Influence of Co\textsuperscript{3+} spin-state on optical properties of LaCoO\textsubscript{3} and HoCoO\textsubscript{3}

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Abstract. Optical properties of the isoelectronic compounds LaCoO\textsubscript{3} and HoCoO\textsubscript{3} has been experimentally and theoretically investigated. We’ve measured the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function, reflectance $R(\omega)$ and optical conductivity at room temperature. The shift of the most pronounced spectral features to the high energy region on 0.3 eV associated with larger distortions due to the smaller rare earth ionic radii in HoCoO\textsubscript{3} in comparison with LaCoO\textsubscript{3} was observed. Also there was found an enhancement of absorption intensity in the range 1.3-2.3 eV in all kinds of spectra in HoCoO\textsubscript{3}, which can be attributed basing on the results of LDA+U calculations to the different spin-states of Co\textsuperscript{3+} ion in these compounds. The shift of the onset of the absorption from less than 0.1 eV in LaCoO\textsubscript{3} to 0.7 eV in HoCoO\textsubscript{3} and an absorption intensity enhancement in a narrow spectral range 1.2-2.6 eV in HoCoO\textsubscript{3} are clearly seen from the calculated convolution of partial densities of states obtained in the LDA+U approach. Such changes are assumed to be induced by the different Co\textsuperscript{3+} spin-state in these compounds at room temperature.

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1. Introduction

At present a temperature dependence of structural and magnetic properties of $\text{LaCoO}_3$ is usually described within a three-spin-states model. In the ground state $\text{LaCoO}_3$ is a nonmagnetic insulator and all $\text{Co}^{3+}$ ions have a low spin-state configuration (LS, $t_{2g}^6e_g^0, S=0$)\(^6\).

There are two transitions at approximately 100 and 500 K in $\text{LaCoO}_3$ with the increase of temperature. At 100 K this compound undergoes the spin-state transition to a paramagnetic state, as evidenced by a steep increase of magnetic susceptibility\(^6\) and can be interpreted as a spin-state transition to the intermediate spin-state (IS, $t_{2g}^5e_g^1, S=1$) or to a mixture of low and high spin-state (HS, $t_{2g}^4e_g^2, S=2$)\(^7\). The second transition at 500 K is associated with a metal-insulator (MI) transition. Band structure calculations within LDA+U approximation demonstrated that IS is the lowest in energy spin-state after the first transition\(^8\). In contrast to the expectation from the simple ionic model IS is stabilized by a strong $p-d$ hybridization and possible orbital ordering in $e_g$ shell of $\text{Co}^{3+}$ ions\(^8\).

From experimental point of view there are gradual changes in x-ray absorption spectroscopy\(^11, 12\) at the first spin-state transition. Up to now optical spectroscopy as well as an electroresistivity investigation have not found any significant changes in the electronic structure of $\text{LaCoO}_3$ in the low temperature region\(^13\). Change of the optical conductivity spectrum was observed only near MI transition. However, infrared spectroscopy revealed anomalous splitting of the phonon modes and change of their intensities with the increase of temperature, which was associated with local distortions due to the spin-state transitions\(^14\).

In this paper we’ve performed experimental and theoretical investigations of the changes in electronic structure, occurring at the spin-state transition. We’ve chosen two isoelectronic compounds: $\text{LaCoO}_3$ and $\text{HoCoO}_3$, which have different spin-state configurations at room temperature due to a chemical pressure happening with substitution of La ions by smaller Ho ions and hence increasing of a crystal field $t_{2g} - e_g$ energy splitting\(^10\). Observed changes in the optical properties of $\text{HoCoO}_3$ in comparison with $\text{LaCoO}_3$ can be associated with larger lattice distortions in $\text{HoCoO}_3$ and with different spin-state stabilization of $\text{Co}^{3+}$ ions in these compounds.

2. Experimental details

In order to grow $\text{LaCoO}_3$ and $\text{HoCoO}_3$ single crystals a kind of anodic electrodeposition technique was used. In particular, McCarrol approach\(^15\) was modified\(^16\) to use seeded flux melt growth based on $\text{Cs}_2\text{MoO}_4$-$\text{MoO}_3$ mixture in the ratio 2.2 : 1 as solvent. Appropriate solute quantity was added into a 100 cm\(^3\) platinum crucible contained the mixture to grow these single crystals with a seed served as anode at $\sim$ 950-1000 °C under current density in the range 0.5-0.7 mA/cm\(^2\). Simultaneously the crucible serves as cathode in a such electrochemical cell.
The typical dimensions of the samples were 2x2x1 mm$^3$. According to X-ray data they were single phase. Optical measurements were performed on a cleaved mirror as well as on mechanically polished by diamond powder (with grains less than 0.5 $\mu$m) surface. In this paper we use experimental data for a cleaved surface, because in this case numerical data for the reflectance were higher and spectral features had a better resolution.

