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Charge ordering driven metal-insulator transition in the layered cobaltite $HoBaCo_2O_{5.5}$

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In this Brief Report we report high-resolution synchrotron x-ray diffraction and x-ray pair-distribution-function analysis as a function of temperature on the $HoBaCo_2O_{5.5}$ cobaltite. These investigations provided a direct evidence of a structural phase transition from an orthorhombic to a monoclinic phase in the $HoBaCo_2O_{5.5}$ layered cobaltite which occurs concomitantly with the metal to insulator transition. The structural data suggest a possible charge ordered state in the monoclinic phase which may be responsible for the insulating character at low temperature.

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Layered perovskite oxides of transition metal (TM) ions are extremely fascinating materials due to their rich structural, electronic, and magnetic phase diagrams which is a consequence of the strong coupling between charge and spin degrees of freedom.[1–5] Recently, much attention has been devoted to the investigation of REBaCo$_2$O$_{5+\delta}$ systems (RE =rare earth) where, differently from other compositions, the Co ions add a further degree of freedom related to the Co spin state. In addition, the δ value can theoretically vary from 0 to 1 thus allowing a continuous doping of the square-lattice CoO$_2$ planes which not only influences the mean Co valence state but also the carrier nature, the Co spin state and the bandwidth. In the REBaCo$_2$O$_{5.5}$ samples all the Co ions are in the +3 oxidation state and this composition is characterized by an equal number of ordered CoO$_6$ octahedra and CoO$_5$ square pyramids.

One of the most interesting member of the layered cobaltites is the HoBaCo$_2$O$_{5+\delta}$ system for δ=0.50. This composition is characterized by an abrupt metal to insulator transition (MIT) around ~300 K which is also coupled to a drastic change in the inverse magnetic susceptibility $(1/\chi)$.[2,6] Let us remember that the most common view is that in this compounds, at sufficiently low temperature, the Co^{3+} ions adopt the intermediate-spin (IS), configuration ($t_{2g}^5e_g^1$) in the pyramids and the low-spin (LS) configuration (t_{2g}^6) in the octahedra, whereas they are both in the high-spin (HS) or IS state above the MIT.

One still open question is related to the origin of the MIT in HoBaCo$_2$O$_{5.5}$. In 2004 Maignan *et al.*[2] proposed a model, to explain the change in the transport properties, based on a complete or partial conversion of the HS Co^{3+} located in the octahedra to the LS state. This conversion "immobilizes" the electron charge carriers due to the phenomenon of spin blockade, and the latter is replaced by an activated regime for holes (LS Co^{4+}) moving in the much narrower t_{2g} band.[4] A recent neutron diffraction investigation[7] has shown that the MIT above 305 K occurs concomitantly with the melting of the orbital order in the pyramids and increase in the Co-O-Co bond angle together with unit-cell volume collapse. At the same time, the observed isotope effect ruled out a possible mechanism based on a LS to HS spin state transition in the pyramids as suggested for the GdBaCo$_2$O$_{5.5}$ system.

In this Brief Report we are going to provide experimental evidences of a previously unknown structural phase transition in the HoBaCo$_2$O$_{5.5}$ cobaltite crossing the MIT. In particular, by means of high-resolution synchrotron x-ray powder diffraction (XRPD) and pair-distribution-function (PDF) analysis we will provide a direct evidence of an orthorhombic to monoclinic symmetry change which occurs concomitantly with the MIT. This result provides input and evidences for the consideration and reconsideration of the MIT in layered cobaltites and, in general, in strongly correlated electron systems with a layered perovskite structure. We stress that in other members of the REBaCo$_2$O$_{5.5}$ family a structural transition has been observed as well. This was reported for the Tb, Nd, and Gd compounds where a *Pmmm* to *Pmma* phase transition was observed together with the MIT.[8,9] However, the very interesting point is that, for the HoBaCo$_2$O$_{5.5}$ cobaltite only (at least considering the REBaCo$_2$O$_{5.5}$ samples investigated so far), the presence of a *Pmma* symmetry in the insulating phase is not compatible with the structural changes observed (as it will be shown later). On the other hand, the HoBaCo$_2$O$_{5.5}$ cobaltite is the only one showing a six order of magnitude increase at the MIT which can be correlated with the different structural behavior reported here.

