X-ray and neutron diffraction studies of coupled structural phase transitions in DyBaCo$_2$O$_{5.5}$

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Abstract

A structural transition at $T \approx 322$ K from the $P mmm$ to $P mma$ phase is found to coincide with an anomaly of resistivity. Another structural phase transition doubling the lattice parameter $c$, which has been postulated earlier to accompany a low-temperature magnetic transition in TbBaCo$_2$O$_{5.5}$, is observed in a single crystal DbBaCo$_2$O$_{5.5}$ by means of the X-ray and neutron diffraction. The low temperature phase does not belong to the space group $P cca$ that has been chosen earlier as the highest subgroup of the $P mma$. The transition is of the first order with the temperature hysteresis, between $T \approx 100$ and $T \approx 200$ K, which probably explains anomalous magnetic properties in this temperature range.

Key words: Cobaltites, Phase transitions, X-ray diffraction, Neutron diffraction

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1. Introduction

The rare-earth ($R$) oxides $R$BaCo$_2$O$_{5+\delta}$ have a double-perovskite structure, with all the cobalt ions formal oxidation being 3+ at $\delta = 0.5$. A competition between the intra-atomic exchange and the crystal field results in three possible spin states of the Co$^{3+}$ ions: the low-spin (LS, $t_{2g}^6$, $S = 0$), the intermediate-spin (IS, $t_{2g}^5e_{g}^1$, $S = 1$), and the high-spin (HS, $t_{2g}^4e_{g}^2$, $S = 2$) \[1\]. The small energy differences between these states as well as a twofold degeneracy of the IS electronic configuration leads to the quite unusual magnetic properties including coupled phase transitions (structural/ spin-order/ spin-state-order/ orbital-order) and, probably as a consequence, the giant magnetoresistance. These properties best of all develop themselves in the crystals with well ordered alternating planes $(0,1,0)$ at $y = 0$ and $y = 1/2$ of the Co$^{3+}$ ions in the oxygen pyramids and octahedra, respectively, as shown schematically in Fig. 1 by the grey and white circles. We consider in this paper the only case of $\delta \approx 0.5$ that corresponds to the superstructure $a_2 \approx a_p$, $b_2 \approx 2a_p$, $c_2 \approx 2a_p$, where $a_p$ is a perovskite lattice parameter (Fig. 1). If $\delta$ differs considerably from 0.5, an additional degree of freedom, the charge, should be added, which may be ordered giving unusual superstructures.

The regular study, e.g. \[2\], of the crystal lattice dependence on the oxygen content for a number of slowly cooled $0.17 < \delta < 0.79$ and rapidly quenched $0.23 < \delta < 0.71$ samples PrBaCo$_2$O$_{5+\delta}$ has shown that for the samples, which are expected to be most disordered, the unit cell is close...
to a tetragonal one with the lattice parameters \( a_1 \approx a_p, b_1 \approx a_p, c_1 \approx 2a_p \). Various superstructures, mainly with short-range ordering, were observed \(^3\) in the family \( R = \text{Pr} - \text{Ho} \), with \( \delta \) being varied from 0.3 to 0.7. However, even at the ideal oxygen content, \( \delta = 0.5 \), the ordering of the apical oxygen atoms \( O_1, O'_1, O_2, O_3 \) shown in Fig. 1 by the black circles controls the ordering degree of the alternating octahedral and pyramidal \( \text{Co}^{3+} \) ions. As an example \(^4\), we give the apical oxygen distribution in two single crystals \( \text{Tb}_{0.9}\text{Dy}_{0.1}\text{BaCo}_2\text{O}_{5+\delta} \) observed \(^5\) below \( T_{S1} = 341.5(2) \) K give an evidence of the second order structural phase transition. The unit cell below the \( T_{S1} \) has the lattice parameters \( a_3 \approx 2a_p, b_3 \approx 2a_p, c_3 \approx 2a_p \), and the systematic extinction of the superstructure reflections corresponds to the space group \( Pmna \). Atomic displacements found from the intensities of the superstructure reflections indicate an orbital/spin-state ordering. The neutron powder diffraction patterns of \( \text{TbBaCo}_2\text{O}_{5.53(1)} \) have been successfully treated in the frame of this group \(^6\). Although small atomic displacements cannot influence a powder diffraction pattern, the distribution of the equivalent \( \text{Co}^{3+} \) ions over octahedral and pyramidal sites is completely different in comparison with the \( Pmna \) group. Among the pyramidal cobalt ions, the ions 1 and 4 as well as 2 and 3 are equivalent in the \( Pmma \), while all four ions are equivalent in the \( Pmna \). The octahedral ions 5 and 8 as well as 6 and 7 yield a similar chess-board-like order (Fig. 1). This difference is very important for the magnetic/spin-state/orbital ordering, and the group \( Pnma \) has been later verified \(^4\) with a twin-free single crystal of \( \text{Tb}_{0.9}\text{Dy}_{0.1}\text{BaCo}_2\text{O}_{5.54(3)} \), the material that is expected to have the properties similar to the Tb ones studied in \(^6\). The first objective of our work is to check whether this phase transition is typical for the \( R\text{BaCo}_2\text{O}_{5.5} \) materials.