The refractive index $n$ and absorption constant $k$ were measured in the spectral range 0.5-5.0 eV by ellipsometric technique at the room temperature. The automated ellipsometer for measurements on small samples was assembled on the basis of the KSVU-12 spectrometer. For energies less than 0.5 eV absorption constant $k$ abruptly decreases and an error of measured values rises. Thus we had to break off our measurements at 0.5 eV. The relative experimental errors were 2%-4%. From $n$ and $k$, the real $\varepsilon_1(\omega) = n^2 - k^2$ and imaginary $\varepsilon_2(\omega) = 2nk$ parts of the complex dielectric constant $\varepsilon(\omega)$, the optical conductivity $\sigma(\omega) = nk\omega/2\pi$ and the reflectance $R(\omega) = [(n - 1)^2 + k^2]/[(n + 1)^2 + k^2]$ were derived.

3. Experimental results

The real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function for LaCoO$_3$ and HoCoO$_3$ are presented in figure 1. As seen from behaviour of $\varepsilon_2(\omega)$ function, there is a strong absorption region in the energy range 1.0-5.0 eV for both compounds. Two maxima for HoCoO$_3$ are clearly observed at 1.7 and 2.9 eV. For LaCoO$_3$ such features are broaden and shifted to the low energy region on $\sim$ 0.3 eV. The dispersion of $\varepsilon_1(\omega)$ near these peaks has anomalous behavior and positive values show that optical properties are defined by interband transitions. Another one feature is revealed more distinctly in the spectrum of the reflectance $R(\omega)$ for HoCoO$_3$, which has a maximum at 4.5 eV (figure 1, inset).

Changes in the optical charge gap values for the direct optical transitions and consequently the shift of the main spectral features with decrease of the rare earth ionic radii have been already observed in the series of compounds RCoO$_3$ where R was changed from La to Gd[17]. It can be explained in a following way. With decreasing of the rare earth ionic radii Co-O-Co bond angles deviate much more from 180° and Co-O bond length reduces. Since overlap between Co-3d and O-2p orbitals is determined by Co-O distances and Co-O-Co bond angles, it affects the $d-p-d$ interaction. As a result such distortions cause the band width to decrease and hence band gap to increase.

Right panel of figure 1 shows a variance analysis of the imaginary part of the dielectric function $\varepsilon_2(\omega)$, which has been expanded on 4 Lorentz oscillators ($A_1$, $A_2$, $A_3$, $A_4$). Except the shift of oscillators maxima (on 0.04, 0.30, 0.21 and 0.33 eV respectively) to the high energy region there is a strong enhancement (in 3 times) of $A_3$ oscillators strength in HoCoO$_3$ in comparison with LaCoO$_3$. At the same time other oscillator intensities are changed not more than on 30%.

Presumably, such strong enhancement of the optical absorption can be associated
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Figure 1. Left panel: the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function for LaCoO$_3$ and HoCoO$_3$. The inset in left panel shows the reflectance $R(\omega)$. Right panel: the variance analysis of $\varepsilon_2(\omega)$ for HoCoO$_3$ and LaCoO$_3$.

with different spin-state configurations of Co$^{3+}$ ions in these compounds. At room temperature Co$^{3+}$ ions in HoCoO$_3$ are in LS, but in LaCoO$_3$ a most part of them (about 80% from [13]) are in IS. In this case absorption slackening in the range 1.3-2.3 eV in LaCoO$_3$ may be evidence of some transitions blocking and as a result of suggestive changes in the band structure for IS in comparison with LS. For LaCoO$_3$ similar effect of the spectral feature intensity decreasing with temperature across spin-state transition near 1 eV was observed in photoemission experiment [18].

In order to compare experimental results with the band structure calculations presented below, let us discuss the optical conductivity spectra $\sigma(\omega)$ shown in figure 2. The optical conductivity spectrum for our LaCoO$_3$ crystals is in a good agreement with the literature data on numerical values and dispersion [17]. Optical properties for HoCoO$_3$ were investigated for the first time. The shift to the high energy region and an appearance of addition absorption were observed in optical conductivity $\sigma(\omega)$ as well as in $\varepsilon_2(\omega)$ spectra. Optical properties of the series of compounds RCoO$_3$ (R=La, Pr, Nd, Sm, Gd) were investigated by Yamaguchi et al [17] using reflectance measurements with Kramers-Kronig analysis in the spectral range $E < 2$ eV at $T$=9 K, where all compounds have the same LS state. Let us analyze this paper results and supplement them by our
results for HoCoO$_3$. If an intensity of the optical conductivity for LaCoO$_3$ at 1.7 eV will be considered as 1, then for the series of RCoO$_3$ compounds, where R=La, Pr, Nd, Sm, Gd, Ho it is increased as a whole with a drastic drop on Nd like 1, 1.47, 1.30, 1.07, 1.27, 1.86. Similar tendency has the temperatures of the spin-state transitions with decrease of the rare earth ionic radii [19].

