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The influence of the Co^{3+} spin state on the optical properties of $LaCoO_3$ and $HoCoO_3$

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Abstract

The optical properties of the isoelectronic compounds $LaCoO_3$ and $HoCoO_3$ have been experimentally and theoretically investigated. We have measured the real ($\varepsilon_1(\omega)$) and imaginary ($\varepsilon_2(\omega)$) parts of the dielectric function, the reflectance $R(\omega)$ and the optical conductivity at room temperature. A shift of the most pronounced spectral features to the high energy region by 0.3 eV associated with larger distortions due to the smaller rare earth ionic radii in $HoCoO_3$ in comparison with $LaCoO_3$ was observed. Also there was found an enhancement of the absorption intensity in the range 1.3–2.3 eV in all kinds of spectra of $HoCoO_3$, which can be attributed on the basis of the results of LDA+U calculations to the different spin states of the Co^{3+} ion in these compounds. The shift of the onset of the absorption 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 in $HoCoO_3$ 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^{3+} spin states in these compounds at room temperature.

1. Introduction

Currently, the temperature dependence of the structural [1, 2] and magnetic [3–5] properties of $LaCoO_3$ is usually described within a three-spin-state model. In the ground state $LaCoO_3$ is a nonmagnetic insulator and all 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 $LaCoO_3$ with increase of temperature. At 100 K this compound undergoes a spin state transition to a paramagnetic state, as evidenced by a steep increase of the magnetic susceptibility [6], which can be interpreted as a spin state transition to the intermediate spin state (IS: $t_{2g}^5 e_g^1$, $S = 1$) or to a mixture of low and high spin states (HS: $t_{2g}^4 e_g^2$, $S = 2$) [7]. The second transition at 500 K is associated with a metal–insulator (MI) transition. Band structure calculations within the LDA+U approximation demonstrated that IS is the spin state lowest in energy after the first transition [8–10]. In contrast to the expectation from the simple ionic model, IS is stabilized by a strong p–d hybridization and possible orbital ordering in the e_g shell of Co^{3+} ions [8].

From the experimental point of view there are gradual changes in the x-ray absorption spectra [11, 12] at the first spin state transition. Up to now, optical spectroscopy as well as electroresistivity investigations 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 the MI transition. However, infrared spectroscopy revealed anomalous splitting of the phonon modes and change of their intensities with increase of temperature, which was associated with local distortions due to the spin state transitions [14].

In this paper we have performed experimental and theoretical investigations of the changes in electronic structure occurring at the spin state transition. We have chosen two isoelectronic compounds: $LaCoO_3$ and $HoCoO_3$, which have different spin state configurations at room temperature due to a chemical pressure arising with replacement of La ions by smaller Ho ions and hence increase of the crystal field t_{2g}–e_g energy splitting [10]. Observed changes in the optical properties of $HoCoO_3$ in comparison with those of $LaCoO_3$ can be associated with larger lattice distortions in $HoCoO_3$ and with different spin state stabilizations 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, the McCarrol approach [15] was modified [16] to use seeded flux melt growth based on a Cs_2MoO_4–MoO_3 mixture in the ratio 2.2:1 as the solvent. An appropriate solute quantity was added into a 100 cm^3 platinum crucible containing the mixture to grow these single crystals with a seed serving as the anode at $\sim$950–1000 °C under a current density in the range 0.5–0.7 mA cm^{-2}. Simultaneously, the crucible serves as the cathode in such an electrochemical cell.

The typical dimensions of the samples were $2 \times 2 \times 1$ mm^3. According to x-ray diffraction data collected at room temperature from powdered crushed single crystals, $HoCoO_3$ reveals orthorhombic crystal structure with space group $Pbnm$ and lattice parameters $a = 5.1524$ Å, $b = 5.4471$ Å and $c = 7.3914$ Å, while $LaCoO_3$ has close to cubic rhombohedral structure (space group $R\bar{3}c$) and lattice parameters $a = 3.8264$ Å and $\alpha = 90.6°$ at 295 K. The optical measurements were performed on a cleaved mirror as well as on a mechanically polished (with diamond powder, with grains smaller than 0.5 μm) surface. In this paper we use experimental data for a cleaved surface, because in this case the numerical data for the reflectance were higher and the 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 an ellipsometric technique at room temperature. The automated ellipsometer used for measurements on small samples was assembled on the basis of the KSVU-12 spectrometer. For energies less than 0.5 eV the absorption constant k abruptly decreases and the error in the 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.

