1. INTRODUCTION

The discovery of high-temperature superconductivity in cuprates and, a short time later, colossal magnetoresistance in manganites have aroused great interest in layered oxides of transition metals. Among layered oxides, cobaltites stand out by a particular variety of properties and complex phase diagrams, including regions with various structural, charge, orbital, and spin orders. This is associated, first, with their structural diversity: layered cobaltites can be formed not only based on CoO₂ planes with a square lattice (for example, La₂₋ₓSrₓCoO₄ [1]) but also can include CoO₂ planes with a triangular lattice (for example, Na₄CoO₂ [2, 3]) or a kagome lattice (for example, YBaCo₅O₇₋ₓ [4]). Second, the specific feature of cobalt ions is an additional degree of freedom for a fixed charge state associated with the possibility of electron redistribution over orbitals and, correspondingly, the change in the spin states of ions [5]. Specifically, the Co³⁺ ions can be in three different spin states with close energies, i.e., the low-spin (S = 0), intermediate (S = 1), and high-spin (S = 2) states. The thermal excitation or change in the local crystal environment of the cobalt ions can transform them from one spin state to another state, thus resulting in the appearance of unusual spin superstructures and additional phase transitions [5].

In recent years, cation-ordered phases of layered cobalt oxides RBaCo₅O₇₋ₓ (where R is a rare-earth element) have attracted considerable attention of researchers [6–16]. Unlike half-substituted cubic perovskites of the composition A_b₄A'_5BO₃₋ₓ in which the A and A' ions are randomly distributed over positions, in cation-ordered phases with a structure shown in Fig. 1, the A and A' cations are grouped in layers that alternate along the c axis, which leads to the doubling of the unit cell along the c axis. For an oxygen content in the vicinity of x = 0.5, the oxygen ions in the GdO₅ layers are aligned in filled and empty chains along the a axis, which results in the formation of alternating ac planes composed of the cobalt ions with the octahedral oxygen environment and pyramidal environment (where one-half of the apical oxygen ions is absent).
of the unit cell. The driving force of the cation ordering is a difference between the ionic radii, specifically of the Ba$^{2+}$ and R$^{3+}$ ions. The “parent” compounds $R$BaCo$_2$O$_{5+x}$ at low temperatures are band-gap insulators with all cobalt ions in one charge state of 3+. A wide range of possible oxygen contents $x$ makes it possible to perform electron ($x < 0.5$) and hole ($x > 0.5$) doping of parent insulators $R$BaCo$_2$O$_{5.5}$ in order to modify their properties [12]. However, it turns out that, even without change in the stoichiometry, the insulating state in the $R$BaCo$_2$O$_{5.5}$ compounds becomes unstable with an increase in the temperature and the compounds transform into a metallic state at temperatures $T_{MI} \approx 270–370$ K depending on the rare-earth element $R$ and the accuracy in setting of the oxygen stoichiometry $x = 0.50$ [6–14]. For example, this transition in the GdBaCo$_2$O$_{5.5}$ compound is observed at the temperature $T_{MI} \approx 360–365$ K [7, 9–13].

Despite the performed careful investigations, the mechanism of the metal–insulator transitions in the $R$BaCo$_2$O$_{5.5}$ compounds has remained unclear to date. Initially, this transition was interpreted as a result of the ordering of oxygen into chains along the $a$ axis (Fig. 1) and a related distortion of the crystal structure [7]. Subsequent structural and magnetic investigations showed that the transition into the metallic state can be associated with the spin transition of Co$^{3+}$ ions located in octahedral positions from the low-spin state (at $T < T_{MI}$) to the high-spin state (at $T > T_{MI}$) [10–12]. However, the phenomenological model of magnetic transitions, which was proposed by Taskin et al. [11, 12], was also questioned using the neutron and muon scattering data [15, 16]. In particular, according to the data obtained by Luetkens et al. [16], the high-spin state of the Co$^{3+}$ ions is retained at $T < T_{MI}$ and the spin transitions occur in a stepwise manner at considerably lower temperatures. As a result of discrepancies in the description of the spin transitions, mutually contradictory models have been proposed for explaining the transport and magnetotransport properties of $R$BaCo$_2$O$_{5+x}$ cobaltites.