Thus LS state becomes more stable with decrease of the rare earth ionic radii and one can see, that the higher temperature of transition from nonmagnetic LS state to IS state is the bigger values of the spectral features intensities are observed in the narrow spectral range 1.3 - 2.3 eV. That is naturally reflected in the electronic structure reorganization: an additional channels of interband transitions appearance.

4. Computational details

In order to find out an origin of the difference in the optical conductivity spectra in LaCoO$_3$ and HoCoO$_3$ we’ve performed band structure calculations within the LDA+U approximation [20]. The calculation scheme was realized in the framework of the linear muffin-tin orbitals (LMTO) [21] method based on the Stuttgart TBLMTO-47 computer code.
Temperature was introduced in our calculations only by the change of lattice parameters and atomic positions. Corresponding crystal data for room temperature were taken from Radaelli et al. (for LaCoO$_3$)\cite{11} and Liu et al. (for HoCoO$_3$)\cite{19}. Co(4s,4p,3d), O(3s,2p) and La,Ho(6s,6p,5d) were included to the orbital basis set in our calculations. In contrast to reference 10 almost empty La-$4f$ states as well as partially filled $4f$ states of Ho were treated as pseudo-core states.

It is important to describe La-$4f$ states correctly because in the present work we need to have as more precise density of states (DOS) as possible, since it is used for the optical properties calculations. An attempt to describe La-$4f$ states as valence one in the framework of LDA calculation leads to the appropriate La-$4f$ states peaks appearance in the low energy region near the Fermi level (see figures 3 - 5 in reference 10) in contrast to the experiment, where it placed at $\sim 9.0$ eV above $E_F$\cite{22}.

However, we have found that the presence or the absence of La-$4f$ states in the basis set has not effect on total energies difference of the various spin-state configurations. There are two ways to describe La-$4f$ states properly: to apply LDA+U correction on these states or to treat them as a pseudo-core. We’ve chosen the second way.

On-site Coulomb interaction parameter and Stoner exchange parameter were taken to be 7.0 eV and 0.99 eV respectively for Co-3$d$ shell. The Brillouin-zone (BZ) integration in the course of the self-consistency iterations was performed over a mesh of 27 $k$ points in the irreducible part of the BZ. DOS as well as CPDOS (see below) were calculated by the tetrahedron method with 512 $k$ points in the whole BZ.

There are two ways to calculate optical properties ab-initio. First of all, one can calculate optical conductivity using the Kubo formula\cite{23, 24} and matrix elements of momentum operator $<k'n| -i\Delta_{\alpha}| kn>$ . But such rather difficult and time-consuming procedure requires knowledge of the band structure with a better accuracy than that provided by LMTO-ASA method\cite{25}. Second, it is possible to calculate joint density of states (JDOS)\cite{26}, defined as

$$J(h\omega) = \sum_k N(\epsilon_k)N(-\epsilon_k + h\omega),$$

where $N(\epsilon_k)$ is a total DOS. However, JDOS calculations do not take into account selection rules and as a result their comparison with an experiment usually is not good. In this paper optical absorption is estimated to be proportional to the convolution of partial density of states (CPDOS)

$$C(\omega) = \frac{1}{h\omega} \sum_\sigma \int_0^{h\omega} N_A^\sigma(\epsilon)N_B^\sigma(\epsilon - h\omega)d\epsilon,$$

where $N_A^\sigma(\epsilon)$ and $N_B^\sigma(\epsilon - h\omega)$ are partial densities of states (PDOS) respectively for the energy arguments above and below of the Fermi level and $\sigma$ is spin projection. In this way one should use a "proper" PDOS to satisfy the selection rules. Due to such rules $N_A^\sigma(\epsilon)$ and $N_B^\sigma(\epsilon - h\omega)$ should be the partial DOS of the same atom, have the same spin index $\sigma$ and their orbital quantum numbers should differ only on $\Delta l =$
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$\pm 1$. Thus, this approximation can be compared with a conventional constant matrix elements approximation\cite{26}.

