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# The effect of oxygen disorder on magnetic properties of PrBaCo<sub>2</sub>O<sub>5.50</sub> layered cobaltite

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## Abstract

Oxygen vacancy disorder is very common in RBaCo<sub>2</sub>O<sub>5+ $\delta$</sub>  cobaltites with large rare earths (R). This disorder affects the magnetic interactions and, obviously, the magnetic properties of these compounds. In this work we report the preparation and characterization of a well ordered PrBaCo<sub>2</sub>O<sub>5.50</sub> sample that has allowed us to study their magnetic properties and (by means of neutron powder diffraction) their low temperature magnetic structure in the absence of disorder. By comparison with a sample presenting 10% of oxygen vacancy disorder its effect on the studied properties has been determined.

## 1. Introduction

Research on cobalt oxides has become a very attractive field during the last years. Within the field of transition metal oxides, cobalt oxides are especially appealing because cobalt shows a great facility to present different spin states at different temperatures. This capacity has been a puzzling problem that has given rise to controversy for several years [1–5]. This additional degree of freedom (spin state) is strongly coupled with lattice, magnetic and transport properties, making cobalt oxides even more complex than other transition metal oxides where this degree of freedom is quenched. As an example of a direct effect of spin state degree of freedom we must mention the large Seebeck coefficient of different misfit cobaltites [6, 7].

Recently, there has been much interest in the study of layered RBaCo<sub>2</sub>O<sub>5+ $\delta$</sub>  (R = rare earth;  $0 \leq \delta \leq 1$ ) cobaltites [8–20]. These compounds present two characteristic structural features. The first one is that R and Ba ions in the A position of the perovskite do not form a solid solution but order in alternate planes along the (001) direction. The second one is that these compounds show a great tendency to present oxygen

vacancies that locate in R planes forming ordered structures. These structural features give rise to an ordered distribution of Co in pyramidal and octahedral coordination.

Maignan *et al* [9] showed that the oxygen content of these compounds can be tailored by heat treatments in different atmospheres. In general, small rare earths tend to stabilize smaller values of  $\delta$ . The role of oxygen content is crucial in this family. It controls not only the mean valence of Co ions (that can vary from 3.5+ for  $\delta = 1$  to 2.5+ for  $\delta = 0$ ) but also the coordination of Co (pyramidal or octahedral). It is of relevance to remark that d-level splitting due to the crystal field is determined by the environment. This makes  $\delta$  strongly influence the spin state of Co ions. On the other hand, the spin state is directly related to the orbital occupancy of the outermost d-electrons that will determine the superexchange magnetic interactions (Goodenough–Kanamori rules). Consequently the magnetic and transport properties of these compounds are strongly influenced by the oxygen content and the environment of Co ions. Less studied is the possible influence of the size of the rare earth. This parameter also influences the crystal field on Co ions and hence it can also affect their spin state.

In this work we center our attention on the role of oxygen vacancy ordering. The influence of this order has not been

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studied in depth. The reason for this is that most of the previously studied compounds (namely those with small rare earths) do not present disorder of oxygen vacancies. Studies on larger rare earths like Pr show that the order between oxygen ions and vacancies is often not perfect and that this parameter strongly influences the magnetic properties [21–23].

The role of this order is of special interest in the case  $\delta = 0.50$  where a certain controversy regarding the ordered magnetic structures and the spin state of  $\text{Co}^{3+}$  ions has appeared (see [23] and references therein). Whether or not magnetic structures can change with the rare earth is a quite unexplored problem. Comparison of results in [24] with those in [15, 23] strongly suggest such a dependence. However, vacancy disorder is present in the sample studied in [23] and, in view of results presented here, it must also be present (but not reported) in the sample studied in [15].

The goal of this work is twofold. First, to investigate the magnetic properties and low temperature magnetic structure of well ordered  $\text{PrBaCo}_2\text{O}_{5.50}$ , and second to elucidate the role of oxygen disorder in  $\delta = 0.50$  compounds. Dealing with these goals is mandatory to elucidate the effect of R size in magnetic and transport properties, as far as disorder is preferentially present for large rare earths.

## 2. Experimental details

A  $\text{PrBaCo}_2\text{O}_{5.50}$  sample with a relatively high amount of oxygen vacancy disorder was prepared as reported in [25]. This previous study, by means of neutron and synchrotron x-ray powder diffraction, revealed that the degree of disorder is 10% (thus, 10% of vacancy positions are occupied by oxygen ions and vice versa). Hereafter, we will refer to this sample as PBC-D.

