Metal–Insulator Transition in Double Cobaltites RBAOCO_{5.5}
(R = Eu, Gd): Specific Features of Their Optical Properties

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Abstract—The temperature dependence of the optical properties of GdBAOCO_{5.5} in the region of the metal–insulator transition was studied in the spectral range $\lambda = 4.0–0.258 \mu m (E = 0.3–4.8 eV)$ by the spectroscopic ellipsometry method. The electronic structure of the crystal at $T = 300 K$ was calculated by the linearized muffin-tin orbital method in the local-density approximation with inclusion of on-site Coulomb interaction (LDA + U). The general features of the behavior of the optical properties of GdBAOCO_{5.5} and EuBAOCO_{5.5} are discussed. It is shown that the optical response on the metal side of the metal–insulator transition is determined by the redistribution of the optical-conductivity spectral weight in going from high to low energies and is significantly incoherent in character. The optical band gap width of the GdBAOCO_{5.3} is experimentally determined to be $E_g = 0.26 eV$, which is close to a theoretical estimate. The type of interband transitions is determined from analyzing the temperature dependence of the optical functions for absorption bands.

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1. INTRODUCTION

The specific features of the behavior of the physical properties of double cobaltites RBAOCO_{5+\delta} (R is a rare-earth metal, $0 \leq \delta \leq 1$), which are strongly correlated compounds, are associated with the complicated magnetic phase diagram of these compounds. This diagram is determined by the structural, electronic, and magnetic subsystems, which are strongly coupled because of the considerable overlapping of the 3d orbitals of the transition metal with the oxygen 2p orbitals. These compounds undergo a sequence of phase transitions, such as antiferromagnet–ferromagnet, ferromagnet–paramagnet, metal–insulator (MI), and structural transitions, and exhibit colossal magneto-resistance (see [1–8] and references therein).

The RBAOCO_{5+\delta} compounds have a layered crystal structure consisting of square layers arranged along the $c$ axis in the order [BaO]–[CoO$_3$]–[RO$_{1–\delta}$]–[CoO$_3$]. The oxygen content $\delta$ controls the mixed valence state and coordination (pyramidal or octahedral) of the cobalt ions. The valence of Co ions varies from $+2.5$ at $\delta = 0$ (pyramidal environment of Co ions) to $+3.5$ at $\delta = 1$ (octahedral environment of Co ions). At $\delta = 0.5$, one might expect that only Co$^{3+}$ ions will be present (alternating pyramidal and octahedral environments). As the oxygen content is varied, the CoO$_2$ planes are doped either with electrons (Co$^{2+}$ states) or holes (Co$^{4+}$ states), which has a significant effect on the electrical, magnetic, and structural properties [2–5]. The change in the band gap width caused by the difference in the rare-earth ion radius can also influence the magnetic properties and parameters of the electronic band structure [8, 9]. In compounds with $\delta > 0.5$, magnetic phase separation can occur [4].

The RBAOCO_{5+\delta} compounds are derivatives of the LaCoO$_3$ system, in which the Co$^{3+}$ is nonmagnetic in the ground state. In this compound, it is believed that this ion is in a low-spin (LS) state $t_{2g}^6e_{g}^0 (S = 0)$. As the temperature increases, the crystal-field splitting decreases and two excited states can be populated, namely, an intermediate spin (IS) state $t_{2g}^5e_{g}^1 (S = 1)$ and a high-spin (HS) state $t_{2g}^4e_{g}^2 (S = 2)$ [10, 11]. Since these spin states are very close in energy, transitions with a change in the spin state can occur with variation in temperature or with deformation of the crystal lattice. In the RBAOCO_{5+\delta} compounds, transitions with a change in the spin state can also occur. Until recently, the best founded opinion based on experimental data was that Co$^{3+}$ ions in these compounds at low temperatures are in the IS or LS state in the pyramids and in the LS state in the octahedra and that, above the MI transi-
tion temperature, Co$^{3+}$ ions in both of these positions are in the HS or IS state [12, 13]. Moreover, it is believed that the MI transition is closely related to a change in the spin state of Co$^{3+}$ ions [1–3, 14]. For example, when studying GdBaCo$_2$O$_{5+\delta}$, it was found in [3] that the MI transition is accompanied by an increase in the Co–O bond length in the octahedral positions of Co$^{3+}$ ions and by a decrease in this length in the pyramidal environment. The MI transition was related in [3] to the LS $\rightarrow$ HS transition in the octahedra, because the ionic radius of the Co$^{3+}$ ion in the HS state is larger than that in the LS state.