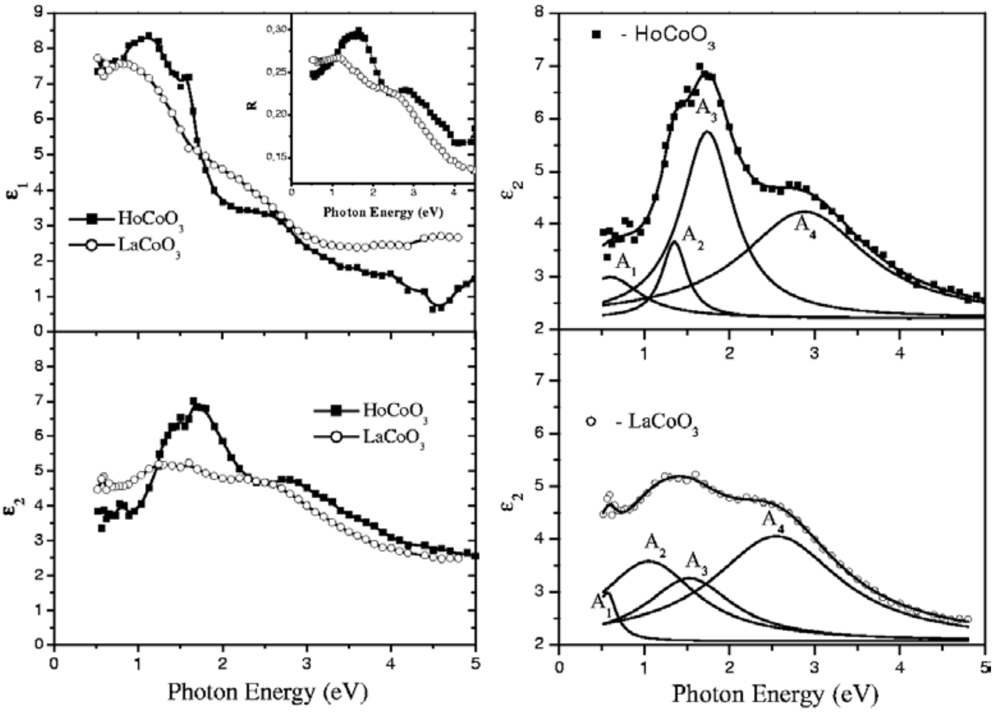

Figure 1. Left panel: the real ($\varepsilon_1(\omega)$) and imaginary ($\varepsilon_2(\omega)$) parts of the dielectric function for $LaCoO_3$ and $HoCoO_3$. The inset in the left panel shows the reflectance $R(\omega)$. Right panel: the variation analysis of $\varepsilon_2(\omega)$ for $HoCoO_3$ and $LaCoO_3$.

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 the behaviour of the $\varepsilon_2(\omega)$ 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 $LaCoO_3$ these features are broadened and shifted to the low energy region by $\sim$0.3 eV. The dispersion of $\varepsilon_1(\omega)$ near these peaks has anomalous behaviour and positive values show that the optical properties are governed by interband transitions. Another 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 already been observed in the series of compounds $RCoO_3$ where R was changed from La to Gd [17]. This can be explained in the following way. With the decrease of rare earth ionic radii, the Co–O–Co bond angles deviate much more from 180° and the Co–O bond length reduces. Since the overlap between the Co 3d and O 2p orbitals is determined by the Co–O distances and Co–O–Co bond angles, the d–p–d interaction is changed. As a result, such distortions cause the bandwidth to decrease and hence the band gap to increase.

The right panel of figure 1 shows a variation analysis of the imaginary part of the dielectric function $\varepsilon_2(\omega)$, which has been expanded over four Lorentz oscillators (A_1, A_2, A_3, A_4). This was done to distinguish the changes in absorption intensity in four features of $LaCoO_3$ and $HoCoO_3$ spectra. These are the peak at $\sim$3 eV, the broad double-humped feature in the spectral