HoBaCo$_2$O$_{5.5}$ has been prepared by means of solid-state reaction and the oxygen content fixed and checked as described by Diaz-Fernandez *et al.*[6] High-resolution synchrotron x-ray diffraction (XRD) and total scattering measurements have been carried out on the ID31 beamline at ESRF (Grenoble-France). XRD patterns have been refined by means of the Rietveld method with FULLPROF software.[10] To obtain the PDFs, the data were processed using PDFGETX2 (Ref. 11) while the structural modeling was carried out using the program PDFFIT2.[12]

Figure 1 presents some selected XRD patterns collected on the HoBaCo$_2$O$_{5.5}$ cobaltite in a temperature range from 318 to 245 K with temperature steps of about 5 °C. As can be appreciated very clear peaks splitting occurs starting from 291 K together with a sudden and significant change in the lattice parameters. The (single) phase is observed at 286 K since the point at 291 K shows the simultaneous presence of both phases. This phase behavior clearly indicates a first-order phase transition type between the two polymorphs. Close inspection of the low-temperature patterns indicates that reflection such as the $(h,2k,0)$ are clearly splitted in two peaks. Let us remember that the room-temperature structure is orthorhombic [*Pmmm* space group (sg)] with lattice constants of a=3.82529(3) Å, b=7.86112(7) Å, c

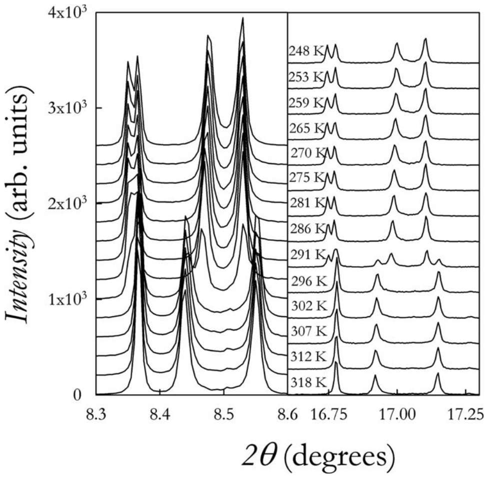

FIG. 1. XRD patterns of HoBaCo$_2$O$_{5.5}$ as a function of temperature in two selected regions of the 2θ range.

$=7.52529(7)$ Å, and $V=226.094(4)$ Å^3 as determined from the Rietveld refinement using the XRPD patterns collected at room temperature. A suitable and complete description of the observed low-T structure has been obtained by refining the data with the monoclinic $P112/m$ space group. Figure 2 shows the pattern at 200 K refined by means of the Rietveld method for the $P112/m$ symmetry (panel A) and for the $Pmma$ symmetry (panel B—found for the other REBaCo$_2$O$_{5.5}$ cobaltites investigated so far in the literature).[8,9] Both space groups are symmetry related to the $Pmmm$ sg through a group-subgroup relation but the plot presented in Fig. 2 clearly shows that in the insulating phase the HoBaCo$_2$O$_{5.5}$ cobaltite adopts the monoclinic $P112/m$ symmetry. The phase is characterized by a γ which differs from 90° with respect to the orthorhombic structure together with a significant change in lattice parameters. Refined structural parameters for the data at 286 K are: $a=3.85271(3)$ Å, $b=7.81948(7)$ Å, $c=7.50963(6)$ Å, $\gamma=90.067(7)°$, and $V=226.237(3)$ Å^3. A sketch of the lattice constants, cell volume, and γ angle variation as a function of temperature is reported in Fig. 3. The trend of lattice parameters is in good agreement with some recent structural data reported on the HoBaCo$_2$O$_{5.5}$ cobaltite as a function of temperature which have been determined by means of high-resolution neutron diffraction.[7] However, in that paper the authors could not see the phase transition occurring at the MIT due to the intrinsic lower resolution of neutron diffraction with respect to synchrotron data and, in particular, of the data presented in this Brief Report (collected at $\lambda=0.3998$ Å). Probably, the only possible evidence of the structural phase transition in a neutron diffraction experiment could be a slight peak broadening in the temperature interval of existence of the monoclinic phase.