To date, another model has been proposed based on experimental spectroscopic (optical [15] and photoemission [16, 17]) data and on isotope-effect and neutron diffraction data [18, 19]. According to this model, the transition from metal to insulator in the GdBaCo$_2$O$_{5+\delta}$ compounds (at least those with rare-earth ions in the middle of the lanthanide series) is caused by delocalization of carriers in a high-spin state.

We are aware of only two publications concerning optical study of the R BaCo$_2$O$_{5+\delta}$ compounds. In [20], the properties of a SmBaCo$_2$O$_{5+\delta}$ crystal were analyzed by measuring the reflectivity and then calculating the optical conductivity spectrum from the Kramers–Kronig relations. In [15], we studied the optical properties of an EuBaCo$_2$O$_{5+\delta}$ crystal in the region of the MI transition using spectroscopic ellipsometry.

In this work, we study the changes in optical properties and electronic structure associated with the transition from metal to insulator in the GdBaCo$_2$O$_{5+\delta}$ compound. Then, we compare the optical properties of two compounds having different rare-earth ions ($R =$ Eu, Gd) in order to elucidate general features of the behavior of the optical response of the R BaCo$_2$O$_{5+\delta}$ compounds.

2. DETAILS OF THE EXPERIMENT AND BAND STRUCTURE CALCULATIONS

A GdBaCo$_2$O$_{5+\delta}$ single crystal ($\delta = 0.47 \pm 0.02$) was grown from a high-temperature melt using a nonstoichiometric mixture of the corresponding oxides. The details of the growth procedure can be found in [5]. For brevity, this composition will be referred to as GdBaCo$_2$O$_{5.5}$ in what follows. After the sample was annealed in oxygen, it had orthorhombic crystal symmetry. Samples of the same series were used in [5, 6] to perform electrical, magnetic, and structural studies. With increasing temperature, a sequence of phase transitions was observed to occur, namely, a MI transition at $T_{\text{MI}} = 360$ K, a transition to a phase with a double orthorhombic cell at $T_{\text{SN}} = 341$ K, a transition to an antiferromagnetic (AFM) phase at $T_N = 275$ K, and two magnetic transitions at $T = 250$ and 150 K. The superstructure observed to arise between $T_{\text{MI}}$ and $T_N$ (at $T_{\text{SN}} = 341$ K) involves atomic displacements and was assumed to be caused by HS $\rightarrow$ IS ordering of the Co$^{3+}$ ions in the pyramidal environment, with all Co ions in the octahedral environment being in the IS state [6].

We studied the optical properties of the GdBaCo$_2$O$_{5.5}$ single crystal by the ellipsometric method at 80–430 K. The indices of refraction ($n$) and absorption ($k$) were measured on an automated ellipsometer in the range of wavelengths $\lambda = 4.0–0.258$ $\mu$m ($E = h\omega = 0.3–4.8$ eV) with an accuracy of 2–4%. Using the measured values of $n$ and $k$, we calculated the real part $\varepsilon_r = n^2 – k^2$ and the imaginary part $\varepsilon_i = 2nk$ of the complex permittivity $\varepsilon(\omega)$, the optical conductivity $\sigma(\omega) = n k \omega / 2 \pi$, and the reflectivity $R(\omega) = [(n – 1)^2 + k^2] / [(n + 1)^2 + k^2]$, where $\omega$ is the cyclic frequency of light with wavelength $\lambda$. The optical properties were studied for the clean (001) plane of the crystal with dimensions of $2.0 \times 1.5$ mm.

