# Magnetic properties of novel R₂BaCoO₅ oxides (R = Pr, Nd, Ho)

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## Abstract

The new $Pr_2BaCoO_5$ crystallizes with orthorhombic symmetry, space group *Immm* and the lattice parameters are: $a = 3.8246(3)$ Å, $b = 5.9942(5)$ Å and $c = 11.8539(9)$ Å. Magnetic susceptibility measurements reveal the existence of one-dimensional antiferromagnetic interactions around the room temperature in the $Co^{2+}$ sublattice for the isostructural $Nd_2BaCoO_5$ oxide. Below 20 K neutron diffraction data show three-dimensional antiferromagnetic ordering in which both the $Co^{2+}$ and $R^{3+}$ sublattices are involved. This transition involves a propagation vector $k = [1/2, 0, 1/2]$ in the case of the neodymium oxide; while the wave vector corresponding to the magnetic structure for the $Ho_2BaCoO_5$, which crystallizes in the *Pnma* space group, can be described as $k = [0, 1/2, 1/2]$.

## 1. Introduction

The $R_2BaCoO_5$ oxides form a family of compounds for which only a few members have been characterized and their magnetic properties remain unexplored. From the structural point of view, it is worth noting that these oxides crystallize with two different structural types, depending on the size of the rare earth ion $R^{3+}$ [1–6]. The brown colored $R_2BaCoO_5$ (R = Nd–Dy) oxides show orthorhombic symmetry, space group *Immm*, with the existence of one-dimensional chains of $(CoO_6)$ distorted octahedra along the crystallographic $a$-axis as the main structural feature [1–4]. In the case of yttrium and the heaviest rare earth ions, R = Ho–Lu, the $R_2BaCoO_5$ oxides crystallize in the so-called "Green phase" structure also with orthorhombic symmetry, but space group *Pnma* and it is characterized by the fivefold coordination of $Co^{2+}$ located in isolated $(CoO_5)$ square pyramids [1,2,5]. Moreover, the existence of dimorphism has been reported recently for some members of this family of compounds, namely for R = Tb, Dy, Ho, Er and Tm [4–6].

Previous magnetic susceptibility measurements revealed the existence of strong one-dimensional antiferromagnetic interactions in the case of the brown *Immm* $R_2BaCoO_5$ oxides, while a three-dimensional antiferromagnetic ordering, in which both the $R^{3+}$ and $Co^{2+}$ sublattices are involved, has been detected below 20 K for both structural types [4,5].

In this paper, the synthesis and characterization of the new $Pr_2BaCoO_5$ oxide is described and studies of the magnetic properties of $Nd_2BaCoO_5$ and $Ho_2BaCoO_5$ are discussed based on magnetic susceptibility and neutron diffraction measurements.

## 2. Experimental details

$R_2BaCoO_5$ oxides were prepared by direct reaction in the solid state of a stoichiometric mixture of the high purity starting materials $BaCO_3$ (A.R. Grade), $CoCO_3 \cdot nH_2O$ (99.999%), $Ho_2O_3$ (99.9%), $Nd_2O_3$ (99.99%) and $Pr(CH_3COO)_3 \cdot 3H_2O$ (99.9%). In all cases, the samples were obtained as polycrystalline materials and the synthesis was carried out in alumina crucibles under an argon flow due to the instability of $Co^{2+}$ at high temperatures. The times of firing were 24 h in various thermal treatments with interruptions

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for regrinding in order to maximize surface areas, the homogeneity and hence reaction rates. For the neodymium and holmium compounds, the preparation was done at temperatures up to 1350 °C, while in the case of the praseodymium compound, a temperature of 1150 °C was used in order to avoid melting of the mixture, which takes place at slightly higher temperatures.

The magnetic susceptibility measurements were performed in the temperature range 4.2–300 K, with a fully automatic DSM8 magneto-susceptometer based on the Faraday method. The setup was calibrated with $Hg[Co(SCN)_4]$, $Gd_2(SO_4)_3 \cdot 8H_2O$ and $NH_4Cr(SO_4)_2 \cdot 12H_2O$ as standards. The maximum magnetic field was 14 kG with $HdH/dz \approx 24$ $kG^2$ $cm^{-1}$. The data were corrected for ionic diamagnetism taking the values in emu $mol^{-1}$ of: $-18 \times 10^{-6}$ for $R^{3+}$, $-32 \times 10^{-6}$ for $Ba^{2+}$, $-16 \times 10^{-6}$ for $O^{2-}$ and $-12 \times 10^{-6}$ for $Co^{2+}$ [7].