To this rule satisfy transitions $6s - 6p$ and $6p - 5d$ for Ho and La ions, $3s - 2p$ for O, $4s - 4p$ and $4p - 3d$ for Co ions. On the contrary, the valence band in both compounds is defined by O-$2p$ states which hybridize with a partially filled Co-$3d$ band, but O-$3s$ states are much far away from the Fermi level (approximately on 30 eV higher) and hence oxygens $3s - 2p$ transitions also should be neglected.

Thus there are Co $4s - 4p$, $4p - 3d$ and La,Ho $6s - 6p$, $6p - 5d$ transitions which can be taken into account in the calculation of (2). However, there is a strong hybridization between Co-$4p$ and O-$2p$ states due to a large spatial extension and a sizable overlap between these orbitals on neighboring Co and O ions. So in this way excitations from occupied Co-$4p$ into unoccupied Co-$3d$ band can be considered in a certain way as O-$2p$ – Co-$3d$ transitions.
5. LDA+U results

Recently, using the results of LDA+U calculations Nekrasov et al.\cite{10} have shown that a different spin-state stabilizes in LaCoO$_3$ (IS) and in HoCoO$_3$ (LS) at room temperature due to a chemical pressure happening with substitution of La ions by small Ho ions and hence increasing of a crystal field $t_{2g} - e_g$ energy splitting.

Calculated in the present work PDOS for IS state in LaCoO$_3$ and LS state in HoCoO$_3$ are presented in figure 3. Both compounds should be insulators in the calculations at room temperature. However, IS state for LaCoO$_3$ gave a metallic state in LDA+U in contrast to the experiment\cite{13}. This contradiction have been explained by a prediction of a possible orbital ordering of partially filled $e_g$ orbitals of Co$^{3+}$ ions in IS state \cite{8}. A band gap for HoCoO$_3$ in LS state is found to be 0.7 eV in agreement with experiment, where it is estimated to be $\leq$ 0.7 eV (see left panel of figure 2, inset). Local magnetic moment on Co ion in LaCoO$_3$ is equal to 2.2 $\mu_B$.

The results of optical convolution calculations are presented in right panel of figure 2. Due to the presence of a sizable band gap in HoCoO$_3$ there are no electronic transitions below 0.7 eV, while LaCoO$_3$ is a metal in our calculation (insulator with very small band gap $\sim$0.1 eV in experiment\cite{17}). As a result in LaCoO$_3$ the electronic excitations, which form optical conductivity, appear already at very small energies. Drastic increase of the absorption is observed at $\sim$ 2.3 eV for LaCoO$_3$ and at $\sim$ 1.1 eV for HoCoO$_3$.

The origin of such different behavior one can find in two interrelated features of O–2$p$ and Co–3$d$ PDOS for both compounds. From one side the $p – d$ hybridization for majority spin is stronger for IS configuration because of partial filling of $e_g$–band in IS in comparison with LS. It leads to the increase of valence oxygen 2$p$ band width in IS and to the decrease of PDOS just below the Fermi level (compare left and right panels in figure 3). From other side there is a sizable $\sim$ 2.3 eV gap in PDOS for Co–3$d$ and O–2$p$ minority spin, because in general they are placed on different sides from the Fermi level and almost do not hybridize. Thus, there is a small intensity of the optical absorption in LaCoO$_3$ due to only one (majority) spin contribution to this absorption in the low energy range till $\sim$ 2.3 eV. In this case ”drastic growing” of the intensity of O2$p$ – Co3$d$ transitions in optical conductivity spectra appears for IS state of Co$^{3+}$ ions in LaCoO$_3$ at the higher energies than for LS Co$^{3+}$ in HoCoO$_3$. Such shift and absorption intensity enhancement in the range 1.2–2.6 eV results in the crossing of CPDOS for LaCoO$_3$ and HoCoO$_3$ at $\sim$ 1.2 eV in a good agreement with experiment (see left panel of figure 2).

Thus, analysis of the LDA+U calculation results shows that there are qualitative changes in the electronic structures connected with the shift of the onset of the absorption and absorption intensity enhancement due to the different spin-state configuration at room temperature. It is important to note that the structural modifications by itself without changing of the spin-state configuration do not lead to the considerable changing of the electronic structure (see figures 3 and 4 in reference 10).
6. Conclusion

In this paper, we've reported the results of the optical properties investigations of isoelectronic compounds LaCoO$_3$ and HoCoO$_3$ with the aim to clarify the influence of the different spin-state stabilization on electronic structure as a whole and on the optical properties in particular.

We've measured the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function, reflectance $R(\omega)$ and optical conductivity and found several differences in the optical spectra between LaCoO$_3$ and HoCoO$_3$ at room temperature.