The electronic structure of GdBaCo$_2$O$_{5.5}$ was calculated by the linearized muffin-tin orbital method [21] in the local-density approximation with inclusion of on-site Coulomb interaction (LDA + U) [22]. Integration over the Brillouin zone was carried out using a grid consisting of 64 points in an irreducible part of the zone. The basis set included the following states: Co(4s, 4p, 3d), O(2s, 2p, 3d), Ba(6s, 6p, 5d, 4f), and Gd(6s, 6p, 5d). The Gd(4f) states were considered as pseudo core states. The crystal structure at $T = 300$ K was taken from [8]. The on-site Coulomb repulsion energy $U$ and the intraatomic exchange energy $J_H$ were taken to be 7.00 and 0.99 eV, respectively [23]. In the magnetic lattice chosen, the interaction of all neighboring Co ions was AFM in character (as in a $G$-type antiferromagnet).

The results of our calculations show that the solution with a minimum total energy corresponds to the case where the octahedral Co ions are in the LS state and the pyramidal Co ions are in the HS state. This solution will be referred to as the LS–HS state. The HS state is stabilized in the pyramids because one of the oxygen ions is absent in a pyramid as compared with an octahedron and, as a result, the crystal-field energy decreases significantly.

It should be noted that, at present, there are several publications in which band calculations were carried out in order to determine which of the spin states is stable at a given temperature from comparing the total energies of various spin configurations. Unfortunately, even calculations performed by the same full-potential linearized augmented plane wave (FP-LAPW) method give different results [9, 13]. Our studies in this field show that the relative total energies of different spin states are fairly strongly dependent on the choice of the specific form of the LDA + $U$ functional (the existing versions of LDA + $U$ are discussed in detail in [24]), the included relaxation of the crystal lattice (because different spin states differ in terms of ionic radius), the type of magnetism, and the method used to solve the equations of the density functional theory. For this rea-
son, we believe that it is not correct to compare the calculated total energies of different spin configurations in this case, because these energies depend significantly on the details of the calculations. In this paper, we compare the theoretical densities of states of the LS–HS configuration with the results of optical measurements. It should be noted that, for the other possible combinations of spin states (IS–HS and HS–HS), the positions of the main optical bands vary insignificantly.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the dependences of the real and imaginary parts of the complex refraction index $N = n - ik$ of GdBaCo$_2$O$_{5.5}$ on photon energy in the energy range 0.3–4.8 eV measured at temperatures of 80, 300, and 430 K. It is seen that, on the transition from the insulator to metal phase, the most noticeable change in the optical constants with temperature occurs in the spectral range $E < 1.5$ eV. The sharp increase in the index of absorption $k$ at energies above 0.3 eV in the insulator phase (80 and 300 K) is associated with the onset of strong interband absorption. The values and dispersion of $n$ and $k$ near the low-energy limit of the spectral range studied indicate the transition to the metallic phase.

The temperature dependence of the optical-conductivity spectrum of GdBaCo$_2$O$_{5.5}$ is shown in Fig. 2. In the low-temperature (insulator) phase (at $T = 80$ K), the $\sigma(E)$ curve has three specific features: a strong broad absorption band with a maximum at $\sim 2.6$ eV, a less strong narrow band centered at 1.3 eV, and a nonmonotonic variation near $-3.4$ eV. The high values of the optical conductivity in the range $E = 0.3$–4.8 eV are due to interband transitions. Figure 3 shows the electron density of states (DOS) calculated in LDA + $U$ for the LS–HS state. It is clearly seen that, in this energy range, transitions should occur between the strongly hybridized O(2$p$)–Co(3$d$) electron states above and below the Fermi level. The results of a more detailed analysis of the DOS presented in Fig. 3 show that, indeed, one might expect the contribution from the O(2$p$) $\rightarrow$ Co(3$d$) optical transitions to reach a maximum at energies of $\sim 2.5$ eV. This conclusion is confirmed by the experimental data on photoemission [16, 17]. Therefore, the RBaCo$_2$O$_{5.5}$ compounds can be related to charge-transfer insulators, according to the Zaanen–Sawatzky–Allen classification [25].

