Magnetic ordering in Dy$_{1-x}$Ca$_x$BaCo$_2$O$_{5.5}$ for $x = 0.0$ and $0.1$

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Abstract. The crystal and magnetic structures of Dy$_{1-x}$Ca$_x$BaCo$_2$O$_{5.5}$ for $x = 0.0$ and $0.1$ have been studied by neutron powder diffraction and the crystal structures of both compounds were found to be best described in space group $Pnmm$ with a $a_p \times 2a_p \times 2a_p$ unit cell, where $a_p$ is the lattice parameter of the cubic perovskite unit cell. Oxygen is absent in the R layers and different from the observed magnetic structures of TbBaCo$_2$O$_{5.5}$ and HoBaCo$_2$O$_{5.5}$ despite the proximity of Tb, Dy and Ho in the periodic table. It is a relatively complex antiferromagnetic structure with both pyramidal and octahedrally coordinated Co ions in the intermediate spin state. It contains both ferro- and antiferromagnetic interactions and the magnetic moments are canted in the $a$, $b$-plane. The canting angles between the magnetic moments and the $b$-axis are 6.6 and 50.0° at 20 K for the pyramidal and octahedrally coordinated Co ions, respectively. The high and low temperature magnetic phases were found to coexist at 230 K.

PACS. 75.25.+z Spin arrangements in magnetically ordered materials – 61.66.Fn Inorganic compounds – 71.30.+h Metal-insulator transitions and other electronic transitions

1 Introduction

The rare earth cobaltites R BaCo$_2$O$_{5+\delta}$ ($R = Y$, or rare earth element) are examples of systems with strongly correlated electrons and they therefore exhibit phenomena such as coupling between charge, orbital and spin degrees of freedom and the R BaCo$_2$O$_{5+\delta}$ family of compounds have therefore recently been intensively studied. The large allowed oxygen range ($0 \leq \delta \leq 1$) leads to mixed valence states of the cobalt ions (oxidation states 2+, 3+ and 4+) resulting in different crystal structures and magnetic ordering accompanied by colossal magnetoresistance as well as metal-insulator (MI) transitions [1–5]. The structure of R BaCo$_2$O$_{5+\delta}$ compounds with $\delta = 0$ is an oxygen deficient perovskite structure derived from the basic cubic perovskite structure by a doubling of the primitive unit cell and it is described as an $a_p \times a_p \times 2a_p$ structure, where $a_p \approx 3.9$ Å refers to the lattice parameter of the cubic perovskite unit cell. Oxygen is absent in the R layers and all cobalt atoms are pyramidal coordinated. Compounds with $\delta = 1$ have octahedrally coordinated cobalt atoms and the layered structure just exists for compounds with complete ordering of the rare earth and barium atoms. The crystal structure of compounds with $\delta \neq 0$ and 1 in many cases still not clearly established and especially for $\delta = 0.5$ conflicting results have been obtained. Compounds with $\delta = 0.5$ have been described using different space groups and unit cells e.g. $Pnmm$ ($a_p \times 2a_p \times 2a_p$), $Pnma$ ($2a_p \times 2a_p \times 2a_p$) and $Pcca$ ($2a_p \times 2a_p \times 4a_p$) with the Co$^{3+}$ ions equally distributed in square pyramidal and octahedral coordination [1,2,5,6]. The difference between space group $Pnmm$ and subgroups of lower symmetry such as e.g. $Pnma$ and $Pcca$ is due to minor atomic displacements away from special positions in $Pnmm$. The determination of the correct space group has proven difficult, especially when based on neutron powder data but is of importance as it imposes symmetry constraints on the possible magnetic structures [6].

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Rather complex magnetic structures have been observed for RBaCo$_2$O$_{5+\delta}$ and here we will just be concerned with compounds with $\delta \approx 0.5$ which contain Co$^{3+}$ ions only, thereby preventing accompanying charge ordering phenomena. The complex magnetic structures of the RBaCo$_2$O$_{5+\delta}$ compounds are partly due to the fact that the number of possible magnetic ground states is expanded as the Co$^{3+}$ ions are able to adapt different spin states. Co$^{3+}$ is a 3d$^6$ ion and as a result of the competition between intra-atomic exchange and the effect of the crystal field, it can exist in the low-spin state (LS, $t_{2g}^6$, $S = 0$), the intermediate-spin state (IS, $t_{2g}^5e_g^1$, $S = 1$) as well as the high-spin state (HS, $t_{2g}^4e_g^2$, $S = 2$) [7]. The gaps between these states are rather small and in the range 30 to 100 meV [8,9] which allows for changes from the LS to the IS and HS states as the temperature increases. Several studies of the magnetic structures of RBaCo$_2$O$_{5+\delta}$ compounds with $\delta \approx 0.5$ have recently been performed.

