5.24), no change in the spin state was found.

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CONFLICT OF INTEREST
The authors declare that they have no conflicts of interest.

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