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Neutron powder diffraction study on Nd_2BaCuO_5 oxide

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Abstract

The magnetic behaviour of Nd_2BaCuO_5 oxide has been studied by means of neutron powder diffraction at low temperatures. This oxide behaves as antiferromagnetic with a Néel temperature of 7.8 K, and the magnetic structure can be described on the basis of a propagation vector $\mathbf{k} = [0, 0, 1/2]$. The Cu^{2+} magnetic moments are aligned along the *c*-axis of the crystal structure, while the Nd^{3+} magnetic moments lie in the *ab*-plane. The experimental values of the ordered moments at 1.7 K are 0.84 (8) and 0.78 (4)μ_B for copper and neodymium ions, respectively.

Keywords: Antiferromagnetism; Neutron diffraction; Magnetic structure

1. Introduction

R_2BaCuO_5 oxides (R = rare earth) crystallize into two different structural types depending on the lanthanide trivalent cation size. Most of the previous structural and magnetic studies have been performed for R_2BaCuO_5 oxides, where R stands for samarium to lutetium and yttrium, that crystallize with the Sm_2BaCuO_5 structural type showing orthorhombic symmetry and space group *Pnma* [1]. Their main structural feature is the presence of isolated distorted square pyramids $[CuO_5]$. Bond valence calculations based on neutron diffraction data show that the structural instability increases with the rare earth cationic radius. The calculated instability index would be very large for the bigger R^{3+} cations (R = La, Pr and Nd), and the *Pnma* structure is not stable for these three cations [1]. In fact the lanthanum, praseodymium and neodymium derivatives present tetragonal symmetry and crystallize with the Nd_2BaPtO_5 aristotype, space group *P*4/*mbm* [2]. Its characteristic feature is the location of the copper atoms in isolated square planar $[CuO_4]$ units, forming a quasi bi-dimensional arrangement.

These latter oxides present a rather unusual magnetic behaviour among the copper oxides, since La_2BaCuO_5 oxide behaves as ferromagnetic with a Curie temperature (T_C) of 5.7 K [3], and the substitution of the diamagnetic La^{3+} by paramagnetic Pr^{3+} and Nd^{3+} ions produces important changes in the magnetic behaviour of the isostructural Pr_2BaCuO_5 and Nd_2BaCuO_5 oxides. In fact, the Pr_2BaCuO_5 oxide shows ferromagnetic interactions below 15 K [4], while Nd_2BaCuO_5 oxide is antiferromagnetic with a Néel temperature (T_N) of 7.8 K [5]. In our previous studies, we have carried out a detailed study of the mechanism of the magnetic interactions that take place in the neodymium oxide, based on both powder and single crystal magnetic and calorimetric measurements [6]. The main purpose of this paper is to study the magnetic structure that the Nd_2BaCuO_5 oxide presents by means of temperature-dependent neutron powder diffraction and, concomitantly, to determine possible significant differences between the room-temperature and low-temperature crystal structure. Comparisons will be established with our previous single-crystal X-ray diffraction results [6].

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2. Experimental

Nd_2BaCuO_5 powder sample was prepared by a solid state reaction following the synthesis method described elsewhere [7]. Neutron diffraction data were collected in the D2B neutron diffractometer using the high flux reactor facilities of the Institut Laue-Langevin in Grenoble, France. The wavelength used was 2.46 Å and neutron diffraction patterns were collected at 150, 50 and 1.7 K. The data were analyzed with the Rietveld method using the FULLPROF program [8]. The specific heat was measured by the heat phase-relaxation method in a Quantum Design PPMS.