First of all, the shift of the main spectral features to the high energy region on 0.3 eV associated with smaller rare earth ionic radii and as a result with larger distortions in HoCoO$_3$ in comparison with LaCoO$_3$ was found. As well, there is an increase of the absorption in the range 1.3-2.3 eV in all kinds of spectra in HoCoO$_3$, which can be attributed basing on the results of LDA+U calculations to the different spin-state stabilization in these compounds.

We've performed convolution of partial density of states computations obtained in the framework of the LDA+U approach taking into account dipole-dipole selection rules. As a result we've found qualitative changes in the electronic structures, which is reflected in the optical spectra as the shift of the onset of the absorption edge from less than 0.1 eV in LaCoO$_3$ to 0.7 eV in HoCoO$_3$ and an absorption intensity enhancement in a narrow spectral range 1.2-2.6 eV. Such changes are assumed to be induced by the different Co$^{3+}$ spin-state in these compounds at room temperature.

Acknowledgments

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Influence of Co$^{3+}$ spin-state on optical properties of LaCoO$_3$ and HoCoO$_3$

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1. Introduction

At present a temperature dependence of structural[1, 2] and magnetic[3, 4, 5] properties of LaCoO$_3$ is usually described within a three-spin-states model. In the ground state LaCoO$_3$ is a nonmagnetic insulator and all Co$^{3+}$ ions have a low spin-state configuration \((\text{LS}, t^6_2 e^0_g, S=0)\)[6].

There are two transitions at approximately 100 and 500 K in LaCoO$_3$ with the increase of temperature. At 100 K this compound undergoes the spin-state transition to a paramagnetic state, as evidenced by a steep increase of magnetic susceptibility[6] and can be interpreted as a spin-state transition to the intermediate spin-state (IS, \(t^5_2 e^1_g, S=1\)) or to a mixture of low and high spin-state (HS, \(t^4_2 e^2_g, S=2\))[7]. The second transition at 500 K is associated with a metal-insulator (MI) transition. Band structure calculations within LDA+U approximation demonstrated that IS is the lowest in energy spin-state after the first transition[8, 9, 10]. In contrast to the expectation from the simple ionic model IS is stabilized by a strong \(p - d\) hybridization and possible orbital ordering in \(e_g\) shell of Co$^{3+}$ ions [8].

From experimental point of view there are gradual changes in x-ray absorption spectroscopy[11, 12] at the first spin-state transition. Up to now optical spectroscopy as well as an electroresistivity investigation have not found any significant changes in the electronic structure of LaCoO$_3$ in the low temperature region[13]. Change of the optical conductivity spectrum was observed only near MI transition. However, infrared spectroscopy revealed anomalous splitting of the phonon modes and change of their intensities with the increase of temperature, which was associated with local distortions due to the spin-state transitions[14].

In this paper we’ve performed experimental and theoretical investigations of the changes in electronic structure, occurring at the spin-state transition. We’ve chosen two isoelectronic compounds: LaCoO$_3$ and HoCoO$_3$, which have different spin-state configurations at room temperature due to a chemical pressure happening with substitution of La ions by smaller Ho ions and hence increasing of a crystal field \(t_{2g} - e_g\) energy splitting [10]. Observed changes in the optical properties of HoCoO$_3$ in comparison with LaCoO$_3$ can be associated with larger lattice distortions in HoCoO$_3$ and with different spin-state stabilization of Co$^{3+}$ ions in these compounds.

2. Experimental details

In order to grow LaCoO$_3$ and HoCoO$_3$ single crystals a kind of anodic electrodeposition technique was used. In particular, McCarrrol approach [15] was modified [16] to use seeded flux melt growth based on Cs$_2$MoO$_4$-MoO$_3$ mixture in the ratio 2.2 : 1 as solvent. Appropriate solute quantity was added into a 100 cm$^3$ platinum crucible contained the mixture to grow these single crystals with a seed served as anode at \(\sim 950-1000\) °C under current density in the range 0.5-0.7 mA/cm$^2$. Simultaneously the crucible serves as cathode in a such electrochemical cell.
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The refractive index $n$ and absorption constant $k$ were measured in the spectral range 0.5-5.0 eV by ellipsometric technique at the room temperature. The automated ellipsometer for measurements on small samples was assembled on the basis of the KSVU-12 spectrometer. For energies less than 0.5 eV absorption constant $k$ abruptly decreases and an error of measured values rises. Thus we had to break off our measurements at 0.5 eV. The relative experimental errors were 2%-4%. From $n$ and $k$, the real $\varepsilon_1(\omega) = n^2 - k^2$ and imaginary $\varepsilon_2(\omega) = 2nk$ parts of the complex dielectric constant $\varepsilon(\omega)$, the optical conductivity $\sigma(\omega) = nk\omega/2\pi$ and the reflectance $R(\omega) = [(n - 1)^2 + k^2]/[(n + 1)^2 + k^2]$ were derived.