The value of \( T_{S1} \) measured for \( \text{GdBaCo}_2\text{O}_{5.47(2)} \) is close to the metal-insulator transition \( T_{MI} = 359 \) K for the same oxygen content \(^7\). Since the transport properties should depend on the orbital ordering \(^8\), the second objective is to verify whether these critical temperatures coincide when measured for the same crystal in identical temperature conditions.

To explain the magnetic structure at \( T = 100 \) K of \( \text{TbBaCo}_2\text{O}_{5.53(1)} \) we have postulated \(^9\) a structural phase transition at about 170 K to the phase with the lattice parameters \( a_4 \approx 2a_p, b_4 \approx 2a_p, c_4 \approx 4a_p \), as shown in Fig. 1. Since the experiment was made with a ceramic sample, and no very weak superstructure reflections could be observed for selecting the space group by their extinction, we have suggested a highest subgroup of the \( Pmna \) with the wave-vector \( \mathbf{k} = c_3/2 \), which is \( Pcca \), for the space group of the hypothetical new phase. Our third, the main objective, is to look for the low-temperature struc-

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**Fig. 1.** Four unit cells, observed in \( R\text{BaCo}_2\text{O}_{5.5} \) at different oxygen content, a degree of oxygen ordering and temperature. Cobalt ions in the pyramidal and octahedral sublattices are shown by the grey and white circles, respectively. Oxygen atoms in the apical positions are described by black circles. The other oxygen atoms are in the corners of the coordinating polyhedra. The \( R \) and \( \text{Ba} \) atoms are omitted for simplicity.
tural phase transition, to investigate its character and to verify whether the systematic extinction of the X-ray superstructure reflections yields the $Pcca$ group suggested earlier.

2. Experimental methods

Single crystals of DyBaCo$_2$O$_{5+\delta}$ were grown from an overstoichiometric fluxed melt which was prepared in accordance with optimal composition in the DyO$_{1.5} - \text{Ba}_2\text{Co}_3\text{O}_y$ cross section of the Gibbs triangle [4]. Relatively large (up to $5 \times 6 \times 0.5 \ mm^3$) single crystals of rectangular shape were grown in a furnace with a vertical chamber supplied by Cr-La resistive heaters. A batch of Dy$_2$O$_3$ was put as feeder on the bottom of a 100 cm$^3$ magnesia crucible to keep the flux melt saturated at temperature of about 1200 °C under positive temperature gradient 1–3 °C and to grow a limited number of nuclei for about three weeks of isothermal crystal growth process. The as-grown single crystals were annealed in flowing oxygen for about three days. The cooling with rate of 10 °C/h from 660 °C down to 330 °C and then with rate 20 °C/h down to room temperature was used to get $\delta = 0.50(2)$ according to iodometric titration. One of these oxygenated and twinned crystals DyBaCo$_2$O$_{5.5}$ was used in the X-ray diffraction and resistivity measurements. The total oxygen content and the oxygen ordering were verified by means of X-ray diffraction as explained in the introduction. The X-ray value of $\delta$ coincided with that obtained by the iodometric titration in the limits of a standard deviation. As to the oxygen distribution over the apical sites, a small amount (7 – 10 %) of oxygen was always present in the site O’$_1$ that should be vacant in the ideal case.