NdBaCo$_2$O$_{5+\delta}$ with $\delta \approx 0.5$ has been studied by several groups with different results. Fauth et al. [10] showed in a neutron diffraction study of NdBaCo$_2$O$_{5.47}$ that the IS Co$^{3+}$ spins order in a G-type antiferromagnetic structure at 275 K and a spin state ordering was found to take place at 230 K. In the spin state ordered phase every second octahedral Co$^{3+}$ ion along the $c$-axis is in the diamagnetic LS state while the remaining Co$^{3+}$ ions are in the IS state. Conversely, Burley et al. [5] observed no long range ordering but only weak magnetic diffuse scattering in a study of NdBaCo$_2$O$_5$ but a single crystal neutron diffraction study of this compound showed that it orders antiferromagnetically with a non-collinear G-type structure [11]. In addition, the crystal and magnetic structures of TbBaCo$_2$O$_{5+\delta}$ with $\delta \approx 0.5$ have been studied by several groups starting with the work by Moritomo et al. and no magnetic structure was determined at 50 K in this study [12]. Thereafter, the magnetic structure of this compound was studied by Khalyavin et al. and it was shown that TbBaCo$_2$O$_{5.4}$ orders antiferromagnetically in a canted G-type structure [13]. Furthermore, it was demonstrated that the magnetic ordering process depends on the degree of oxygen order and thereby on the cooling rate of the samples during synthesis. In addition, Plakhty et al. have performed a detailed study of the spin structure magnetic phase transitions in TbBaCo$_2$O$_{5.5}$ [6]. It was found that TbBaCo$_2$O$_{5.5}$ orders ferrimagnetically at $T \approx 290$ K and this magnetic phase transforms to an antiferromagnetic phase at $T \approx 255$ K and a second antiferromagnetic phase was observed below 170 K. YBaCo$_2$O$_{5.5}$ has recently been studied by neutron powder diffraction by Khalyavin et al. [14]. The crystal structure was refined in space group $Pnma$ for $T > 190$ K and a spin state ordered magnetic phase was observed in the temperature range from 190 to 265 K. The magnetic phase contains octahedrally coordinated Co$^{3+}$ ions in the LS and HS states, forming chessboard-like spin state ordered a, c-planes while the pyramidal coordinated Co$^{3+}$ ions adopt the HS state. In addition, HoBaCo$_2$O$_{5.5}$ has recently been studied by neutron powder diffraction and it was shown that it orders in complex antiferromagnetic structure for $T \leq 265$ K similar to the structure observed for TbBaCo$_2$O$_{5.5}$ below 170 K [15]. In this study we present a neutron powder diffraction study of the magnetic ordering in Dy$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5.5}$ and DyBaCo$_2$O$_{5.5}$.

2 Experimental details

The Dy$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5.5}$ and DyBaCo$_2$O$_{5.5}$ samples were prepared by solid state synthesis by mixing stoichiometric amounts of Dy$_2$O$_3$, CaCO$_3$, BaCO$_3$ and Co$_3$O$_4$. The mixture was heated to 1000°C for 12 h in air several times with intermediate grinding steps and finally to 1070°C in O$_2$ flow for 12 h. The neutron diffraction data were collected on the DMC diffractometer at the Swiss spallation neutron source SINQ using a wavelength of 2.5657 Å. Dysprosium has a large neutron absorption cross section and the sample was loaded into a helium filled vanadium can composed of two concentric cylindrical tubes with diameters of 14.5 and 13.5 mm, respectively. The 1 mm thick sample layer created in this setup diminishes the effects of absorption. The filled vanadium containers were mounted on a closed cycle helium refrigerator and powder patterns were collected in the temperature range from 20 to 365 K. The linear absorption coefficients were subsequently measured in transmission measurements and used in the Rietveld refinements. Data analysis was performed by the Rietveld method using the FullProf program package [16], with the use of its internal tables for neutron scattering lengths and magnetic form factors.

3 Results and discussion

Inspection of the measured powder patterns for Dy$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5.5}$ and DyBaCo$_2$O$_{5.5}$ showed that magnetic ordering was present in these compounds for $T \lesssim 305$ and 290 K, respectively. Several trial refinements of the non-magnetic phases of both compounds were carried out in different space groups. These refinements showed that the non-magnetic phases of both compounds were best described in space group $Pmmm$ using a $a_p \times 2a_p \times 2a_p$ unit cell. The limited $q$-range ($q_{max} = 3.6$ $\AA^{-1}$) of the present data sets prevented reliable refinements in space groups of lower symmetry than $Pmmm$. No changes in the symmetry of the crystal structures of both compounds were observed and all structural refinements were therefore performed in space group $Pmmm$ within the investigated temperature range. The occupancies of Dy and Ca were fixed at 90 and 10%, respectively in the case of Dy$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5.5}$ and trial refinements showed that the oxygen content is 5.5 oxygens per formula unit within the experimental uncertainty (obtained stoichiometries: Dy$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5.49(1)}$ and DyBaCo$_2$O$_{5.49(8)}$), and it was therefore fixed at this value in the subsequent refinements. In the case of Dy$_{0.9}$Ca$_{0.1}$BaCo$_2$O$_{5.5}$ it was found that the magnetic reflection observed for $T \lesssim 305$ K