3. Experimental results

The real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function for LaCoO₃ and HoCoO₃ are presented in figure 1. As seen from behaviour of $\varepsilon_2(\omega)$ function, there is a strong absorption region in the energy range 1.0-5.0 eV for both compounds. Two maxima for HoCoO₃ are clearly observed at 1.7 and 2.9 eV. For LaCoO₃ such features are broaden and shifted to the low energy region on ~ 0.3 eV. The dispersion of $\varepsilon_1(\omega)$ near these peaks has anomalous behavior and positive values show that optical properties are defined by interband transitions. Another one feature is revealed more distinctly in the spectrum of the reflectance $R(\omega)$ for HoCoO₃, which has a maximum at 4.5 eV (figure 1, inset).

Changes in the optical charge gap values for the direct optical transitions and consequently the shift of the main spectral features with decrease of the rare earth ionic radii have been already observed in the series of compounds RCoO₃ where R was changed from La to Gd[17]. It can be explained in a following way. With decreasing of the rare earth ionic radii Co-O-Co bond angles deviate much more from 180° and Co-O bond length reduces. Since overlap between Co-3d and O-2p orbitals is determined by Co-O distances and Co-O-Co bond angles, it affects the $d-p-d$ interaction. As a result such distortions cause the band width to decrease and hence band gap to increase.

Right panel of figure 1 shows a variance analysis of the imaginary part of the dielectric function $\varepsilon_2(\omega)$, which has been expanded on 4 Lorentz oscillators ($A_1$, $A_2$, $A_3$, $A_4$). Except the shift of oscillators maxima (on 0.04, 0.30, 0.21 and 0.33 eV respectively) to the high energy region there is a strong enhancement (in 3 times) of $A_3$ oscillators strength in HoCoO₃ in comparison with LaCoO₃. At the same time other oscillator intensities are changed not more than on 30%.

Presumably, such strong enhancement of the optical absorption can be associated
Influence of Co$^{3+}$ spin-state on optical properties of LaCoO$_3$ and HoCoO$_3$

Figure 1. Left panel: the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function for LaCoO$_3$ and HoCoO$_3$. The inset in left panel shows the reflectance $R(\omega)$. Right panel: the variance analysis of $\varepsilon_2(\omega)$ for HoCoO$_3$ and LaCoO$_3$.

with different spin-state configurations of Co$^{3+}$ ions in these compounds. At room temperature Co$^{3+}$ ions in HoCoO$_3$ are in LS, but in LaCoO$_3$ a most part of them (about 80% from [13]) are in IS. In this case absorption slackening in the range 1.3-2.3 eV in LaCoO$_3$ may be evidence of some transitions blocking and as a result of suggestive changes in the band structure for IS in comparison with LS. For LaCoO$_3$ similar effect of the spectral feature intensity decreasing with temperature across spin-state transition near 1 eV was observed in photoemission experiment[18].

In order to compare experimental results with the band structure calculations presented below, let us discuss the optical conductivity spectra $\sigma(\omega)$ shown in figure 2. The optical conductivity spectrum for our LaCoO$_3$ crystals is in a good agreement with the literature data on numerical values and dispersion[17]. Optical properties for HoCoO$_3$ were investigated for the first time. The shift to the high energy region and an appearance of addition absorption were observed in optical conductivity $\sigma(\omega)$ as well as in $\varepsilon_2(\omega)$ spectra. Optical properties of the series of compounds RCoO$_3$ (R=La, Pr, Nd, Sm, Gd) were investigated by Yamaguchi et al [17] using reflectance measurements with Kramers-Kronig analysis in the spectral range $E < 2$ eV at $T=9$ K, where all compounds have the same LS state. Let us analyze this paper results and supplement them by our
results for HoCoO₃. If an intensity of the optical conductivity for LaCoO₃ at 1.7 eV will be considered as 1, then for the series of RCoO₃ compounds, where R=La, Pr, Nd, Sm, Gd, Ho it is increased as a whole with a drastic drop on Nd like 1, 1.47, 1.30, 1.07, 1.27, 1.86. Similar tendency has the temperatures of the spin-state transitions with decrease of the rare earth ionic radii[19].

Thus LS state becomes more stable with decrease of the rare earth ionic radii and one can see, that the higher temperature of transition from nonmagnetic LS state to IS state is the bigger values of the spectral features intensities are observed in the narrow spectral range 1.3 - 2.3 eV. That is naturally reflected in the electronic structure reorganization: an additional channels of interband transitions appearance.