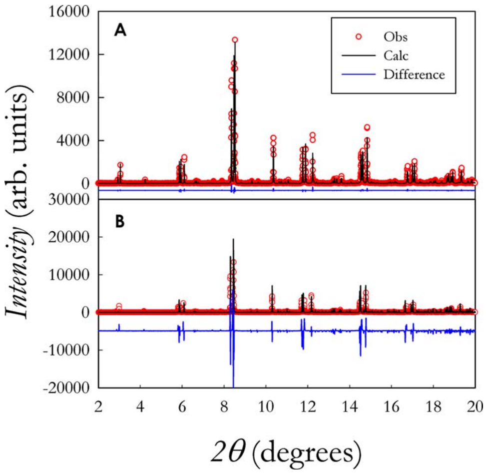

FIG. 2. (Color online) XRD pattern of HoBaCo$_2$O$_{5.5}$ at 200 K refined by means of Rietveld method by assuming a monoclinic symmetry (panel A) and an orthorhombic symmetry (panel B). Red (gray) empty circles represent the experimental pattern, black line the calculated one. The lower horizontal blue (dark gray) line shows the difference between the calculated and experimental patterns.

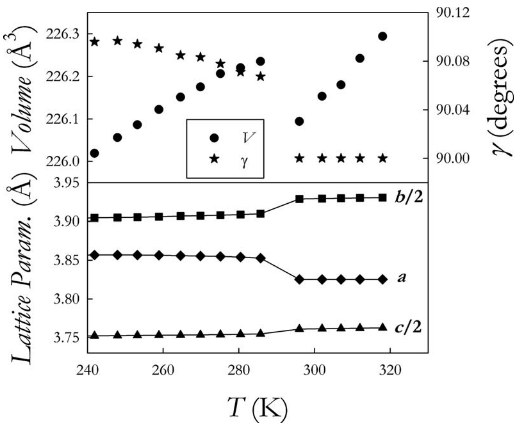

FIG. 3. Variation in structural parameters of HoBaCo$_2$O$_{5.5}$ as a function of temperature.

The relevant structural modifications induced by the phase transition can be nicely seen in the bond lengths changes occurring in the CoO$_5$ and CoO$_6$ polyhedra. Let us remember that at this oxygen content (5.5) there is a preferential localization of the extra oxygen atoms (with respect to an oxygen content of 5) at the $(0,\frac{1}{2},\frac{1}{2})$ position ($1g$ in $Pmmm$ sg) instead of a random distribution between this site and the $(0,0,\frac{1}{2})$ site ($1c$ in $Pmmm$ sg). This has also been checked in the present case through neutron diffraction measurements (D1A instrument, ILL–Grenoble) at room temperature followed by Rietveld refinement. It was found that the $(0,\frac{1}{2},\frac{1}{2})$ site is nearly fully occupied (approximately 94%) while the $(0,0,\frac{1}{2})$ site has a very low occupation (approximately 6%). This corresponds to an alternate coordination of the Co ions in pyramids and octahedra along the b direction. In all the XRPD and PDF refinement the oxygen occupancies have been fixed to those determined from neutron diffraction.

Figure 4 shows a sketch of the bond lengths changes at the phase transition by showing the pyramids and octahedra coordination environments at 296 K (A) and 286 K (B). The most relevant change occurring in the monoclinic phase is related to the pyramids where the in-plane bonds show a marked difference between them [1.892(2) and 1.978(9) Å] with respect to the values found in the orthorhombic phase [1.952(3) and 1.967(9) Å]. Overall, the octahedra environ-

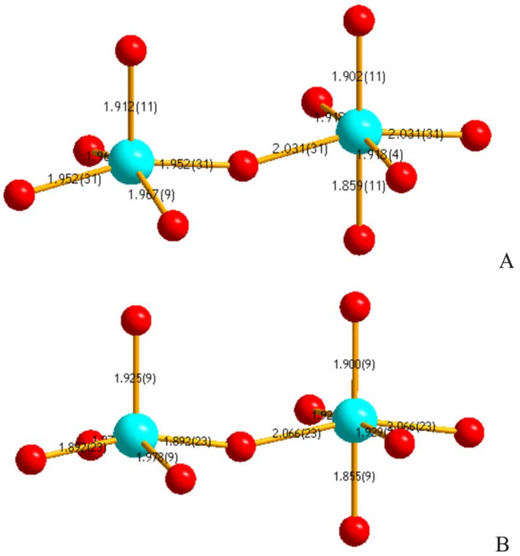

FIG. 4. (Color online) Sketch of the Co-O coordination environment at 296 K (panel A) and 286 K (panel B).

ment shows a slight contraction of the two apical bonds and a small increase in the two in-plane Co-O bond lengths.