The initial  $\text{PrBaCo}_2\text{O}_{5+\delta}$  used to get a well ordered  $\text{PrBaCo}_2\text{O}_{5.50}$  sample was prepared by sol–gel methods. Praseodymium acetate hydrate (Strem Chemicals, Inc.), barium acetate and cobalt acetate tetrahydrate (Alfa Aesar) were dissolved in the correct stoichiometric ratio in distilled water at 60 °C for a few minutes. Then, an excess of citric acid monohydrate (Sigma-Aldrich) was added to the solution until saturation. The mix was held at 110 °C under vigorous stirring in order to evaporate the water solvent and the resultant acetic acid. The final product was a dark violet gel which was thermally fired at 550 °C in a muffle furnace for 5 h in order to eliminate the organic material. The black powder obtained was pressed into pellets at 10 tons and calcined in a tubular furnace at 1075 °C for 80 h under air. The bars were then cooled slowly ( $-60\text{ }^\circ\text{C h}^{-1}$ ) to room temperature (RT). Laboratory x-ray powder diffraction data show that initial  $\text{PrBaCo}_2\text{O}_{5+\delta}$  was well crystallized and free from impurities up to the detection limit of the technique (1 wt%).

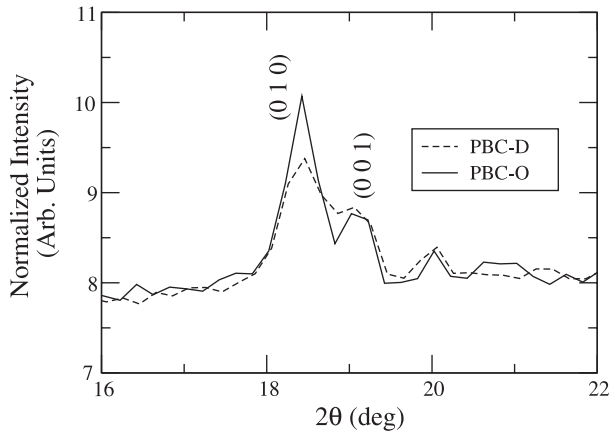
To reduce the as-prepared sample (with  $\delta \simeq 0.75$ ) to  $\delta \simeq 0.50$  to get an optimal vacancy ordering, we introduced the as-prepared  $\text{PrBaCo}_2\text{O}_{5+\delta}$  in a Pyrex ampoule together with a large amount of metallic Cu. We sealed the ampoule, annealed it at 460 °C for 180 h, and then slowly cooled it ( $-3\text{ }^\circ\text{C h}^{-1}$ ) down to RT. This procedure is similar to that used in [22] but based on a different principle. In that work the authors use an

evacuated ampoule with a calculated amount of Cu in order to get exactly the desired value of  $\delta$  (0.50 in the present case) and heated it up to a very high temperature. By this procedure, presumably, the cobaltite reduces below the desired value but the oxygen released by the sample remains in the ampoule and is not completely captured by metallic Cu (the amount of Cu introduced in the ampoule is calculated for this purpose). On cooling the sample recovers the oxygen released and not got by Cu, giving rise to the desired  $\delta$  value. Instead, we have just heated up to 460 °C to equilibrate, in the sample, the desired value of  $\delta$ . All the released oxygen and the oxygen present in the initial atmosphere is trapped by the Cu getter. To estimate the appropriate temperature we have taken into consideration the results reported in [22] and also the results reported in [25] where it is shown that the value of  $\delta$  at different temperatures and different oxygen partial pressures is mainly controlled by the temperature. In addition, reference [26] reports that the order–disorder transition between oxygen ions and vacancies takes place at 500 °C. With this, our annealing temperature is below this transition, so the appearance of order will occur during the annealing, but is sufficiently high to ensure a good mobility of oxygen vacancies. Hereafter we will refer to this sample as PBC-O. The obtained compound was characterized by means of laboratory x-ray diffraction and found to be well crystallized and free from impurities. The refinement of x-ray diffraction data rendered a cell volume per Co ion of  $V/\text{Co ion} \simeq 58.55\text{ \AA}^3$ . According to table 1 in [22] this corresponds to an oxygen content above  $\delta = 0.46$  ( $V/\text{Co ion} \simeq 58.58\text{ \AA}^3$ ) and near  $\delta = 0.50$  ( $V/\text{Co ion} \simeq 58.53\text{ \AA}^3$ ).

