A complex magnetic structure in the magnetoresistive La$_{0.82}$Ba$_{0.18}$CoO$_3$

P Tong$^1$, Q Huang$^2$, M Kofu$^1$*, M C Lehman$^1$, J Yu$^1$ and D Louca$^1$

$^1$University of Virginia, Department of Physics, VA 22904, USA
$^2$NIST Center for Neutron Research, Gaithersburg, MD 20899, USA

Email: tongpeng@virginia.edu

Abstract. The magnetic structure of the perovskite cobaltite La$_{0.82}$Ba$_{0.18}$CoO$_3$ was investigated using powder neutron diffraction. Although macroscopically this composition is thought to be in the spin-glass phase from bulk magnetic measurements, the presence of Bragg-like magnetic features in the neutron diffractograms suggests otherwise. At 4 K, two long-range magnetic orders are observed with two propagation wave vectors, $k_1 = (0,0,0)$ and $k_2 = (0,-0.5,0.5)$, corresponding to ferromagnetic and antiferromagnetic orders, respectively. However, above 100 K, the $k_2$ component almost disappears, while $k_1$ persists.

1. Introduction

The intricate interplay of spin, charge, orbital and lattice degrees of freedom in complex transition metal oxides often leads to emergent behaviours with unusual magnetic and electronic characteristics as in the case of the cobalt perovskite La$_{1-x}$A$_x$CoO$_3$ (A = divalent ion, Ca, Sr or Ba) [1]. The parent compound, LaCoO$_3$, has a non-magnetic insulating ground state, with the Co$^{3+}$ ion in the $t^2_{2g}e^0_g$ (low spin, LS) electronic configuration [2]. However, as the temperature rises, an electronic excitation occurs to a higher spin state, with possibly one of two configurations, $t^5_{2g}e^1_g$ (intermediate spin, IS) or $t^4_{2g}e^2_g$ (high spin, HS). This transition is coupled with a 0.6 meV excitation due to a single-ion effect of the Co$^{3+}$ [3]. From the elastic neutron scattering on single crystals, it was previously shown that dynamic ferromagnetic (FM) and antiferromagnetic (AFM) correlations between the Co$^{3+}$ ions are present, consistent with the thermally excited transition from the LS to the IS state [3]. Upon doping La$_{1-x}$A$_x$CoO$_3$ by divalent ions such as Ba, a long-range FM state is presumed to develop by $x \sim 0.2$. This is followed by an insulator-to-metal transition at $x \sim 0.25$, brought upon the spin-to-charge coupling via the Double Exchange (DE) mechanism [4]. However, this seemingly simple picture fails to describe the true magnetic state when the Ba concentration reaches 18%. In this paper, we report on the magnetic neutron diffraction analysis of a polycrystalline sample of La$_{0.82}$Ba$_{0.18}$CoO$_3$ under magnetic field. Two commensurate magnetic structure with propagation vectors $k_1 = (0,0,0)$ and $k_2 = (0,-0.5,0.5)$ corresponding to the FM and AFM ordering, respectively, were observed [5]. The diffraction patterns were refined and a possible configuration of the magnetic moments is presented and discussed.

* Present address: Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8581, Japan.
2. Methods
The sample was prepared by standard solid state reaction. The powder neutron diffraction experiments were performed using the BT1 diffractometer at the NIST Center for Neutron Research using a 7 Tesla vertical magnet. Very weak λ/3 reflections are observed in the diffraction patterns. The measurements were carried out at two temperatures, 4 and 100 K, with and without the magnetic field turned on. At 4 K, data were also collected in zero-field cooling (ZFC) and field cooling (FC) modes. Each data set was collected for a total of about 18 hours. The programs Fullprof and SARAh [6] were employed for the data analysis. The crystal structure does not change with the magnetic transition within the resolution of our experiment and remains in the rhombohedral phase with the $\overline{R\bar{3}}c$ space group. Based on the nuclear symmetry and the observed magnetic propagation vectors, the basis vectors (BV$s$) for each wave vector were calculated using SARAh following the irreducible representation (IR) theory. The calculated results are listed in table 1 for $k_1$ and $k_2$. In the $\overline{R\bar{3}}c$ symmetry, there are two distinct Co ion sites, with coordinates at (0, 0, 0) for Co1 and (0, 0, 0.5) for Co2. The two characteristic wave vectors may originate either from the same domain or from two different domains. It is possible to combine the two $k$-vectors if originating from a single magnetic domain with a double-$k$ structure. On the other hand, if the two $k$-vectors are independent of each other because they originate from different magnetic domains, then forming single-$k$ structure is more appropriate. The former scenario was assumed in the present case.

3. Results and Discussion
At 4 K, two sets of magnetic peaks are observed, and indexed using two propagation vectors, $k_1=(0, 0, 0)$ and $k_2=(0, -0.5, 0.5)$, as shown in figure 1(a), corresponding to static FM and AFM magnetic structures. The two propagation vectors are commensurate with the crystal unit cell. When the magnetic field is turned on to $H = 7$ T under ZFC mode [figure 1(b)], the peaks of $k_1$ are significantly enhanced, while those of $k_2$ are somewhat suppressed but not absent. Under the FC mode [figure 1(c)], however, the background changes and the $k_1$ peaks become even stronger while the intensity of the $k_2$ peaks is reduced further. By increasing the temperature to 100 K as in figure 1(d), both sets of magnetic diffraction peaks decrease in intensity. Particularly, the diffraction pattern stemming from the $k_2$ structure nearly disappears.