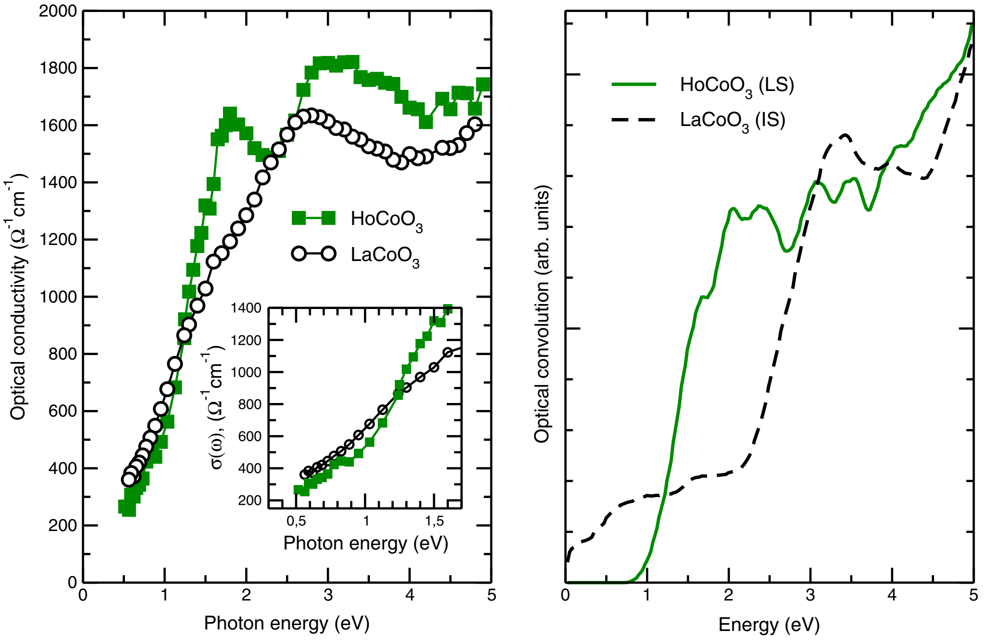

Figure 2. Left panel: the optical conductivity $\sigma(\omega)$ for HoCoO$_3$ and LaCoO$_3$ at 290 K. Right panel: the CPDOS calculated within the LDA + U approach for LaCoO$_3$ (dashed curve) in the IS state and for HoCoO$_3$ (solid curve) in the LS state.

(This figure is in colour only in the electronic version)

range 1–2.5 eV and the low energy shoulder near 0.6 eV. In addition to the shift of the oscillator maxima (by 0.04, 0.30, 0.21 and 0.33 eV respectively) to the high energy region, there is a strong enhancement (by a factor of three) of the A_3 oscillator strength in HoCoO$_3$ in comparison with that in LaCoO$_3$. At the same time, the other oscillator intensities are changed by not more than 30%.

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

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 as regards numerical values and dispersion [17]. The optical properties of HoCoO$_3$ were investigated for the first time. A shift to the high energy region ($E < 1.3$ eV; inset of figure 2, left panel) in HoCoO$_3$ in comparison with LaCoO$_3$ and an increase of absorption ($E > 1.3$ eV) were observed in the optical conductivity $\sigma(\omega)$ as well as in the $\varepsilon_2(\omega)$ spectra.

It was already known [19] that the state LS becomes more stable with decrease of the rare earth ionic radii. Now one can find a correlation between the higher temperature of transition from the nonmagnetic LS state to the IS state in HoCoO$_3$ in comparison with that in LaCoO$_3$ and the larger values of the spectral feature intensities which are observed in the narrow spectral range of 1.3–2.3 eV. As we will show below, the differences in spectra caused by the influence of rare earth ionic radii together with the spin state of the Co ion can be described in the framework of band structure calculations.

4. Computational details

In order to find the origin of the difference in optical conductivity spectra between $LaCoO_3$ and $HoCoO_3$ we have 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 via 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 in the orbital basis set in our calculations. In contrast to the case in 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 precise a density of states (DOS) as possible, since it is used for the optical properties calculation. An attempt to describe La 4f states as valence ones in the framework of LDA calculation leads to the appropriate La 4f state peaks appearing in the low energy region near the Fermi level (see figures 3–5 in [10]) in contrast to the experimental finding, which places them at $\sim$9.0 eV above E_F [22].

However, we have found that the presence or absence of La 4f states in the basis set has no effect on the total energy difference of the various spin state configurations. There are two ways to describe La 4f states properly: applying LDA + U correction to these states or treating them as a pseudo-core. We have chosen the second way.