Thorough structural studies have been carried out using neutron powder diffraction on different beamlines at ILL (D2B,  $\lambda = 1.594\text{ \AA}$ , D1B  $\lambda = 2.52\text{ \AA}$  and D20  $\lambda = 2.42\text{ \AA}$ ), at different temperatures between 5 K and RT; and using synchrotron x-ray powder diffraction (SXRPD) at the ID31 beamline of ESRF (Grenoble, France). A short wavelength  $\lambda = 0.39978(25)\text{ \AA}$ , to reduce the absorption, was selected with a double-crystal Ge(111) monochromator and calibrated with Si NIST ( $a = 5.43094\text{ \AA}$ ). Optimum transmission was achieved by enclosing the finely ground sample in a 0.5 mm diameter borosilicate glass capillary, and appropriate spinning of the capillary in the beam ensured good powder averaging. Diffraction data were analyzed with the Rietveld method using FullProf suite of programs [27]. Magnetic characterization was done using a commercial SQUID magnetometer (Quantum Design).

## 3. Results and discussion

As a result of the difference in the preparation route between PBC-D and PBC-O samples, subtle differences between their NPD patterns can be appreciated. The most evident one is the difference in the intensity of the (0 1 0) diffraction peak, coming from the periodicity introduced by oxygen ordering. This difference is shown in figure 1. As explained in section 2, the joint Rietveld refinement of SXRPD and NPD data for PBC-D [23] showed that, within  $\text{PrO}_{0.50}(001)$  planes, 10% of the oxygen ions are placed occupying vacancy positions and

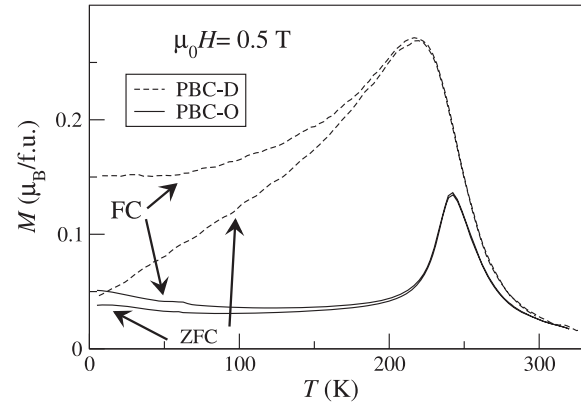


**Figure 1.** Detail of the room temperature NPD patterns showing (010) and (001) peaks (the intensity of the former comes from the order of oxygen ions) of PBC-D and PBC-O samples. The intensity has been normalized using the integrated intensity of the most intense diffraction peak [(122)].

vice versa. For PBC-O room temperature SXRPD and NPD (collected on D1B) patterns can be successfully refined jointly ( $\chi^2 = 6.5$ ,  $R_B = 2.5$  for SXRPD and  $\chi^2 = 7.5$ ,  $R_B = 4.9$  for NPD) using the  $Pm\bar{m}m$  space group ( $a_p \times 2a_p \times 2a_p$  cell). The joint refinement uses the same structural parameters (atomic positions, thermal displacement parameters, occupancies and cell parameters) for both patterns. This joint refinement renders a much smaller concentration of oxygen ion–oxygen vacancy antisites for PBC-O, around 1%, than for PBC-D (10%). To further investigate the significance of this result we have refined diffraction data for the PBC-O sample by imposing a disorder of 10%. This leads to an enhancement of  $R_B$  of the NPD pattern from 4.9 to 5.5. This allows us to conclude that oxygen ordering in the PBC-O sample is nearly perfect in contrast with the PBC-D sample. This joint refinement has also allowed us to corroborate the value of  $\delta$  estimated from the unit cell volume at RT: the refinement of oxygen occupancies gives  $\delta = 0.51(2)$ .