By extrapolating the decreasing $\sigma(E)$ at low energies (inset to Fig. 4), we find the optical band gap to be 0.26 eV for GdBaCo$_2$O$_{5.5}$. For comparison, Fig. 4 also shows the data for the EuBaCo$_2$O$_{5.5}$ compound, for which the band gap is much less, $\sim 0.05$ eV [15]. It is seen that the character of the decreasing $\sigma(E)$ in the low-temperature phase is different for samples with $R = $ Eu and Gd. Later, the experimental temperature dependence of the optical functions near the absorption edge will be used to determine the nature of the band gap.
The observed increased absorption in the infrared region of the spectrum and the fact that the temperature dependence of the resistivity \( \rho(T) \) at low temperatures follows the Mott law \( \rho = \rho_0 \exp(\frac{E_0}{T})^{1/4} \) of the variable-range hopping conduction model of disordered systems [5, 15] suggest that there is a significant disorder in the low-temperature insulator phase of the crystals studied. The disorder can be caused by oxygen ions when the composition is slightly different from \( \delta = 0.5 \) [4]. It is most likely that the difference in the optical response at low energies between the two crystals differing in the rare-earth ion is not an intrinsic property of the double cobaltites but rather is due to the different degree of disorder in them. However, it should be stressed that, as can be seen from Fig. 4, the effect of the rare-earth ion on the \( \sigma(E) \) spectrum in the range of strong interband absorption is negligible in the low-temperature phase.

According to the calculations performed in this work, the band gap width in GdBaCo\(_2\)O\(_{5.5}\) is 0.24 eV. It is clearly seen in Fig. 3 that the bottom of the conduction band is formed by the \( e_g \) states of the Co ions in the pyramidal environment. This is due to the fact that one of the apical oxygen ions is absent (as compared with the octahedral environment) and the hybridization between the O\((2p)\) orbitals and one of the \( e_g \) orbitals \((3z^2 - r^2)\) of the pyramidal Co decreases sharply.

In the metallic phase at \( T = 430 \) K, i.e., above the MI transition point \( T_{\text{MI}} = 360 \) K, the absorption band of GdBaCo\(_2\)O\(_{5.5}\) in the range 1.0–4.5 eV decreases in intensity and the spectral weight is noticeably redistributed to the range \( E < 1 \) eV. The fact that the redistribution of the spectral weight from the higher to lower energy region covers a wide spectral range becomes obvious from the calculated electron DOS function

\[
N_{\text{eff}}(\omega) = \frac{2m^2}{\pi e^2} V_{\text{cell}} \int_{\omega_1}^{\omega_2} \sigma(\omega) d\omega.
\]

Fig. 3. (a) Total and (b–d) partial (b, c) Co(3d) and (d) O(2p) electron DOSs of GdBaCo\(_2\)O\(_{5.5}\) at \( T = 300 \) K. The Co ions in the octahedral environment are in the LS state and those in the pyramidal environment are in the HS state (LS–HS state). Positive (negative) values of the electron DOS correspond to spin up (spin down), respectively. In panels (b, c), the solid lines correspond to the \( t_{2g} \) states and shaded regions correspond to the \( e_g \) states. \( E_F = 0 \) eV.

Fig. 4. Comparison of the optical-conductivity spectra of GdBaCo\(_2\)O\(_{5.5}\) and EuBaCo\(_2\)O\(_{5.5}\) in the insulator phase at 80 K. The inset shows the low-energy range.
where \( m \) and \( e \) are the mass and charge of an electron, respectively, \( V_{\text{cell}} \) is the volume of the unit cell containing one formula unit, \( \hbar \omega_2 = 4.7 \text{ eV} \), and \( \hbar \omega_1 = 0 \) (the \( \sigma(E) \) curve in the vicinity of 0.3 eV was extrapolated to \( \sigma_\text{stat} \) at \( \omega = 0 \)). The quantity \( N_{\text{eff}} \) is proportional to the number of electrons involved in optical transitions up to the energy \( \hbar \omega_2 \) (equal to 4.8 eV in our case) irrespective of their excitation mechanism. The values of \( N_{\text{eff}} \) calculated from \( \sigma(E) \) at 80 and 430 K are plotted in the inset to Fig. 2. The total spectral weight \( N_{\text{eff}} \) increases with temperature up to an energy of \( \sim 4.7 \text{ eV} \); however, the most noticeable change occurs at \( E < 1.5 \text{ eV} \). The values of \( N_{\text{eff}} \) at low energies are small even in the metallic phase. The redistribution of the optical conductivity spectral weight from the higher interband transition range to a lower region of the spectrum was observed on the metal side of the MI transition for many families of strongly correlated oxides of transition metals [26, 27].