3. Results and discussion

3.1. Structural characterization

Neutron powder diffraction patterns obtained at 150 and 1.7 K are shown in Fig. 1. The data have been refined considering the *P*4/*mbm* space group, and the obtained results

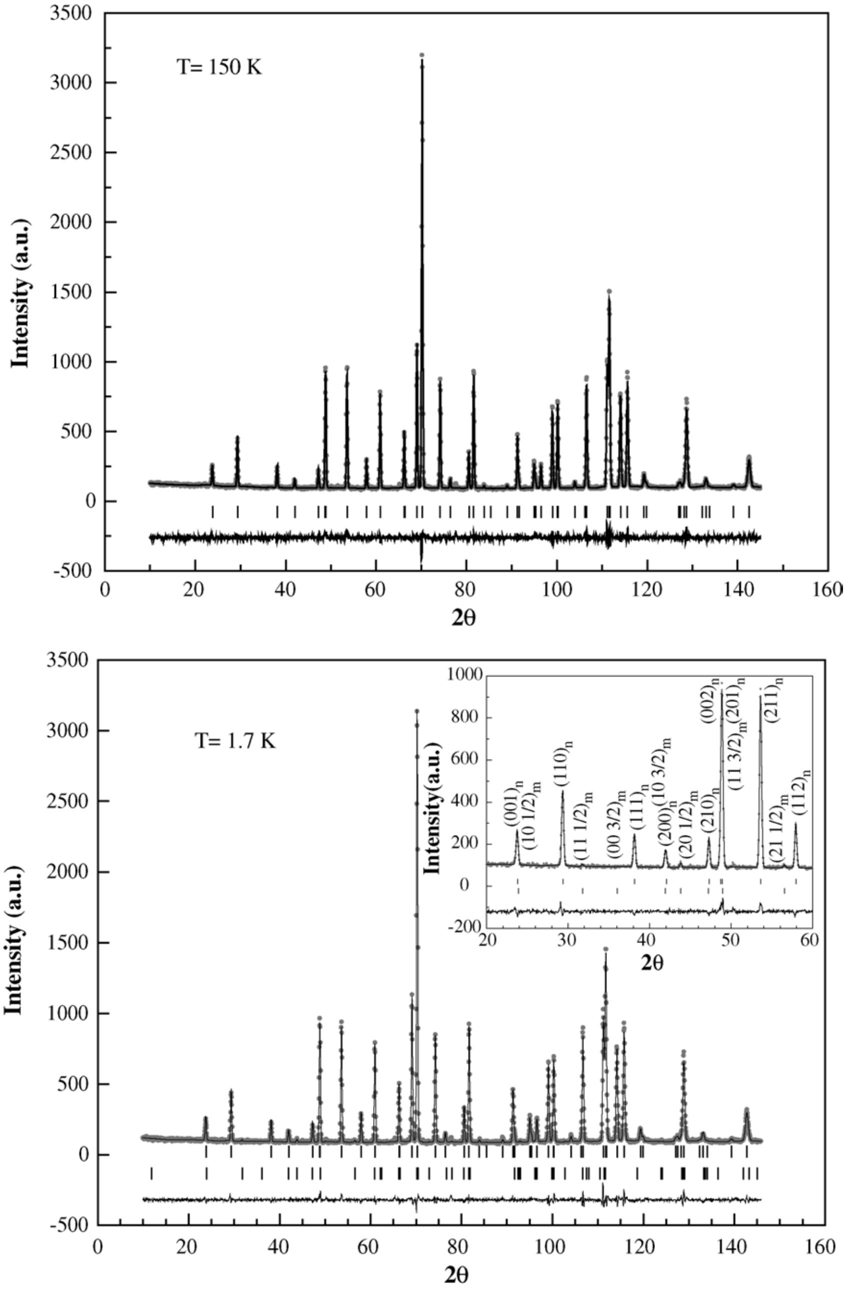

Fig. 1. Neutron powder diffraction patterns obtained at 150 and 1.7 K (dots), and calculated from the Rietveld refinement (solid line) for Nd_2BaCuO_5 oxide. Vertical marks show the position of the nuclear (first row) and magnetic (second row) Bragg reflections. A difference curve is plotted at the bottom of the pattern.