One of the crystals was cut in a rectangular shape and polished. The edges of the crystal were kept parallel to the crystallographic axes with an estimated error less than 5 degree of arc. In order to remove twins the crystal was kept under pressure of about 0.15 – 0.20 GPa in flowing oxygen at 300 – 350 °C and then quickly cooled to room temperature. We have applied pressure along the longest edge of the rectangular sample, and this direction corresponds to the smallest crystallographic a-axis in the resulting twin-free structure of the sample. The polarized-light microscope image and the susceptibility characterization have indicated less than 4% fraction of the sample survived as b-axis oriented after such a procedure.

The in-plane resistivity $\rho$ of a twinned crystal was measured using a standard dc four-probe method. Two current wires, as well as two voltage ones in between, were connected with the room drying silver paste to one natural crystal face. The face polishing could easily destroy the crystal that had visible microscopic cracks. We were aware of the negative factors, like the contact resistance and, in particular important, additional effects of the surface conductivity. However, our aim was to search for an anomaly in the temperature dependence of resistivity, and possible artifacts were not that dangerous as in quantitative measurements of $\rho(T)$ itself. On contrary, we paid attention to the crystal temperature. The temperature difference with the X-ray experiment including its stability was estimated as about 2 K.

It is commonly believed that the structural changes due to the oxygen atoms should be investigated by means of neutron diffraction. This is obvious when taking into account the scattering ability of oxygen in comparison with heavy atoms. In our case, the crystals were too small for investigation of the superstructures due to the oxygen ordering that produce the Bragg reflections a few orders of magnitude weaker than the basic ones. We combined these two methods in our work. The nuclear and magnetic structure as well as the magnetization density were investigated with a twin-free crystal of $4 \times 3 \times 0.4 \ mm^3$ on 5C1 and 6T2 diffractometers at the ORPHEE reactor of the Laboratoire Leon Brillouin (CE Saclay, France). Here we present only the temperature dependence of some Bragg reflections, mainly of the magnetic origin, to be compared with the X-ray and resistivity data. The other results will be published elsewhere. For historical reasons, the neutron studies were made at the beginning, and, because of the cobalt activation by neutrons, we were left for the X-ray and resistivity measurements with a twinned crystal that was checked to have the total oxygen content and distribution over the apical positions as in the first one, before the detwinning procedure. As explained in the next section, a conclusion on the low-temperature crystal symmetry can be made even with a twinned crystal. The crystal had thickness of about 0.2 mm, and was enough transparent for the Mo $K\alpha$ radiation $\lambda = 0.712\AA$. As usually [5], the voltage on a 2 kW X-ray tube was set lower then the high-energy edge of the white spectrum for avoiding any $\lambda/2$ contaminations in the primary beam after a PG monochromator.
3. Results and discussions

The temperature dependence of the peak intensity for the superstructure reflection (3,1,1)+(1,3,1), as well as the basic one (6,2,2)+(2,6,2) from a twinned crystal is displayed in Fig. 2(a), with the indices being given for the unit cell with parameters \(a_3 \approx 2a_p, b_3 \approx 2a_p, c_3 \approx 2a_p\). A continuous structural transition is definitely seen at \(T_{s1} \approx 323\) K, and the temperature variation of both reflections is identical, as shown by a solid line in Fig. 2(a), where two intensities are reduced to one scale by their average value in the temperature range 293 – 321 K. For comparison, a similar transition in GdBaCo\(_2\)O\(_{5.47}(2)\) has been observed at \(T_{s1} \approx 341.5(7)\) K. The X-ray data obtained earlier for a twin-free crystal Tb\(_{0.9}\)Dy\(_{0.1}\)BaCo\(_2\)O\(_{5.54(3)}\) has given unambiguous evidence that at this transition the symmetry changes from \(Pmnm\) with the unit cell \(a_2 \approx a_p, b_2 \approx 2a_p, c_2 \approx 2a_p\) in the high-temperature phase to \(Pmma\) with \(a_3 \approx 2a_p, b_3 \approx 2a_p, c_3 \approx 2a_p\).