In the metal phase, as can be seen from Fig. 2, the Drude character of \( \sigma(E) \) is suppressed. The deviation from the Drude model (in which \( \sigma(E) \) increases with decreasing energy) is likely to indicate that, even in the high-temperature metallic phase, the carriers are localized due perhaps to the large on-site Coulomb repulsion energy. This conclusion is confirmed by the behavior of the permittivity \( \varepsilon_\text{i}(E) \), which decreases sharply at \( E < 1 \text{ eV} \) and takes on negative values (small in magnitude) at the limit of the spectral range studied for both GdBaCo\(_2\)O\(_{5.5}\) and EuBaCo\(_2\)O\(_{5.5}\).

With the value of the dc conductivity in the metallic phase (\( \sigma = 1000 \Omega^{-1} \text{ cm}^{-1} \)), indicated by a cross on the vertical axis of Fig. 2, it is clear that, at \( E \rightarrow 0 \), there is no contribution from coherent motion of carriers. The optical response of carriers in the compounds differing in the rare-earth ion studied is incoherent in character and, therefore, such a state is not metallic. The observed behavior of \( \sigma(E) \) in the metallic phase is most likely to be inherent in the family of double cobaltites.

In order to analyze the temperature dependence of the absorption edge, the \( \varepsilon_\text{i}(E) \) function of GdBaCo\(_2\)O\(_{5.5}\) in the spectral range studied was fitted by five Lorentzians with maxima at 0.58, 0.91, 1.6, 2.6, and 5.3 eV. Figure 5 shows (in more detail than for EuBaCo\(_2\)O\(_{5.5}\) in our previous paper) the temperature dependences of the optical functions of GdBaCo\(_2\)O\(_{5.5}\) at fixed energy values (2.5, 1.0, 0.41 eV). These dependences differ signifi-
cantly in character in the infrared region of the spectrum (at 0.41 eV) near the lowest energy absorption peak. In the range 220 K < T < 340 K, all optical functions change drastically, whereas above T_{MI} ≈ 360 K and below 220 K the optical characteristics vary only slightly with temperature. The temperature range of significant changes in the optical functions (220 K < T < 340 K) coincides with the range where a sequence of AFM phase transitions occurs and where the temperature dependence of the resistivity has discontinuities in slope. Thus, the significant changes in the optical functions are associated with the onset of long-range AFM ordering [5]. The magnetic ordering causes an effective narrowing of energy bands and the formation of a band gap. The weak temperature dependence of the optical functions at T < 220 K suggests that the band gap persists up to 220 K. The upper limit of the temperature range of changes in the optical functions coincides with the temperature of the structural phase transition observed in the GdBaCo_{2}O_{5.5} crystal at 340 K [6], i.e., below the temperature of the transition to the metallic phase.

Based on the difference between the temperature dependences of the absorption bands at 2.6 and ~0.6 eV, we propose the following interpretation of the nature of the optical transitions forming the absorption spectrum of the double cobaltites. The absence of a strong temperature dependence in the vicinity of the intense absorption band at 2.6 eV indicates that the main contribution to this band comes from the charge-transfer transitions O(2p) → Co(3d). The strong temperature dependence of the lowest-energy absorption band in the vicinity of the AFM phase transition points suggests that a considerable contribution to the absorption edge comes from the intersite transitions Co(3d) → Co(3d). It should be noted that, in the perovskite structure, the direct overlapping of the Co(3d) orbitals is small and the intersite transitions will likewise occur via O(2p) orbitals. Indeed, the fairly strong absorption (ε_2 ~ 5 at 0.4 eV) indicates that there is a contribution from charge-transfer transitions O(2p) → Co(3d). Therefore, the double cobaltites are neither pure charge-transfer insulators nor pure Mott–Hubbard insulators. Most likely, the absorption edge has a dual nature.