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

As usual, the optical conductivity is calculated *ab initio* using the Kubo formula [23, 24]. The constant matrix element approximation can be used to calculate the optical conductivity due to the $i \rightarrow j$ interband transitions [25]:

$$\sigma_{ij}(\omega) = \frac{\pi p_{ij}^2}{\omega V} J_{ij}(\omega), \tag{1}$$

where V is the volume of the unit cell, p_{ij} is the dipole matrix element for a given polarization and $J_{ij}(\omega)$ is the joint density of states (JDOS), defined via total DOS $N(\varepsilon_{\mathbf{k}})$ **k** summation as

$$J(\omega) = \sum_{\mathbf{k}} N(\varepsilon_{\mathbf{k}}) N(-(\varepsilon_{\mathbf{k}} + \hbar\omega)). \tag{2}$$

In the present paper the optical conductivity is estimated to be proportional to the convolution of the partial density of states (CPDOS) which, in comparison with JDOS, already takes into account the dipole–dipole selection rules:

$$C(\omega) = \frac{1}{\omega} \sum_{\sigma} \int_0^{\hbar\omega} N_A^{\sigma}(\varepsilon) N_B^{\sigma}(\varepsilon - \hbar\omega)\, d\varepsilon. \tag{3}$$

Here $N_A^{\sigma}(\varepsilon)$ and $N_B^{\sigma}(\varepsilon - \hbar\omega)$ are partial densities of states (PDOS) for the energy arguments above and below the Fermi level respectively and σ is the spin projection. In this way one uses a 'proper' PDOS to satisfy the selection rules. Due to such rules, $N_A^\sigma(\varepsilon)$ and $N_B^\sigma(\varepsilon - \hbar\omega)$ should be the partial DOS of the same atom, have the same spin index σ, and their orbital quantum numbers should differ only by $\Delta l = \pm 1$. In this approach the dipole matrix elements p_{ij} in (1) equal 1 for allowed and 0 for forbidden transitions. Transitions 6s–6p and 6p–5d for Ho and La ions, 3s–2p for O ions, 4s–4p and 4p–3d for Co ions satisfy this rule.

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 far away from the Fermi level (approximately 30 eV higher) and hence oxygen 3s–2p transitions should also 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 (3). However, there is a strong hybridization between Co 4p and O 2p states due to the large spatial extent and the sizable overlap between these orbitals on neighbouring Co and O ions. So in this way excitations from the occupied Co 4p into the 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 different spin states stabilize in $LaCoO_3$ (IS) and in $HoCoO_3$ (LS) at room temperature due to a chemical pressure arising with the replacement of La ions by small Ho ions and hence the increase of the crystal field t_{2g}–e_g energy splitting.

The PDOS for the IS state in $LaCoO_3$ and the LS state in $HoCoO_3$ calculated in the present work are presented in figure 3. Both compounds are insulators at room temperature. However, the IS state for $LaCoO_3$ gave a metallic state in the LDA + U calculation in contrast to the experimental finding [13]. This contradiction has been explained by the prediction of a possible orbital ordering of partially filled e_g orbitals of Co^{3+} ions in the IS state [8]. The band gap for $HoCoO_3$ in the LS state is found to be 0.7 eV—in agreement with experiment, from which it can be estimated as $\sim$0.7 eV by linear extrapolation of the steep slope of $\sigma(\omega)$. The local magnetic moment on the Co ion in $LaCoO_3$ is equal to 2.2 μ_B.

The results of the optical convolution calculations are presented in the 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 (an insulator with very small band gap of $\sim$0.1 eV in experiments [17]). As a result, in $LaCoO_3$ the electronic excitations, which form the optical conductivity, are already appearing at very small energies. A 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 behaviours can be found in two interrelated features of the O 2p and Co 3d PDOS for both compounds. On one hand, the p–d hybridization for the majority spin is stronger for the IS configuration because of partial filling of the e_g band in IS in comparison with LS—this leads to the increase of the valence oxygen 2p bandwidth in IS and to the decrease of the PDOS just below the Fermi level (compare the left and right panels in figure 3). On the other hand, there is a sizable ($\sim$2.3 eV) gap in the PDOS for Co 3d and O 2p minority spin, because in general they are placed on different sides of the Fermi level and almost do not hybridize. Thus, there is a small intensity of optical absorption in $LaCoO_3$ due to only one (the majority) spin type contributing to this absorption in the low energy range until $\sim$2.3 eV. In this case, 'drastic growth' of the intensity of O 2p–Co 3d transitions in the optical conductivity spectra appears for the IS state of the Co^{3+} ions in $LaCoO_3$ at higher energies than for the Co^{3+} LS state in $HoCoO_3$. Such a shift and absorption intensity enhancement in the range 1.2–2.6 eV result in the crossing of the CPDOS for $LaCoO_3$ and $HoCoO_3$ at $\sim$1.2 eV in a good agreement with experiment (see the left panel of figure 2).