### 3.1. Effect of vacancy ordering on magnetic properties

Figure 2 shows the DC magnetization versus temperature measured under an applied field of  $\mu_0 H = 0.5$  T for PBC-D and PBC-O. This figure reveals several differences between the two samples. The magnetic behavior of PBC-O is more similar to that displayed by other  $R\text{BaCo}_2\text{O}_{5.50}$  cobaltites with small R ions like Y, Tb or Gd [9, 12, 13, 28]. This is characterized by the appearance, on cooling, of a small FM signal, followed by its sharp disappearance on further cooling. Following the nomenclature we used in [23] we will refer to the first (on cooling) transition temperature as  $T_{N_1}$ , defined as the point where  $M(T)$  presents an inflection point; and to the second as  $T_{N_2}$ , defined as the point where  $M(T)$  curve presents a maximum. Similar magnetic behavior has been reported for other rare earths [9, 13, 24, 28, 29]. The appearance in these compounds of a FM signal at  $T_{N_1}$  is due to the stabilization of a canted AFM structure [23, 24, 29]. The transition at  $T_{N_2}$  is due to the formation of a fully AFM structure [23, 24]. With

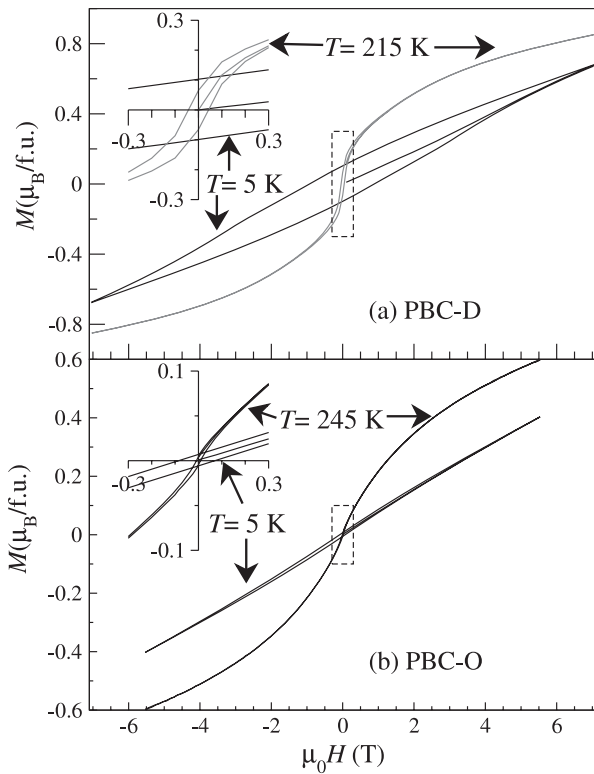


**Figure 2.** ZFC and FC DC magnetization versus temperature for PBC-O (solid lines) and PBC-D (dashed lines) measured under an applied field of  $\mu_0 H = 0.5$  T.

the above definitions, we found: for PBC-D  $T_{N_1} = 245(5)$  K and  $T_{N_2} = 215(5)$  K; and, for PBC-O,  $T_{N_1} = 250(3)$  K and  $T_{N_2} = 242(3)$  K. Remarkably, the magnetic moment measured at  $T_{N_2}$  is considerably smaller for PBC-O ( $0.14(1) \mu_B/\text{fu}$ ) than for PBC-D ( $0.27(2) \mu_B/\text{fu}$ ). It is also worth mentioning that PBC-O presents only tiny differences between ZFC and FC curves in contrast with PBC-D where the differences are huge. Moreover, the transition at  $T_{N_2}$  is quite abrupt for PBC-O and the magnetic moment measured below the transition is very small. Instead, for PBC-D the transition is very wide and the moment below this transition diminishes slowly on cooling.

Differences in the magnetic behavior of the two samples can be understood by considering that oxygen disorder introduces disorder in the magnetic interactions. This disorder shifts down the transition temperature, and makes ZFC and FC magnetization curves very different in PBC-D sample. Disorder can also give rise to a distribution of transition temperatures responsible for the widening of the transitions in PBC-D sample.