The X-ray diffraction data were obtained using a Siemens Kristalloflex K810 diffractometer and a D-500 goniometer equipped with a secondary graphite monochromator and Cu $K\alpha$ radiation. Powder diffraction patterns were recorded by step scanning over an angular range of $10° < 2\theta < 120°$ in increments of $0.04°$ and a counting time of 15 s per step.

Neutron diffraction patterns were collected on the DNS powder diffractometer at the Siloë reactor of the CEN-Grenoble (France). The wavelength was $\lambda = 1.347$ Å and the angular range covered was 80° using

a multidetector composed of 800 cells separated by 0.1°.

Both X-ray and neutron diffraction data were analyzed by the Rietveld method using the program FULLPROF [8], which is based on the Young and Wiles refinement program [9]. The shape of the diffraction peaks was estimated to be well represented by a pseudo-Voigt function. In the refinements of the neutron diffraction patterns at room temperature, other phases were taken into account as impurities corresponding to small amounts of unreacted starting materials, $R_2O_3$ and CoO. The low temperature diffraction patterns were treated using the technique of profile matching without structural and magnetic models. Only profile parameters were refined by least squares while integrated intensities were obtained by an iterative method.

## 3. Results and discussion

Figure 1 shows the observed and calculated X-ray diffraction pattern of the new $Pr_2BaCoO_5$ oxide, the structural order is based on an orthorhombic unit cell, space group *Immm*, and the lattice parameters were: $a = 3.8246(3)$ Å, $b = 5.9942(5)$ Å and $c = 11.8539(9)$ Å. It is worth mentioning that $Pr_2BaCoO_5$ is the first praseodymium oxide reported for the $R_2BaMO_5$ families (M = Co, Ni, Cu and Zn). This could be due to the
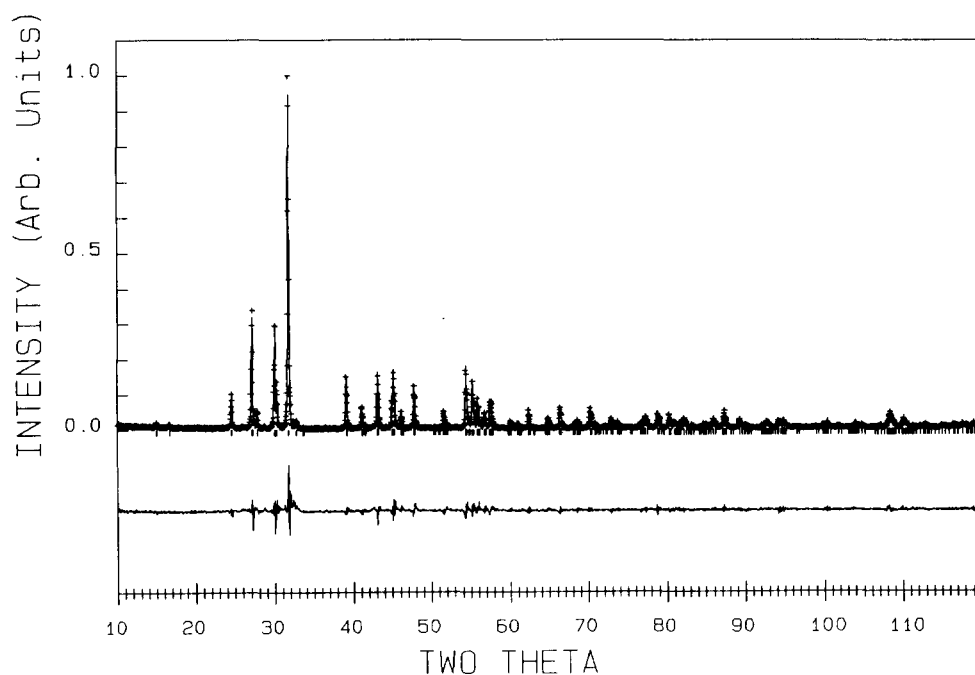


Fig. 1. X-Ray powder diffraction pattern of the new $Pr_2BaCoO_5$ oxide, space group *Immm*. Crosses represent the experimental data and the solid line is the calculated profile. A difference curve is plotted at the bottom. Vertical marks represent the position of allowed Bragg reflections.

difficulty in stabilizing the $Pr^{3+}$ oxidation state. More work is now in progress in order to prepare the remaining $Pr_2BaMO_5$ oxides.