By constraining the population (i.e., phase fraction) of the $k_1$ and $k_2$ components to be equal to that of the nuclear phase, several possible moment configurations have been tested on the basis of symmetry-allowed BV$s$ from table 1. For $k_1$, there are three IR$s$ allowed by the crystal symmetry. Among the six BV$s$, only $\psi_2$ of $I\bar{3}$ can reproduce the observed patterns alone, which means a FM structure with all moments along $c$ axis as shown in figure 2(a). As for $k_2$, there is only one nonzero IR as shown in table 1. We find that $\psi_2$ or $\psi_5$ alone can reproduce the diffraction patterns of $k_2$. The involvement of any other BV$s$ does not lead to an improvement of the refinement. The magnetic structures resulting from $\psi_2$ or $\psi_5$ are non-collinear AFM with moments along [010] and $\pm[110]$ for Co1(0, 0, 0) and Co2 (0, 0, 0.5) sites, respectively. The case of $\psi_5$ is shown in figure 2 (b). The AFM unit cell is doubled along $b$ and $c$ axes, while the FM unit cell is as same as the nuclear one. The refined magnetic moments $\mu(k_1)$ and $\mu(k_2)$ are listed in figure 1 for $k_1$ and $k_2$ phases, respectively. It can be seen that the magnetic field enhanced the Co moment of $k_1$, while it suppressed that of $k_2$. Compared to the 4 K data, at 100 K both the moments of $k_1$ and $k_2$ are suppressed. In comparison with the $k_1$ component, the weaker $k_2$ magnetic intensities yield a higher value of Rietveld factor $R_{mag}$, as shown in figure 1.

If the two $k$-vectors are coupled with each other, the combination of them may give rise to a canted magnetic structure (i.e., a single domain structure). As discussed above, the possible moment of $k_1$ is orthogonal to those of $k_2$, which ensures each Co site has the same magnitude of total moment ($\mu_{total}$) after combination. The values of $\mu_{total}$ are shown in figure 1. Alternatively, if the single-$k$ structure is more applicable, the volume fraction for each $k$-vector can be estimated (not shown here) by supposing that the moment magnitudes are equal in both $k_1$ and $k_2$ domains, and that the whole sample volume is magnetically ordered. At present, however, it is not easy to distinguish between the two
models in our case because whether and how the two \( k \)-vectors modulate with each other are still unclear. In addition, the powder diffraction performed can not distinguish the moment orientation within the \( ab \) plane of such a rhombohedral crystal unit cell. Further studies on other chemical compositions near 18 % and polarized neutron diffraction with the aid of magnetic field on single crystals may shed light on these issues.

Figure 1. (Color online) Rietveld refinements of neutron diffraction patterns. The observed intensities are shown by cross symbols and calculated ones by a solid line. The vertical bars indicate the Bragg peak positions of nuclear phase, \( k_1 \) and \( k_2 \) from top to bottom. The solid line at the bottom of each panel indicates the difference between the observed and calculated intensities. \( R_{\text{mag}} \) is the agreement parameter for magnetic phase. The magnetic moments \( \mu(k_1) \) and \( \mu(k_2) \) are obtained by supposing the single domain structure with two \( k \)-vectors. \( \mu_{\text{total}} \) is the total moment after combination of \( \mu(k_1) \) and \( \mu(k_2) \). An enlarged view of the profiles at low angles is shown in the inset of every panel. The magnetic diffractions from propagation vectors \( k_1=(0, 0, 0) \) (blue asterisk) and \( k_2=(0, -0.5, 0.5) \) (pink plus) are indicated. Some weak diffraction peaks unmarked are due to the \( \lambda/3 \) contamination in the BT1 instrument. Relative intensity of the peak at 2\( \theta \approx 27 \) degree is nearly invariable with temperature and magnetic field, indicating its non-magnetic origin. It may come from a secondary phase, thus was excluded in the indexing and refinement.
Table 1. The calculated irreducible representation ($\Gamma$) and related basis vectors (BVs) at the two Co sites (Co1 and Co2) for $k_1$ and $k_2$ with respect to the space group $R\bar{3}c$. The components of BV, $M_a$, $M_b$ and $M_c$ are given with respect to the crystallographic axes $a$, $b$ and $c$ respectively.

| IR  | BV      | Co(1) | Co(2) | IR  | BV      | Co(1) | Co(2) |
|-----|---------|-------|-------|-----|---------|-------|-------|
| $\Gamma_1$ | $\Psi_1$ | 0     | 0     | 1   | 0       | 0     | -1    |
| $\Gamma_3$ | $\Psi_2$ | 0     | 0     | 0   | 0       | 1     | 0     |
| $\Gamma_6$ | $\Psi_3$ | 1     | 0     | 0   | 0       | 0     | 0     |
| $\Psi_4$   | 0     | 0     | 0     | 0   | 1       | 0     | 0     |
| $\Psi_5$   | 0     | 0     | 2     | 1   | 0       | 0     | 1     |
| $\Psi_6$   | -1    | -2    | 0     | 0   | 0       | 0     | 1     |

Figure 2. (Color online) Possible magnetic structure for $k_1$ (a) and $k_2$ (b) plotted within one nuclear unit cell. The moments at Co (0,0,0) sites are plotted in green, and at Co (0,0,0.5) sites in pink.

4. Summary
To summarize, we report on the powder neutron diffraction on La$_{0.82}$Ba$_{0.18}$CoO$_3$. Two magnetic propagation vectors $k_1 = (0,0,0)$ and $k_2 = (0,-0.5,0.5)$ were observed corresponding to the FM and AFM structures. Further studies are necessary to understand the details of the coupling between the magnetic orders and the orientations of the magnetic moments.

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