Differences found in  $M(T)$  curves are also visible in the isothermal magnetization curves (figure 3). The measures done near  $T_{N_2}$  (mainly the low field region, insets of figure 3) show the great difference in the FM moment between the two samples. Both the remanence and the coercive field are much smaller for PBC-O ( $m_0 = 0.005(1) \mu_B/\text{fu}$  and  $H_C = 95(5)$  Oe) than for PBC-D ( $m_0 = 0.061(5) \mu_B/\text{fu}$  and  $H_C = 410(20)$  Oe). The behavior displayed at 5 K, although quantitatively very different, is qualitatively similar. Both compounds present a wider hysteresis loop at 5 K than at  $T_{N_2}$  (where the maximum of the magnetization takes place). For PBC-D we find  $m_0 = 0.102(5) \mu_B/\text{fu}$  and  $H_C = 9300(200)$  Oe, while for PBC-O these values are  $m_0 = 0.007(1) \mu_B/\text{fu}$  and  $H_C = 750(50)$  Oe. In spite of this, we realize that this does not signal the presence of ferromagnetism at low temperature. The behavior of the first magnetization curve indicates that the magnetic moment is completely induced by the magnetic field rather than being spontaneous. The induced moment does not saturate with strong fields ( $\mu_0 H \geq 6$  T) and the magnetization process is not reversible: the release of the field does not produce a reversal of the  $M(H)$  curve.

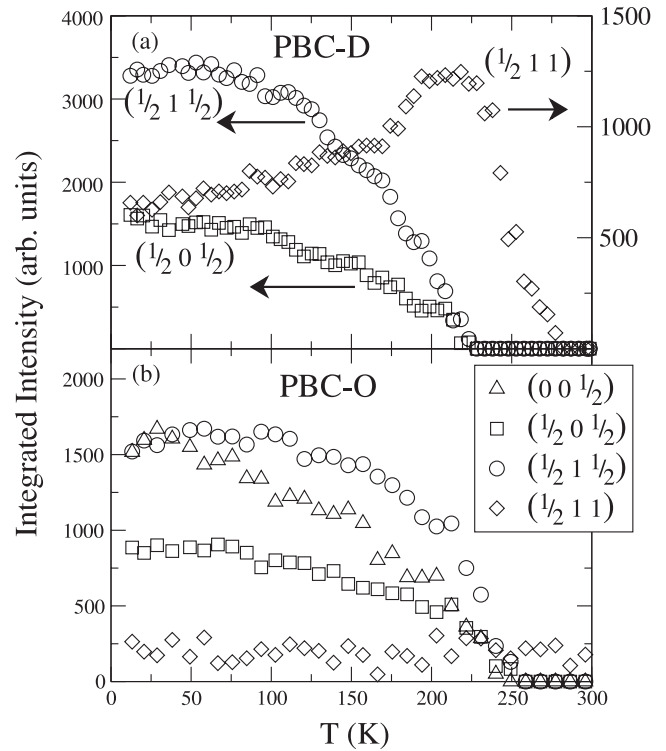


**Figure 3.** Isothermal DC magnetization versus field for PBC-D (a) and PBC-O (b). Measures have been done after zero field cooling from RT at 5 K and near the corresponding  $T_{N_2}$ . Insets show in detail the regions (of the main panels) enclosed in the dashed lines.

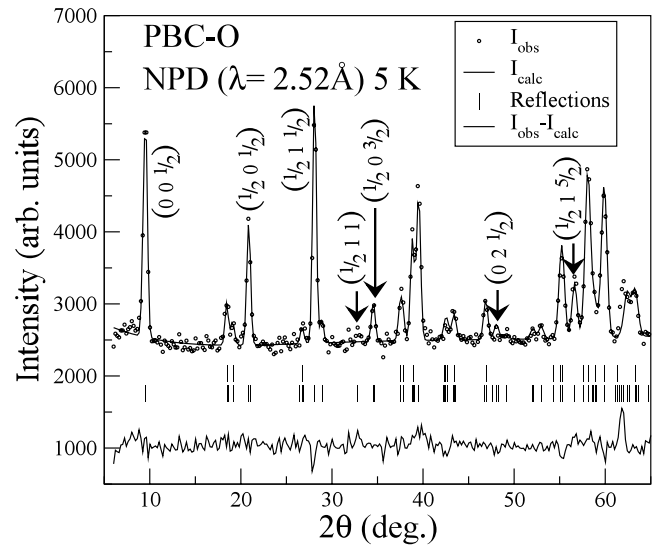
This is rather unusual behavior, specially in the case of the nearly disorder-free sample PBC-O. The low temperature state consists of an AFM arrangement of magnetic moments (see next subsection) with quite a high Néel temperature ( $T_{N_2} = 242(3)$  K). This invariably indicates strong magnetic interactions in the absence of disorder, and one would expect a robust low temperature antiferromagnetic structure. In spite of this, the effect of the magnetic field is a continuously induced ferromagnetic moment. This behavior cannot be attributed to disorder but must be an intrinsic property of this system. Beside this observation, the amount of magnetic moment remaining when the magnetic field is released increases with the amount of disorder and depends on the strength of the applied magnetic field.