Magnetic susceptibility measurements for this $Pr_2BaCoO_5$ oxide revealed the existence of a small ferromagnetic component probably due to the presence of small amounts of amorphous metallic Co, which strongly masks the paramagnetic signal coming from the $Pr^{3+}$ and $Co^{2+}$ ions. New routes of synthesis are being explored to avoid the reduction of $Co^{2+}$ to metallic cobalt, due to the generation of the CO reducing agent in the thermal decomposition of the praseodymium acetate under argon, which is necessary to prevent the oxidation of $Pr^{3+}$ and $Co^{2+}$ to $Pr^{4+}$ and $Co^{3+}$, respectively.

Figure 2 shows the variation of the reciprocal magnetic susceptibility with temperature for the *Immm* $Nd_2BaCoO_5$ oxide. It can be observed that the susceptibility obeys the Curie–Weiss law over a wide temperature range. The magnetic moment, $\mu \approx 3.8$ BM, agrees fairly well with that expected for the $Nd^{3+}$ only contribution. It is worth noting that the $Co^{2+}$ does not contribute to the magnetic moment, which is indicative of the existence of strong one-dimensional antiferromagnetic interactions above room temperature, within the chains of $(CoO_6)$ octahedra present in this compound.

The downward deviations from the Curie–Weiss behavior below 60 K could be due to the splitting of the $^4I_{9/2}$ ground term of $Nd^{3+}$ under the influence of the crystal field. However, this tendency ceases at about 16 K and a net maximum in the susceptibility appears.
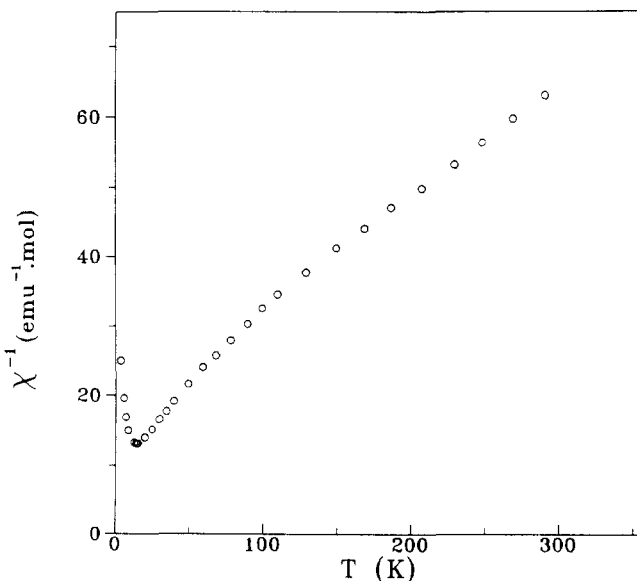
By analogy with the isostructural $R_2BaNiO_5$ oxides [10,11], this behavior can be explained by a three-dimensional antiferromagnetic ordering in which both the $Nd^{3+}$ and $Co^{2+}$ sublattices are involved. In order to confirm this assumption, neutron diffraction data have been obtained at different temperatures.

Figure 3 shows the neutron diffraction patterns measured at 300 K and 2 K. A comparison of both patterns reveals the presence of extra peaks in the 2 K pattern at low Bragg angles, that can be assigned to a three-dimensional magnetic ordering of the sample. The magnetic peaks can be indexed in a commensurate lattice with unit-cell parameters of $a' = 2a$, $b' = b$ and $c' = 2c$; $a$, $b$ and $c$ being the parameters of the chemical cell ($a = 3.8109(4)$ Å, $b = 5.9509(6)$ Å, $c = 11.788(1)$ Å). There is no magnetic contribution to the intensity of the reflections on the nuclear positions. Therefore, the ordered magnetic structure is antiferromagnetic and it can be described in terms of a propagation vector $\mathbf{k} = [1/2, 0, 1/2]$. The one-dimensional antiferromagnetic correlations above room temperature in the $Co^{2+}$ sublattice detected from the magnetic susceptibility data do not produce any Bragg peaks, but a small jump in the background signal at a $2\theta$ angle value corresponding to the one-dimensional antiferromagnetic periodicity along the chain appears.