A further insight into the structure of the $HoBaCo_2O_{5.5}$ cobaltite has been achieved by means of PDF analysis. Total x-ray scattering data have been collected at 320 and 200 K. The aim of the PDF investigation was to look at the short-range order of the cobaltite above and below the MIT and also use this probe to get a further indication of the symmetry change on the local scale.

Figure 5 shows the fit of the 320 K PDF by means of the *Pmmm* structure. The R_w of the refinement is 8.0% which witness a very high quality of the fit. Table I reports the Co-O bond lengths obtained from the Rietveld refinement using the XRPD data at 320 K and those obtained from the PDF fit. There is a general agreement between the two data sets suggesting that the average structure properly describes the local structure. In addition, it can be seen that the average Co-O bond length within the two polyhedra is very close each other which is also true for the average in-plane and out-of-plane lengths.

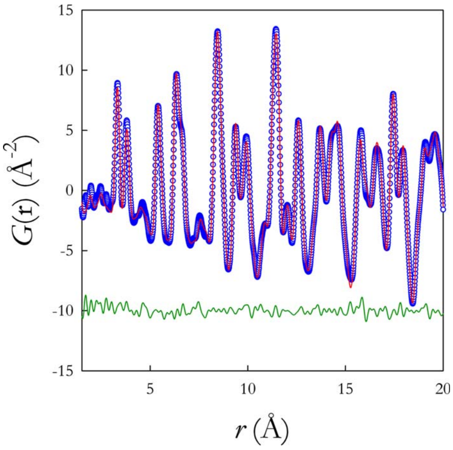

FIG. 5. (Color online) PDF fit of $HoBaCo_2O_{5.5}$ at 320 K with the *Pmmm* model. Blue (dark gray) empty circles represent the experimental *G*, red (gray) line represents the calculated *G*, and the lower horizontal green (light gray) line represents the difference.

TABLE I. Bond lengths of the $HoBaCo_2O_{5.5}$ at different temperatures after Rietveld and PDF refinements. Co1 are the Co ions in the octahedra and Co2 in the pyramids. O5, O6, and O7 are equatorial oxygen atoms while O1, O2, and O3 are axial oxygen atoms. O3 is the oxygen lying in the HoO_δ plane $(0,\frac{1}{2},\frac{1}{2})$.

(Å)/(deg)	320 K Rietveld	320 K PDF	200 K Rietveld	200 K PDF
Co1-O6	1.920(3)	1.890(5)	1.938(3)	1.945(6)
Co1-O7	2.07(2)	2.05(2)	2.08(2)	2.09(4)
Co1-O2	1.901(11)	1.94(1)	1.897(8)	1.906(6)
Co1-O3	1.862(11)	1.881(8)	1.854(8)	1.844(6)
Co2-O5	1.963(9)	1.99(1)	1.980(7)	1.996(9)
Co2-O7	1.92(2)	1.938(5)	1.87(2)	1.88(2)
Co2-O1	1.929(11)	1.93(1)	1.927(8)	1.923(6)
Co1-O7-Co2	159.8(1)	158.6(2)		
⟨Co-O⟩octa	1.957(9)	1.950(1)	1.965(11)	1.970(10)
⟨Co-O⟩pyr	1.939(11)	1.957(1)	1.925(10)	1.935(12)

Figure 6 reports, on panel A, the comparison between the experimental PDFs at 320 and 200 K. As can be appreciated, significant differences are evident between the two data sets. A reliable description of the PDF at 200 K has been obtained by using the monoclinic $P112/m$ space group. The result of the fit of the 200 K data with this starting structure is reported in panel B of Fig. 5. The R_w of the refinement is 9.1%. Selected bond lengths for the structure at 200 K are reported in Table I as well.