Table 1

Lattice parameters, atomic coordinates and reliability factors from the Rietveld refinement of the neutron powder diffraction data obtained at 150, 50 and 1.7 K

a (Å)	c (Å)
6.7544 (5)	5.8709 (5)
6.7490 (5)[a]	5.8683 (5)[a]
6.7483 (5)[b]	5.8684 (5)[b]

Atom	Site	x	y	z
Nd	4h	0.1738 (2) 0.1737 (2)[a] 0.1737 (1)[b]	0.6738 (2) 0.6737 (2)[a] 0.6737 (1)[b]	0.5 0.5 0.5
Ba	2a	0	0	0
Cu	2d	0	0.5	0
O (1)	2b	0	0	0.5
O (2)	8k	0.3603 (1) 0.3601 (1)[a] 0.3601 (1)[b]	0.8603 (1) 0.8601 (1)[a] 0.8601 (1)[b]	0.7591 (2) 0.7587 (2)[a] 0.7591 (2)[b]

Temperature (K)	R_B (%)	χ^2	R_{wp} (%)
150	2.51	2.74	9.99
50	2.44	2.64	9.65
1.7	2.14	2.18	9.74

Numbers in parentheses are estimated standard deviations.

[a] Data at 50 K.

[b] Data at 1.7 K.

at 150, 50 and 1.7 K are given in Table 1. Both lattice parameters and atomic positions agree with those previously reported from our single crystal X-ray diffraction study at room temperature [6], but better accuracy is obtained for the light oxygen atoms. The lattice parameters progressively decrease with the temperature from 150 to 1.7 K as a result of the thermal contraction of the crystal lattice, see Table 1.

The isolated square planar [CuO_4] units present four equal Cu–O distances of 1.945 (1) Å at 1.7 K. This value does not show any temperature dependence, remaining almost constant up to 150 K, and agrees well with that obtained from single crystal X-ray diffraction at room temperature of 1.947 (7) Å [6]. It is worth noting that the [CuO_4] groups have a subtle distortion giving rise to two planar angles O–Cu–O of 86.72 (6) and 93.27 (7)° at 1.7 K. These values remain almost constant up to 150 K and agree with those obtained from single crystal X-ray diffraction at room temperature of 85.7 (4) and 94.3 (4)° [6].

3.2. Magnetic behaviour

Previously reported magnetic susceptibility data for a powdered Nd_2BaCuO_5 sample [6,7] show a Curie–Weiss behaviour over the wide temperature range of 300–50 K, and the obtained magnetic moment agrees well with the calculated one taking into account the Nd^{3+} and Cu^{2+} paramagnetic contributions. Moreover, it is worth noting the absence of any maximum at lower temperatures, see inset of Fig. 2, as could be expected from the antiferromagnetic ordering suggested by means of optical spectroscopy data below 7.8 K [9]. However, our recent anisotropic magnetic susceptibility measurements on a single crystal fully justifies the mentioned lack of any maximum [6], since the clear maximum observed in the parallel susceptibility ($\chi_{||}$) can be masked by the higher values of the perpendicular susceptibility ($\chi_\perp$) in the average susceptibility ($\chi_{av} = (2/3)\chi_{||} + (1/3)\chi_\perp$) that corresponds to the powder sample. On the other hand, bulk specific heat measurements confirms this long-range magnetic order with the presence of a λ-type transition at 7.8 K, as displayed in Fig. 2.