In the case of the green *Pnma* $Ho_2BaCoO_5$ oxide, a three-dimensional antiferromagnetic order has been proposed in a previously reported work based on magnetic susceptibility measurements [5]. That paper shows upward deviations from linearity in the $\chi^{-1}$ vs. $T$ plot and a negative Weiss constant. Nevertheless, these effects can be due to the crystal field splitting of the $^5I_8$ ground term of the $Ho^{3+}$ ion, however the low $\chi T$ value obtained at 4.5 K indicates possible antiferromagnetic order that is fully confirmed by our neutron diffraction data.

As can be seen in Fig. 4, the neutron diffraction pattern of $Ho_2BaCoO_5$ includes strong magnetic reflections at 2 K. These reflections are even more intense than the nuclear ones, which is a consequence of a contribution to the magnetic moment coming from both the $Ho^{3+}$ sublattices (two cations with an expected value of $gJ = 10$ BM) and the $Co^{2+}$ sublattice (with $2S = 3$ BM). These magnetic peaks have been indexed on a cell of dimensions $a \times 2b \times 2c$, and the antiferromagnetic transition involves a propagation vector $\mathbf{k} = [0, 1/2, 1/2]$, with $a = 12.294(1)$ Å, $b = 5.7069(5)$ Å and $c = 7.0669(6)$ Å.

Further work is now in progress in order to determine the magnetic structures, and in a more accurate way, the Néel temperatures of these compounds.