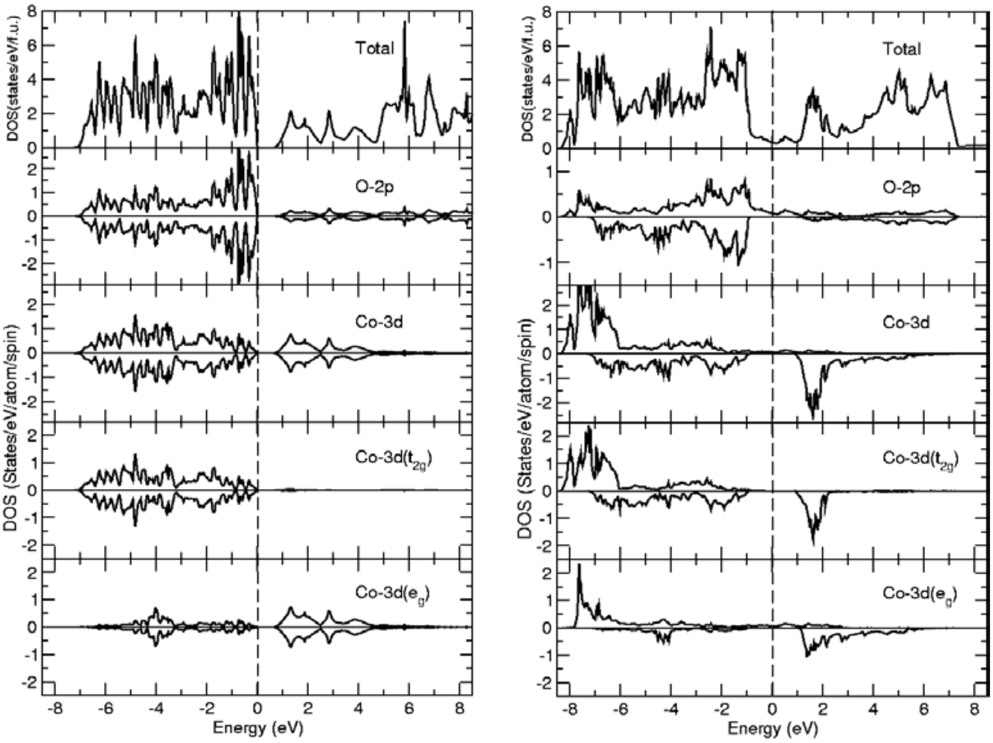

Figure 3. The DOS calculated within the LDA + U approach for the $HoCoO_3$ LS state ($t_{2g}^6e_g^0$) of the Co^{3+} ions (left panel) and the $LaCoO_3$ IS state ($t_{2g}^5e_g^1$) of the Co^{3+} ions (right panel). Parts of the plots with positive (negative) ordinates denote the majority (minority) spin PDOS. The Fermi level is zero energy.

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 configurations at room temperature. It is important to note that the structural modifications by themselves, without change of the spin state configuration, do not lead to the considerable change of the electronic structure (see figures 3 and 4 in [10]).

6. Conclusion

In this paper, we have reported the results of optical property investigations of the isoelectronic compounds $LaCoO_3$ and $HoCoO_3$ made with the aim of clarifying the influence of the different spin state stabilizations on the electronic structure as a whole and on the optical properties in particular.

We have measured the real ($\varepsilon_1(\omega)$) and imaginary ($\varepsilon_2(\omega)$) parts of the dielectric function, the reflectance $R(\omega)$ and the optical conductivity and found several differences in the optical spectra between $LaCoO_3$ and $HoCoO_3$ at room temperature.

First of all, a shift of the main spectral features to the high energy region by 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. Also, there is an increase of the absorption in the range 1.3–2.3 eV in all kinds of spectra of $HoCoO_3$, which can be attributed on the basis of the results of LDA + U calculations to the different spin state stabilizations in these compounds.

We have performed convolution of partial density of states computations in the framework of the LDA + U approach taking into account dipole–dipole selection rules. As a result we have found qualitative changes in the electronic structures, which are reflected in the optical spectra as a shift of the onset of the absorption edge from less than 0.1 eV for $LaCoO_3$ to 0.7 eV for $HoCoO_3$ 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 states in these compounds at room temperature.

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