The neutron diffraction pattern obtained at 1.7 K reveals the onset of a new reflection at about $2\theta = 43.8°$ and the increase in intensity of some nuclear reflections, as can be seen in the inset of Fig. 1. This fact can be ascribed to the occurrence of long-range magnetic ordering. All those magnetic reflections can be indexed in a commensurable lattice related to the crystallographic one by a propagation vector $\mathbf{k} = [0, 0, 1/2]$. Since both Nd^{3+} and Cu^{2+} sublattices become ordered at the same temperature, the basis vectors

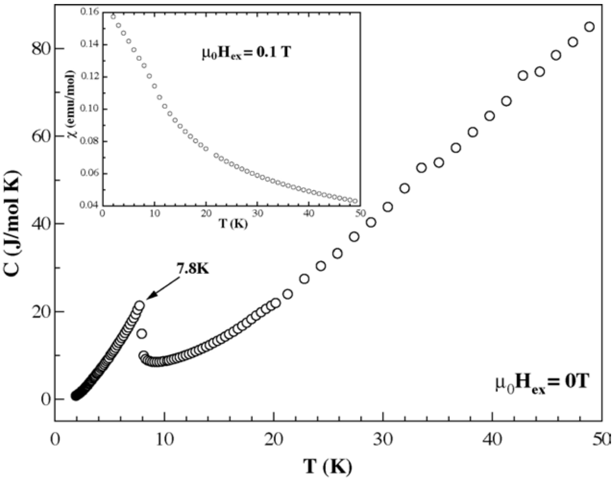

Fig. 2. Temperature dependence of the total specific heat measured in the absence of an external magnetic field ($\mu_0 H_{ex} = 0$ T) for Nd_2BaCuO_5 oxide below 50 K. The inset corresponds to the temperature dependence of the magnetic susceptibility between 2 and 50 K in an external magnetic field of $\mu_0 H_{ex} = 0.1$ T.

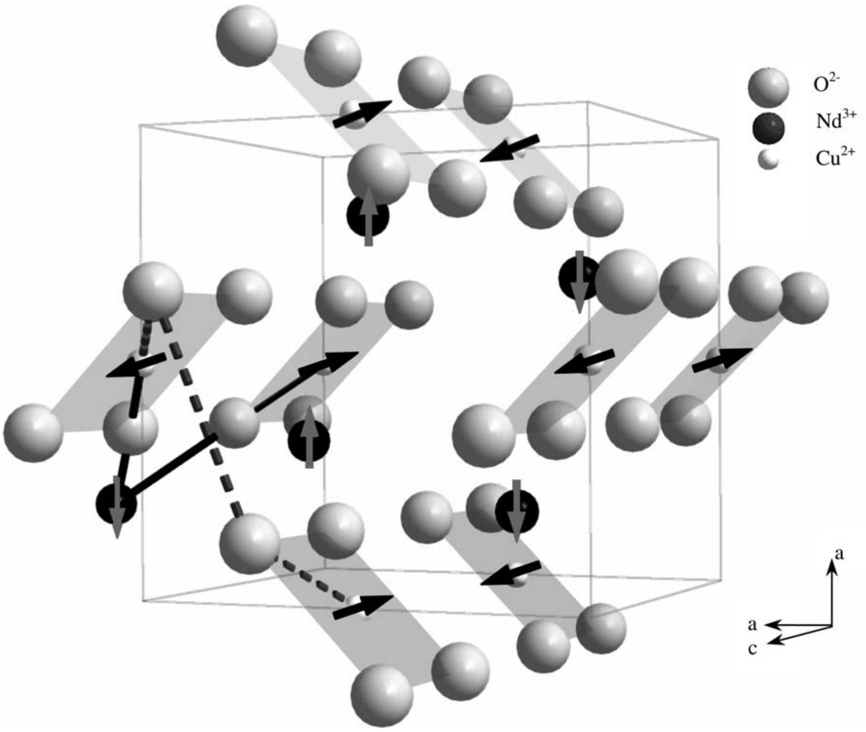

Fig. 3. Proposed magnetic structure for Nd_2BaCuO_5 oxide at 1.7 K, outlined within the crystallographic unit cell.