Fig. 2. Temperature dependence of the reciprocal molar magnetic susceptibility for the $Nd_2BaCoO_5$ oxide, space group *Immm*, $H = 5.6$ kG.
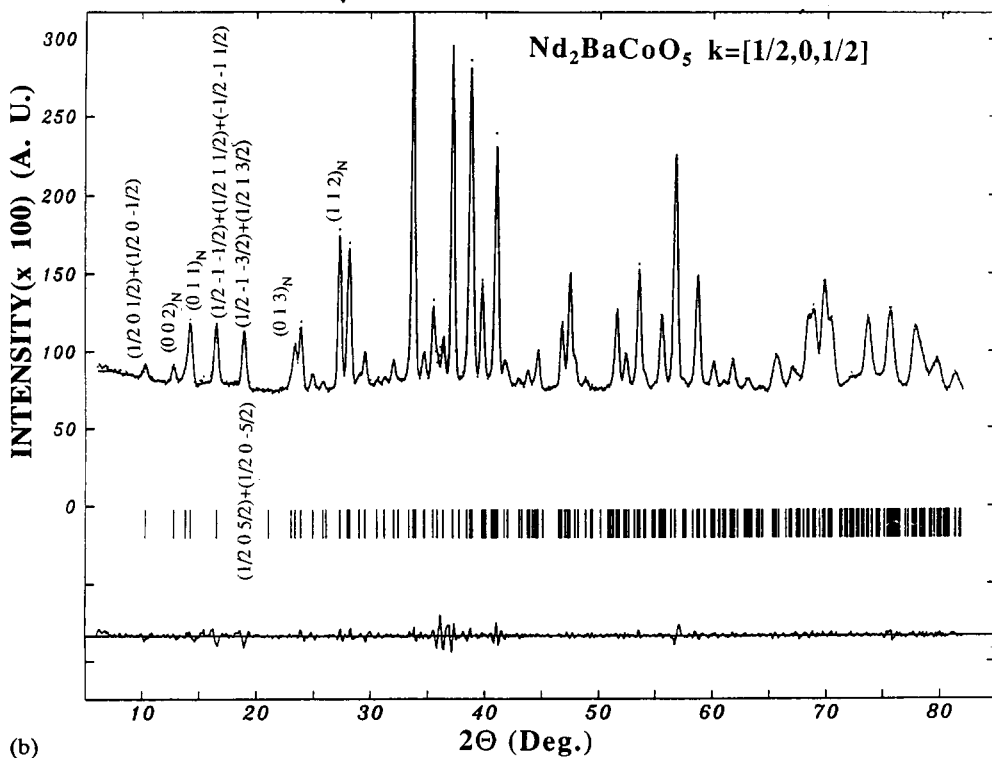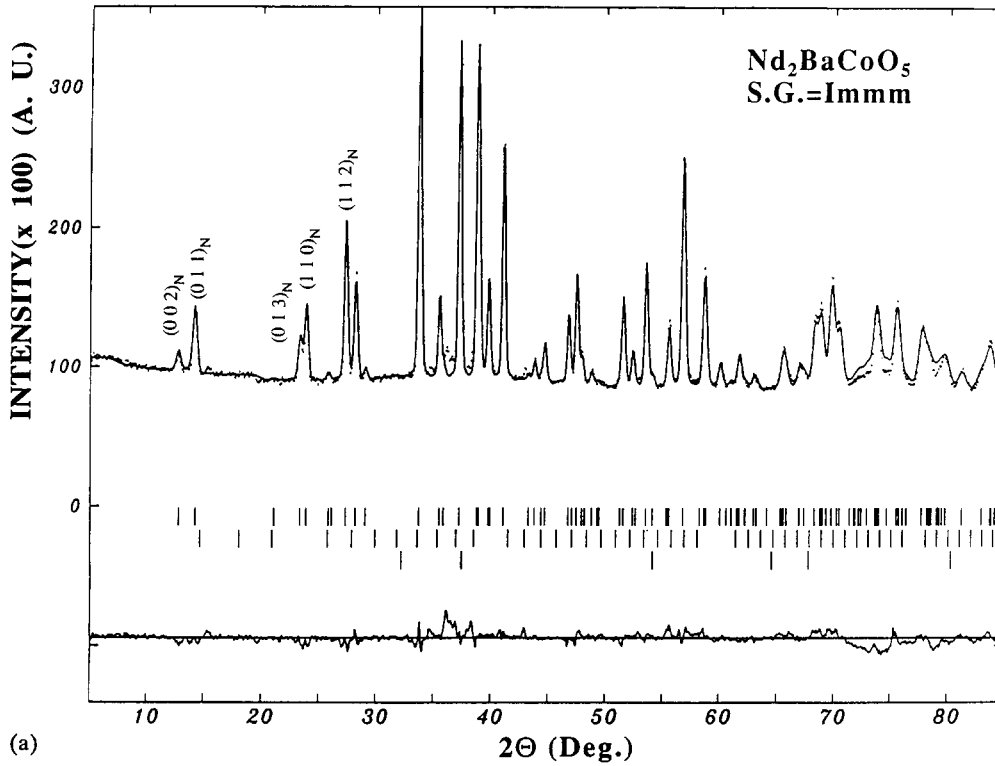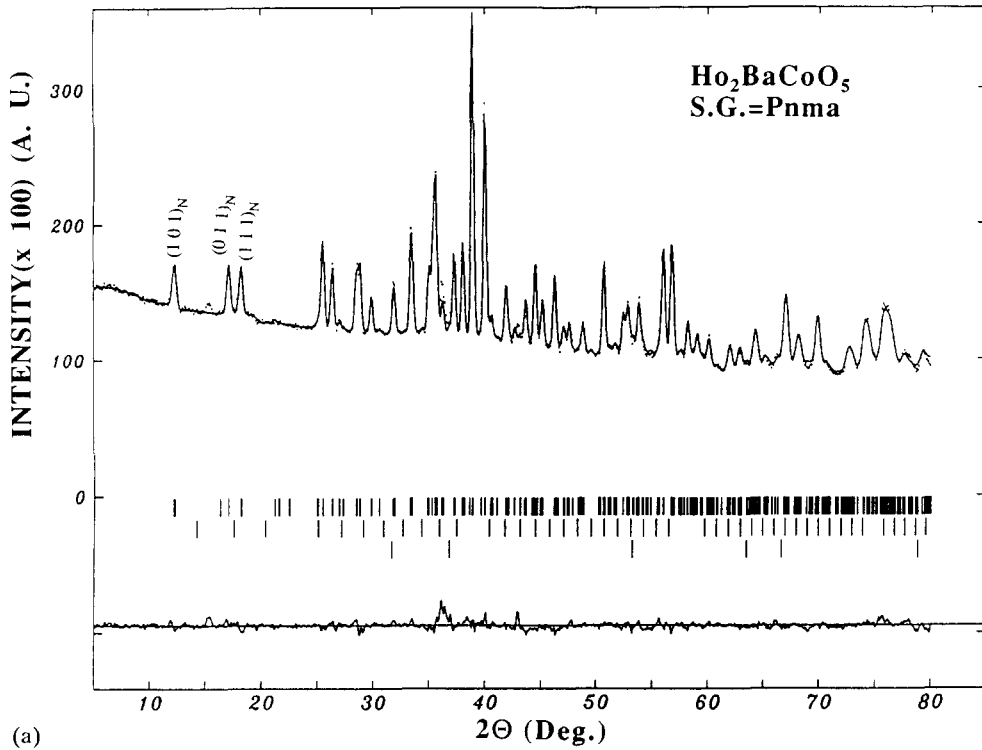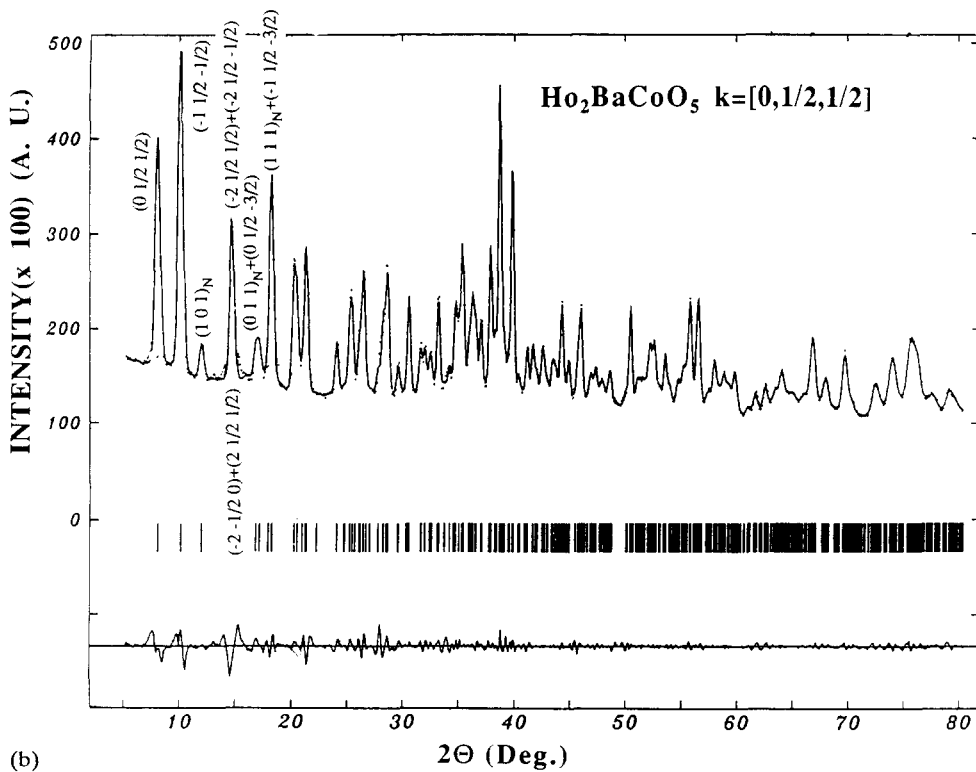
Fig. 3. Observed (points), calculated (solid line) and difference (at the bottom) neutron diffraction profiles for the $Nd_2BaCoO_5$ oxide at the indicated temperatures. (a) The 300 K pattern shows the position of Bragg reflections corresponding to the crystal structures of $Nd_2BaCoO_5$, $Nd_2O_3$ and CoO, respectively. (b) The 2 K pattern has been fitted without structural or magnetic models. The reflections corresponding to the magnetic cell have been generated and the integrated intensities used as parameters. The indices of the main magnetic and nuclear reflections (subscript N) at low angles are displayed.

Fig. 4. Observed (points), calculated (solid line) and difference (at the bottom) neutron diffraction profiles for the $Ho_2BaCoO_5$ oxide at the indicated temperatures. (a) The 300 K pattern shows the position of Bragg reflections corresponding to the crystal structures of $Ho_2BaCoO_5$, $Ho_2O_3$ and $CoO$, respectively. (b) The 2 K pattern has been fitted without structural or magnetic models. The reflections corresponding to the magnetic cell have been generated and the integrated intensities used as parameters. The indices of the main magnetic and nuclear reflections (subscript N) at low angles are displayed.

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