### 3.2. Effect of vacancy ordering on magnetic ordering

Low temperature NPD diffraction patterns of both PBC-D and PBC-O samples present magnetic peaks. In accordance with results previously reported for other rare earths [15, 24], these magnetic peaks can be indexed with a magnetic cell that doubles both  $a$  and  $c$  lattice parameters (for both samples). Figure 4 shows the integrated intensity of the most intense magnetic peaks found in NPD patterns for both samples. This figure anticipates deep differences between the magnetic ordering in PBC-D and PBC-O samples. A dissimilarity that, from our point of view, is very relevant concerns the evolution

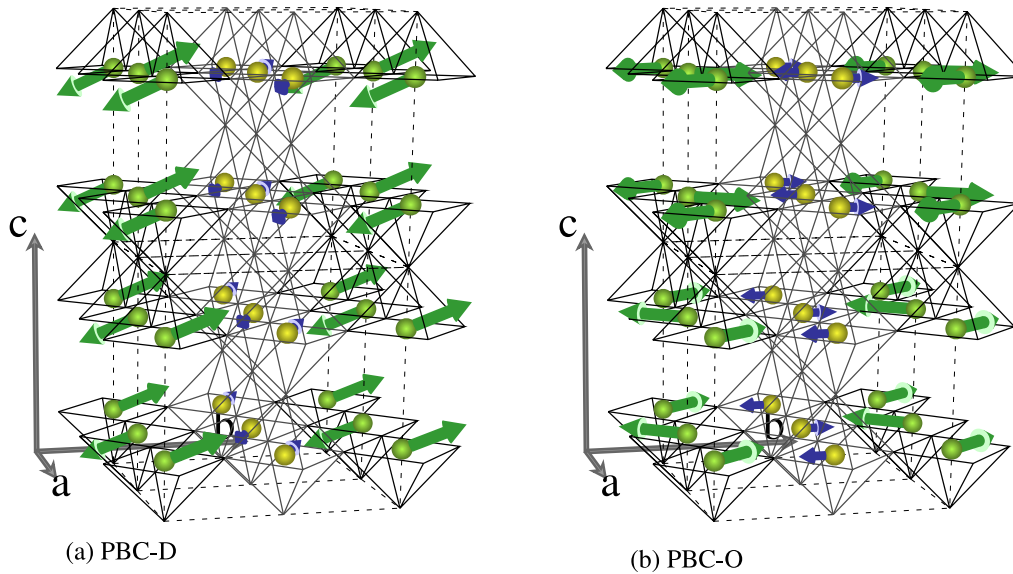


**Figure 4.** Integrated intensity, as a function of temperature, of the most intense magnetic peaks found by NPD for (a) PBC-D and (b) PBC-O samples.



**Figure 5.** Low angle region of the NPD pattern of the PBC-O sample collected at 5 K using the magnetic structure depicted in figure 6(b), showing the magnetic reflections. The most important magnetic peaks are indexed. For clarity, we have also indicated the position of  $(\frac{1}{2} 1 1)$  reflection.

of  $(\frac{1}{2} 1 1)$  reflection. In PBC-D this peak appears (on cooling) at  $T_{N_1}$ , it starts to shrink slowly at  $T_{N_2}$  and is still present at low temperature. A very similar behavior of this reflection is found for  $\text{NdBaCo}_2\text{O}_{5.50}$  [15]. In both cases [15, 23] the



**Figure 6.** Magnetic structures found for (a) PBC-D and (b) PBC-O at low temperature. For the PBC-D sample regions with the sketched magnetic structure coexist with regions presenting another magnetic structure, as explained in [23]. For simplicity only Co ions are plotted. (This figure is in colour only in the electronic version)

low temperature magnetic peaks have been accounted for by assuming the coexistence of two different magnetic structure at different regions of the samples. One phase (the majority) has a magnetic cell doubling both  $a$  and  $c$  cell parameters, while the second only doubles  $a$ . The existence of this second phase is directly related to the persistence of the  $(\frac{1}{2}11)$  magnetic peak at low temperature. In contrast, for PBC-O, the thermal evolution of this peak shows no variation with temperature. If this evolution exists, it is below the error bar of our data. Consequently, we have described the low temperature magnetic structure using a single phase, as in smaller rare earths [24].