This interpretation is in agreement with the results of recent studies of MI transitions in systems related to insulators with a charge-transfer band gap according to the Zaanen–Sawatzky–Allen classification [25]. For nickel monoxide, which is a typical insulator with a charge-transfer band gap, it was shown in [28] that the quasiparticle peak at the Fermi level in the metallic phase is mainly associated with Ni(3d) states, which are strongly hybridized with oxygen, in contrast to the states in Mott–Hubbard systems. In systems with a large on-site Coulomb repulsion energy U, as well as in the cobaltites studied (U ~ 7 eV), the capacity of the quasiparticle peak is fairly small. Therefore, disorder in a system will cause strong suppression of the conductivity, as is the case in the GdBaCo_{2}O_{5.5} compound in the metallic phase.

Earlier, we theoretically and experimentally studied the change in the optical properties caused by a change in the spin state of the Co^{3+} ion in the isoelectronic compounds LaCoO_{3} (IS) and HoCoO_{3} (LS) [23]. It was found that, in HoCoO_{3}, the optical conductivity in the narrow spectral range 1.3–2.3 eV increases by a factor of 3 as compared with that in LaCoO_{3}, which was explained by the difference in the spin state of the Co^{3+} ion. In EuBaCo_{2}O_{5.5} and GdBaCo_{2}O_{5.5}, the specific feature (plateau) centered at ~1.6 eV changes in intensity within 14% upon the MI transition. However, we believe that this is most likely due to the transformation of the spectral weight caused by the delocalization of carriers in the metallic phase as a result of the change in the spin state of the Co^{3+} ion. We note that the plateau in the range 1.2–1.8 eV decreases in intensity (in comparison with the peak at ~3 eV) upon the change (LS, 80 K) → (HS, 430 K) in the spin state of the Co^{3+} ion in the (Eu, Gd)BaCo_{2}O_{5.5} compounds.

4. CONCLUSIONS

The results of the study of the variations in the optical properties with temperature and the calculations of the electronic structure of the double cobaltites RBaCo_{2}O_{5.5} (R = Eu, Gd) in the vicinity of the metal–insulator (MI) phase transition are as follows:

(1) It has been shown that the changes in the optical properties and, hence, in the electronic structure associated with the MI transition in these compounds are caused by a redistribution of the optical spectral weight from the higher energy range of interband (charge-transfer) transitions to the lower energy range covering a wide interval, 1.0–3.5 eV. At present, such a behavior is believed to be due to the strongly correlated metal state.

(2) In the paramagnetic metallic phase, the Drude contribution has been found to be suppressed. The optical response on the metal side of the MI transition is significantly incoherent in character, which is the specific feature of the metallic phase of the family of double cobaltites (i.e., it is independent of the rare-earth ion) and can be explained by the fact that the narrow quasiparticle peak at the Fermi level is significantly suppressed by the inevitable disorder in the samples of the system studied.

(3) In the temperature range 220–340 K, wherein a sequence of magnetic phase transitions occurs, we have observed a strong temperature dependence of the optical functions for the low-energy absorption band centered at ~0.6 eV (in GdBaCo_{2}O_{5.5}) and 0.2 eV (in EuBaCo_{2}O_{5.5}) [15] and a weak temperature dependence in the vicinity of the main absorption band at 2.6 eV. These dependences were used to identify the type of
interband transitions. It was assumed that the $R_BaCo_2O_{4.5}$ compounds do not belong to pure charge-transfer insulators or pure Mott–Hubbard insulators.

(4) The optical band gap width has been estimated to be 0.05 eV in $Eu_BaCo_2O_{5.5}$ and 0.26 eV in $GdBaCo_2O_{5.5}$. This difference can be due to the different quality of the crystals.

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