The structural investigation reported in this Brief Report clearly shows that the MIT occurring in the $HoBaCo_2O_{5.5}$ cobaltite is accompanied to a structural phase transition from an orthorhombic to a monoclinic structure. In addition, a

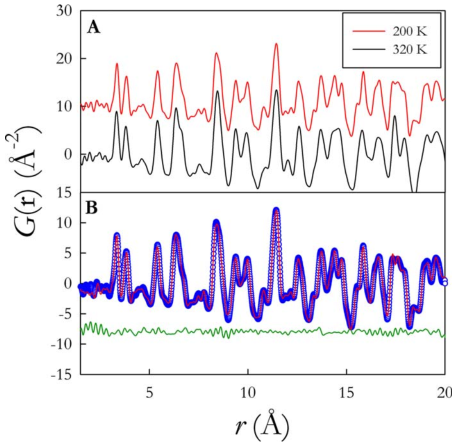

FIG. 6. (Color online) Panel A: Comparison of PDFs at 320 (black line) and 200 K (dark gray line). Panel B: fit of $HoBaCo_2O_{5.5}$ at 200 K with the $P112/m$ model. Blue (dark gray) empty circles represent the experimental *G*, red (gray) line represents the calculated *G*, and the lower horizontal green (light gray) line represents the difference.

dramatic change in the Co coordination environment is found passing from the metallic to the insulating phase. Apart from the single Co-O lengths changes in the polyhedra, a remarkable difference can be observed in the average Co-O bonds in the octahedra and in the pyramids in the orthorhombic phase (data at 320 K) and in the monoclinic phase (200 K). In the monoclinic phase the two $\langle$Co-O$\rangle$ values differs of more than 0.04 Å while they are very similar (within the estimated error) at high temperature, i.e., in the orthorhombic phase. The other remarkable feature is the presence of two significantly different in-plane lengths for the pyramidal Co ions in the monoclinic phase with respect to the orthorhombic phase.

The overall data collected and presented in this Brief Report shed a light on the changes occurring concomitantly with the MIT in the $HoBaCo_2O_{5.5}$ cobaltite. A plausible *scenario* that may account for the observed physical properties changes and structural variations at the MIT points toward a charge-separation phenomenon within the layered cobaltite. The presence of nearly equal $\langle$Co-O$\rangle$ lengths between octahedra and pyramids in the orthorhombic phase is indicative of a similar average Co oxidation state and—most probably—of spin state in the two polyhedra. In the monoclinic phase, the inequivalence of the two Co sites suggests that the average Co oxidation in the pyramids and octahedra is different and, in a purely ionic and localized picture it could be seen as Co^{4+} ions in the pyramids and Co^{2+} ions in the octahedra. Values of the average Co-O lengths in the octahedra in the monoclinic phase are closer to the average value of the Co-O bond found, for example, in the CoO oxide (1.965 Å), while for the pyramids the $\langle$Co-O$\rangle$ value moves toward an average lengths found in CoO_2 (1.920 Å). A similar trend and results have been found recently in several Ni-containing perovskite systems where high-resolution x-ray diffraction studies allowed the observation of structural phase transition from orthorhombic to monoclinic phases at the MIT accompanied by a charge disproportionation and ordering.[13–15]

Within the charge-separated systems the Co^{4+} ions (in the pyramids) will adopt a LS state while the Co^{2+} ions (in the octahedra) will be in the HS state. This electronic arrangement does not allow an easy electron exchange between Co ions thus resulting in an insulating state. This situation is in agreement with the proposed "spin-blockade" mechanism suggested by Maignan *et al.*[4] In addition, the charge ordering proposed in this work most probably occurs together with an orbital ordering in the *ab* plane as also suggested by other authors[7] and confirmed by the peculiar variation in the in-plane bond lengths in the monoclinic phase.

In addition, the structural phase transition found for the Ho cobaltite at the MIT differs from the phase transition found at the MIT for all the others cobaltites studied up to now. This unique feature of the Ho-containing sample is of great importance in order to understand its behavior with respect to the conductivity and magnetic data. As mentioned before, this cobaltite is the only one presenting an impressive six orders of magnitude rise of resistivity at the MIT. Such a behavior can be understood in the framework of the monoclinic more distorted structure with distinct Co-O environments found for this sample with respect to the Gd, Tb, and Nd containing cobaltites which show a less distorted *Pmma* orthorhombic structure below the MIT.[8,9]

In conclusion, we have provided direct evidence of a structural phase transition from an orthorhombic to a monoclinic phase in the $HoBaCo_2O_{5.5}$ layered cobaltite which occurs concomitantly with the metal to insulator transition. The structural data suggest a possible charge ordered state in the monoclinic phase which may be responsible for the insulating character at low temperature. These results provide an input for the understanding of MIT in layered cobaltites and open the way to exciting question and further experimental and theoretical work to be done on this specific system and, in general, on the layered cobaltites.

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