which describe the magnetic structure must belong to the same irreducible representation. In this sense, the representation analysis within the framework of group theory and following the method proposed by Bertaut [10] arrives at different magnetic structures compatible with the crystal symmetry [11]. The best fit of the experimental data has been obtained considering the Nd^{3+} magnetic moments (m_{Nd}) coupled antiferromagnetically in the *ab*-plane and the Cu^{2+} ones (m_{Cu}) aligned antiferromagnetically along the *c*-axis of the structure, as depicted in Fig. 3. Since the crystal structure remains tetragonal down to 1.7 K, all possible directions of the neodymium magnetic moments in the *ab*-plane are magnetically equivalent. Furthermore, m_{Nd} and m_{Cu} are perpendicular while in the case of the homologous R_2BaNiO_5 oxides the R^{3+} and Ni^{2+} magnetic moments are mainly parallel. For example, a collinear structure has been reported for Nd_2BaNiO_5 oxide, where the neodymium and nickel magnetic moments are located along the *c*-axis [12]. This difference could be an indication of the relatively high intrinsic magnetic anisotropy of the neodymium ion in Nd_2BaCuO_5 oxide, as compared with the possible anisotropy coming from the Nd–Cu magnetic interactions.

The mechanism through which the foregoing magnetic structure is established can be explained considering the possible pathways for the different magnetic interactions. Firstly, the dipolar Nd–Nd interactions are extremely weak and can be neglected in the Nd_2BaCuO_5 compound, as implied by the lack of long-range magnetic order down to 4.2 K in the Nd_2BaZnO_5 oxide [9], and by the relatively large Nd–Nd distance of 3.528 (1) Å. Besides that, in the superexchange Cu–O–O–Cu interactions, noted by a dashed line in Fig. 3, the orbital overlap is hindered by the values of the bond angles involved in the superexchange pathways (75.60 (4)° for Cu–O–O and 129.79 (5)° for O–O–Cu), together with the O–O bond distance of 3.687 (1) Å. It is well established that these interactions, in which the half-filled $d_{x^2-y^2}$ and filled d_{z^2} orbitals of Cu^{2+} are involved, give rise to the low temperature ferromagnetic behaviour ($T_C = 5.7$ K) [13] observed in the case of the La_2BaCuO_5 compound, according to the Goodenough–Kanamori–Anderson rules [14]. However, the presence of the paramagnetic Nd^{3+} atoms leads to consider the superexchange Cu–O–Nd interactions, denoted by a bold line in Fig. 3, which are strongly favoured by both the bond angle of 173.88 (5)° and the total distance for this pathway of 4.279 (1) Å. Consequently, the magnetic ordering is mainly governed by the effective orbital overlap of Cu–O–Nd interactions, where the half-filled $d_{x^2-y^2}$ orbital of the Cu^{2+} ions is involved.

The observed magnetic moment for the copper ions in the ordered state takes the value of 0.84 (8)μ_B at 1.7 K, which agrees with the expected value of $2S = 1\mu_B$. The small difference may be assigned to covalency effects associated with the Cu–O bonds. However, in the case of the neodymium ions the experimental magnetic moment, 0.78 (4)μ_B, is significantly smaller than the expected one for the free ion, $g_J \times J = 4.20\mu_B$. This fact has been explained in a previous work by considering the *g*-values derived from the crystal field simulation [6]. The perpendicular component of the *g*-tensor ($g_\perp$) for the crystal-field ground state takes a value of 2.2, so that its corresponding neodymium magnetic moment is $m_{\mathrm{Nd}} = 0.5 \times g_{\perp} \times \mu_{\mathrm{B}} = 1.1\mu_{\mathrm{B}}$. The first excited crystal-field state is placed at 95 K from the ground term [6], so that it does not contribute significantly to the Nd^{3+} magnetic moment in the ordered state. That value for the ordered magnetic moment coming from the ground state is relatively close to the experimental one obtained at 1.7 K of 0.78 (4)μ_{B}. The difference could be attributed to the Zeeman splitting below the Néel temperature of the doublet crystal-field ground term, caused by the magnetic interaction of the magnetic moment associated with the 4f electronic cloud with the molecular field present at the neodymium site.

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