In order to refine the low temperature NPD (D1B) patterns, we have restricted the cell positions to those found by the Rietveld refinement of SXRPD data. Figure 5 shows the low angle part of the refined pattern together with the indices of several magnetic peaks. We have found that the 5 K NPD pattern can be very well refined ( $\chi^2 = 4.2$ ,  $R_M = 14.0$ ) with the magnetic ordering presented in figure 6. This figure also presents, for the sake of comparison, the magnetic structure found for PBC-D (majority phase) [23].

This magnetic structure is characterized by the fact that the Co moment depends only on the Co environment: we have used one magnetic moment for all pyramids ( $\mu_p = 2.7(5) \mu_B$ ) and another for octahedra ( $\mu_o = 1.2(4) \mu_B$ ). This contrasts with other works like that of Fauth *et al* for  $\text{NdBaCo}_2\text{O}_{5.50}$  [15] or that of Plakhty *et al* for  $\text{TbBaCo}_2\text{O}_{5.50}$  [24]. We have tried to release this constraint by refining different moments in different positions with the same environment. However, the refinement does not improve, or even gets worse ( $R_M = 14.9$ ). Different moments on the same environment would signal different spin states of Co ions placed in this environment. In the present case, this is not supported by our SXRPD measurements.

#### 4. Summary and conclusions

The first conclusion of the present work is that, by means of the procedure described in the experimental section, we have been able to prepare a  $\text{PrBaCo}_2\text{O}_{5+\delta}$  sample (labeled as PBC-O) with a very high degree of anion vacancy order (around 99%) and a value of  $\delta$  very near 0.50. This has allowed us to determine the intrinsic (not affected by the disorder) magnetic properties of  $\text{PrBaCo}_2\text{O}_{5.50}$ . Through comparison with the sample studied in [23] presenting 10% oxygen vacancy disorder (labeled as PBC-D), we have also determined the effect of this disorder on magnetic properties and magnetic ordering.

Magnetization versus temperature is strongly influenced by disorder. It is characterized by the appearance, on cooling, of a small ferromagnetic moment (at  $T_{N_1}$ ) followed by the disappearance of this magnetization (at  $T_{N_2}$ ). Both  $T_{N_1}$  and  $T_{N_2}$  are influenced by the degree of disorder. The disorder decreases  $T_{N_1}$  (as one would expect) but it enlarges the magnetization signal and the temperature range where this signal is present by reducing the second transition temperature  $T_{N_2}$ . As a result, ferromagnetism (or the canted AFM structure) is strongly favored by oxygen disorder (at least in the regime of disorder characterized here, up to 10%). The most relevant differences in  $M(T)$  curves are found below the second transition. In the PBC-O sample this transition is sharp while in PBC-D this transition is very smooth and, in fact, a certain ferromagnetic signal is kept down to very low temperatures. This behavior must be attributed to the disorder in magnetic interactions.

Concerning the low temperature isothermal magnetization versus field, we have found that the continuous induction of a FM moment with the field displayed by PBC-D [23] is also found in the PBC-O sample. Thus, this is an intrinsic property of this system rather than a result of the disorder.

At low temperature, our NPD data show that, in PBC-O, only one magnetic structure exists in the system. Thus, the coexistence of magnetic structures reported for PBC-D is a result of the vacancy disorder. This strongly indicates that the NdBaCo<sub>2</sub>O<sub>5.50</sub> sample studied in [15] (presenting also a coexistence of two magnetic structures) also had a certain amount of disorder. The low temperature NPD pattern can be very well described by means of the magnetic structure depicted in figure 6. This is characterized by the strong AFM coupling of magnetic moments through the pyramids sharing the apical oxygen ion as expected from the orbital occupancy in IS pyramids [23]. The magnitude of the magnetic moment is determined by the environment. We have found a moment  $\mu_p = 2.7(5) \mu_B$  for pyramids, slightly larger than that expected for Co<sup>3+</sup> in an intermediate spin state ( $2 \mu_B$ ) but clearly below that of the high spin state ( $4 \mu_B$ ). For octahedra, we have found a moment  $\mu_o = 1.2(4) \mu_B$  that is above the moment for the low spin state but below that of the intermediate spin state. Further research is necessary to clarify the spin state of Co<sup>3+</sup> ions in these systems.

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