One of the possible approaches to the determination of the position of spin transitions consists in studying the thermal expansion coefficient, because the spin transition, i.e., the electron redistribution over orbitals, changes the ionic radius and, hence, should lead to a change in the unit cell volume [17, 18]. At presence, the data on the temperature dependence of the unit cell volume for the $R$BaCo$_2$O$_{5.5}$ compounds with a resolution required for determining the spin transitions have been scarce and, sometimes, contradictory. For example, in direct experiments on the thermal expansion of GdBaCo$_2$O$_{5+x}$, a decrease in the volume was observed upon heating above the transition point $T_{MI} \approx 359$ K and comparable changes in the volume were also observed at $T_k \approx 163$ K. However, as follows from X-ray diffraction data, the transition to the metallic state in the GdBaCo$_2$O$_{5+x}$ compounds is accompanied by an increase in the volume [7, 8, 10]. Furthermore, both a stepwise increase and a decrease in the unit cell volume at the temperature $T_{MI}$ were observed for compounds with other rare-earth elements [13, 14].

Precise measurements of the temperature dependence of the unit cell volume for $R$BaCo$_2$O$_{5+x}$ samples with the accurately specified stoichiometry $x = 0.50$ would make it possible to determine the temperature or the temperature range of the spin transition and to elucidate the mechanism of magnetic transitions and magnetotransport phenomena. It should be noted that, in order to solve this problem, the use of ceramic samples is more preferable. In the measurement of $R$BaCo$_2$O$_{5+x}$ single crystals, it is difficult to exclude the problems associated with both the orthorhombic twinning of crystals [11, 12] and the necessity of their triple thermal cycling (for measurements of all components of the anisotropic expansion) in the temperature range with a high mobility of oxygen ions [12, 19].

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Polycrystalline samples of the GdBaCo$_2$O$_{5+x}$ compound were prepared using the solid-phase synthesis. The initial reactants Gd$_2$O$_3$ (ITO MGr grade), BaCO$_3$ (special purity grade), and Co$_3$O$_4$ (analytical grade) preliminarily annealed at 800°C (Gd$_2$O$_3$), 700°C (Co$_3$O$_4$), and 500°C (BaCO$_3$) were mixed in a stoichiometric ratio and sequentially sintered at 900, 950, and 1000°C for 20 h at each temperature. After each annealing, the mixture was carefully ground with the use of acetone. Finally, the prepared powder was pressed in pellets and annealed for 35 h at 1045°C. The X-ray diffraction pattern of the prepared single-phase sample GdBaCo$_2$O$_{5.5}$ corresponds to the known X-ray diffraction patterns for representatives of this family (GdBaCoCu$_2$O$_y$, GdBaCuFeO$_5$, and LnBaCo$_2$O$_{5+x}$). The necessary oxygen content $x \approx 0.50$ in the GdBaCo$_2$O$_{5+x}$ samples was produced with the use of subsequent annealing and quenching with the technique described in detail in [12]. An extremely high mobility of oxygen in the GdBaCo$_2$O$_{5+x}$ compound [12, 19] allowed us to achieve a uniform oxygen distribution in dense samples $\approx 1$ cm$^3$ in size.

The electrical resistance was measured by the conventional four-probe technique with the use of rectangular bars sawn from the GdBaCo$_2$O$_{5.5}$ pellet. The dilatometric investigations were performed by the capacitance method [20] with the pellet 10 mm in diameter and 12 mm in height. The end surfaces of the pellet were made parallel to each other and polished. A measuring cell represented a plane-parallel capacitor. One plate of the capacitor was immovably fixed to the