We may conclude that this phase transition is a common phenomenon, at least for the \(R\)BaCo\(_2\)O\(_{5.5}\) materials with \(R\) ions from the middle of the rare-earth period. It has been suggested that the structural changes are driven by the orbital/spin-state ordering of the \(Co^{3+}\) ions, which may be expected to influence the transport properties. Possible mechanisms, like spin blockade, are suggested in the unusual magnetic properties of field-cooled and zero-field-cooled crystals in the temperature range \(120 < T < 210\) K, when the crystal is heating. On the crystal cooling this transition begins at \(T = 200\) K and ends at \(T = 150\) K. The variation of the basic reflection \((8,0,0) + (0,8,0)\) shown in Fig. 3(c) is similar to that of the superstructure pair \((3,0,1) + (0,3,1)\).

In the range of this wide temperature hysteresis, the unusual magnetic properties of field-cooled and zero-field-cooled crystals in the temperature range \(120 < T < 210\) K, probably, may be due to coexistence of two phases with different crystal and magnetic structures.

In spite of the twins, it is definitively proved that \(Pcca\) is not a correct space group for the low-temperature phase. Both reflections, \((3,0,1)\) and \((0,3,1)\), are forbidden in this group. A systematic inspection of the reflections \((h,0,l) + (0,k,l)\) has shown that some of them forbidden by symmetry, namely with \(h\) and \(l\) odd, are observed in contradiction with the extinction law for the space
group $P_{cca}$. We should remind that this group was postulated as a highest subgroup \[15\] of the $P_{mma}$ with the wave-vector $\mathbf{k} = \frac{3c}{2}$. Strictly speaking, this argument can be exclusively used for the second order phase transitions. Having the first order transition, we can but try different groups with the proper extinction laws.

4. Conclusions

1. The structural transition at $T_{S1}$ from the $Pmm$ ($a_p \times 2a_p \times 2a_p$) to $Pmna(2a_p \times 2a_p \times 2a_p)$ phase is observed in three isomorphic materials $R$BaCo$_2$O$_{5+\delta}$, ($R$ = Gd, Tb$_{0.9}$Dy$_{0.1}$, Dy) with $\delta = 0.50(2)$ and the well ordered Co$^{3+}$ sites in pyramidal and octahedral coordination. This phase transition is very likely to be a general phenomenon, at least for the $R$ ions from the middle of the rare-earth period.

2. The temperature of the structural phase transition $T_{S1}$ and the $\rho(T)$ anomaly coincide with a precision of $2 – 3$ K, which gives indication to the orbital ordering at this transition. The details of this ordering, in principle, can be derived from the distances between the cobalt ions and intermediate ligands.

3. A structural phase transition of the first order to the phase with the unit cell $2a_p \times 2a_p \times 4a_p$ is discovered in the magnetically ordered state. This transition occurs at $200 < T < 210$ K on heating, while on cooling it is extended from 150 K to 110 K. Unusual magnetic properties observed in this temperature range \[12,13\] probably may be explained by coexistence of two phases with different crystal and magnetic structures.

4. The systematic extinction of the superstructure reflections in the low-temperature phase does not yield the space group $P_{cca}$ that has been postulated \[6\] as a highest subgroup of $P_{mma}$ with the wave-vector $\mathbf{k} = \frac{c}{2}$, an argument that can be only used in the case of the second order transitions.

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