4. Computational details

In order to find out an origin of the difference in the optical conductivity spectra in LaCoO₃ and HoCoO₃ we’ve performed band structure calculations within the LDA+U approximation[20]. The calculation scheme was realized in the framework of the linear muffin-tin orbitals (LMTO)[21] method based on the Stuttgart TBLMTO-47 computer code.
Temperature was introduced in our calculations only by the change of lattice parameters and atomic positions. Corresponding crystal data for room temperature were taken from Radaelli et al. (for LaCoO$_3$)[1] and Liu et al. (for HoCoO$_3$)[19]. Co(4s,4p,3d), O(3s,2p) and La, Ho(6s,6p,5d) were included to the orbital basis set in our calculations. In contrast to reference 10 almost empty La-4$f$ states as well as partially filled 4$f$ states of Ho were treated as pseudo-core states.

It is important to describe La-4$f$ states correctly because in the present work we need to have as more precise density of states (DOS) as possible, since it is used for the optical properties calculations. An attempt to describe La-4$f$ states as valence one in the framework of LDA calculation leads to the appropriate La-4$f$ states peaks appearance in the low energy region near the Fermi level (see figures 3 - 5 in reference 10) in contrast to the experiment, where it placed at $\sim$ 9.0 eV above $E_F$[22].

However, we have found that the presence or the absence of La-4$f$ states in the basis set has not effect on total energies difference of the various spin-state configurations. There are two ways to describe La-4$f$ states properly: to apply LDA+U correction on these states or to treat them as a pseudo-core. We’ve chosen the second way.

On-site Coulomb interaction parameter and Stoner exchange parameter were taken to be 7.0 eV and 0.99 eV respectively for Co-3$d$ shell. The Brillouin-zone (BZ) integration in the course of the self-consistency iterations was performed over a mesh of 27 $k$ points in the irreducible part of the BZ. DOS as well as CPDOS (see below) were calculated by the tetrahedron method with 512 $k$ points in the whole BZ.

There are two ways to calculate optical properties ab-initio. First of all, one can calculate optical conductivity using the Kubo formula[23, 24] and matrix elements of momentum operator $< k n | - i \Delta_n | k' n >$. But such rather difficult and time-consuming procedure requires knowledge of the band structure with a better accuracy than that provided by LMTO-ASA method[25]. Second, it is possible to calculate joint density of states (JDOS)[26], defined as

$$J(h\omega) = \sum_{k} N(\varepsilon_k)N(-\varepsilon_k + h\omega),$$

where $N(\varepsilon_k)$ is a total DOS. However, JDOS calculations do not take into account selection rules and as a result their comparison with an experiment usually is not good. In this paper optical absorption is estimated to be proportional to the convolution of partial density of states (CPDOS)

$$C(\omega) = \frac{1}{h\omega} \sum_{\sigma} \int_0^{\hbar\omega} N_A^\sigma(\varepsilon)N_B^\sigma(\varepsilon - h\omega)d\varepsilon,$$

where $N_A^\sigma(\varepsilon)$ and $N_B^\sigma(\varepsilon - h\omega)$ are partial densities of states (PDOS) respectively for the energy arguments above and below of the Fermi level and $\sigma$ is spin projection. In this way one should use a “proper” PDOS to satisfy the selection rules. Due to such rules $N_A^\sigma(\varepsilon)$ and $N_B^\sigma(\varepsilon - h\omega)$ should be the partial DOS of the same atom, have the same spin index $\sigma$ and their orbital quantum numbers should differ only on $\Delta l=\ldots$
Figure 3. DOS calculated within the LDA+U approach for HoCoO$_3$ LS state ($t_{2g}^6e_g^0$) of Co$^{3+}$ ions (left panel), LaCoO$_3$ IS state ($t_{2g}^5e_g^1$) of Co$^{3+}$ ions (right panel). Parts of plots with positive (negative) ordinates denote majority (minority) spin PDOS. The Fermi level is zero energy.

±1. Thus, this approximation can be compared with a conventional constant matrix elements approximation[26].

To this rule satisfy transitions $6s-6p$ and $6p-5d$ for Ho and La ions, $3s-2p$ for O, $4s-4p$ and $4p-3d$ for Co ions. On the contrary, the valence band in both compounds is defined by O-2p states which hybridize with a partially filled Co-3d band, but O-3s states are much far away from the Fermi level (approximately on 30 eV higher) and hence oxygens $3s-2p$ transitions also should be neglected.

Thus there are Co $4s-4p$, $4p-3d$ and La, Ho $6s-6p$, $6p-5d$ transitions which can be taken into account in the calculation of (2). However, there is a strong hybridization between Co-$4p$ and O-$2p$ states due to a large spatial extension and a sizable overlap between these orbitals on neighboring Co and O ions. So in this way excitations from occupied Co-$4p$ into unoccupied Co-$3d$ band can be considered in a certain way as O-$2p$ – Co-$3d$ transitions.
5. LDA+U results

Recently, using the results of LDA+U calculations Nekrasov et al.[10] have shown that a different spin-state stabilizes in LaCoO₃ (IS) and in HoCoO₃ (LS) at room temperature due to a chemical pressure happening with substitution of La ions by small Ho ions and hence increasing of a crystal field $t_{2g} - e_g$ energy splitting.

Calculated in the present work PDOS for IS state in LaCoO₃ and LS state in HoCoO₃ are presented in figure 3. Both compounds should be insulators in the calculations at room temperature. However, IS state for LaCoO₃ gave a metallic state in LDA+U in contrast to the experiment[13]. This contradiction have been explained by a prediction of a possible orbital ordering of partially filled $e_g$ orbitals of Co$^{3+}$ ions in IS state [8]. A band gap for HoCoO₃ in LS state is found to be 0.7 eV in agreement with experiment, where it is estimated to be $\leq 0.7$ eV (see left panel of figure 2, inset). Local magnetic moment on Co ion in LaCoO₃ is equal to 2.2 $\mu_B$.

The results of optical convolution calculations are presented in right panel of figure 2. Due to the presence of a sizable band gap in HoCoO₃ there are no electronic transitions below 0.7 eV, while LaCoO₃ is a metal in our calculation (insulator with very small band gap $\sim$0.1 eV in experiment[17]). As a result in LaCoO₃ the electronic excitations, which form optical conductivity, appear already at very small energies. Drastic increase of the absorption is observed at $\sim 2.3$ eV for LaCoO₃ and at $\sim 1.1$ eV for HoCoO₃.

The origin of such different behavior one can find in two interrelated features of O$−2p$ and Co$−3d$ PDOS for both compounds. From one side the $p − d$ hybridization for majority spin is stronger for IS configuration because of partial filling of $e_g$-band in IS in comparison with LS. It leads to the increase of valence oxygen 2$p$ band width in IS and to the decrease of PDOS just below the Fermi level (compare left and right panels in figure 3). From other side there is a sizable $\sim 2.3$ eV gap in PDOS for Co−3$d$ and O$−2p$ minority spin, because in general they are placed on different sides from the Fermi level and almost do not hybridize. Thus, there is a small intensity of the optical absorption in LaCoO₃ due to only one (majority) spin contribution to this absorption in the low energy range till $\sim 2.3$ eV. In this case "drastic growing" of the intensity of O2$p − Co3d$ transitions in optical conductivity spectra appears for IS state of Co$^{3+}$ ions in LaCoO₃ at the higher energies than for LS Co$^{3+}$ in HoCoO₃. Such shift and absorption intensity enhancement in the range 1.2-2.6 eV results in the crossing of CPDOS for LaCoO₃ and HoCoO₃ at $\sim 1.2$ eV in a good agreement with experiment (see left panel of figure 2).

Thus, analysis of the LDA+U calculation results shows that there are qualitative changes in the electronic structures connected with the shift of the onset of the absorption and absorption intensity enhancement due to the different spin-state configuration at room temperature. It is important to note that the structural modifications by itself without changing of the spin-state configuration do not lead to the considerable changing of the electronic structure (see figures 3 and 4 in reference 10).
6. Conclusion

In this paper, we’ve reported the results of the optical properties investigations of isoelectronic compounds LaCoO$_3$ and HoCoO$_3$ with the aim to clarify the influence of the different spin-state stabilization on electronic structure as a whole and on the optical properties in particular.

We’ve measured the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function, reflectance $R(\omega)$ and optical conductivity and found several differences in the optical spectra between LaCoO$_3$ and HoCoO$_3$ at room temperature.

First of all, the shift of the main spectral features to the high energy region on 0.3 eV associated with smaller rare earth ionic radii and as a result with larger distortions in HoCoO$_3$ in comparison with LaCoO$_3$ was found. As well, there is an increase of the absorption in the range 1.3-2.3 eV in all kinds of spectra in HoCoO$_3$, which can be attributed basing on the results of LDA+U calculations to the different spin-state stabilization in these compounds.

We’ve performed convolution of partial density of states computations obtained in the framework of the LDA+U approach taking into account dipole-dipole selection rules. As a result we’ve found qualitative changes in the electronic structures, which is reflected in the optical spectra as the shift of the onset of the absorption edge from less than 0.1 eV in LaCoO$_3$ to 0.7 eV in HoCoO$_3$ and an absorption intensity enhancement in a narrow spectral range 1.2-2.6 eV. Such changes are assumed to be induced by the different Co$^{3+}$ spin-state in these compounds at room temperature.

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