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LETTER TO THE EDITOR

On the magnetic structure of Bi_2CuO_4

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Abstract. We present here the results of Rietveld refinements of our neutron investigation on the magnetic structure of Bi_2CuO_4. On each copper site we measured a magnetic moment of $m = 0.45 \pm 0.02\,\mu_B$ at $T = 19$ K, incompatible with the determination of $m = 0.93 \pm 0.06\,\mu_B$ at $T = 1.5$ K, obtained by Garcia-Muñoz and co-workers. Otherwise, we do in general agree with the conclusions of their work and that of Troc and co-workers, and confirm that the magnetic arrangement below $T_N = 47.5 \pm 1$ K can be viewed as a simple two-sublattice antiferromagnetic structure with rods of parallel moments along the c-axis.

Bi_2CuO_4 is a newly studied magnetic compound in which each copper ion is surrounded by four oxygens forming a square centred plaquette. The coppers interact by super-exchange coupling through Cu–O–Bi–O–Cu bonds as shown in figure 1.

We were ignorant of results obtained previously [1, 2] when a powdered sample of Bi_2CuO_4 provided by one of us (GS) was under investigation at the Orphée reactor of the LLB at Saclay. Neutron diffraction patterns were collected on a multidetector (G6-1) installed on a cold neutron guide. The incident wavelength of $\lambda = 4.725$ Å obtained from a vertically bent monochromator was slightly beyond the cut-off wavelength of aluminium. The beam was filtered by cold beryllium. The position sensitive detector (a bank of 400 cells subtending an angle of 80°, filled with BF3) had to be positioned twice in order to scan the whole accessible diffraction pattern from 20° to 150°.

The sample was mounted in a cylindrical aluminium cell ($d = 5$ mm, $h = 10$ mm) in thermal contact with the cold finger of a closed cycle cryogenerator. Diffraction patterns were recorded at decreasing temperatures, from 300 K down to 19 K.

At room temperature eight nuclear peaks were visible, although (002) was very weak. When lowering the temperature, two smaller peaks appeared indexing as (100) and (210) without changing the unit cell. On the basis of the space group P_4/ncc (No 130) as established by Boivin *et al* [4] the emergence of these two small peaks indicates a breakdown of the reflection condition $hk0$: $h + k = 2n$; now, assuming that the coppers are the only magnetic ions, this points to the fact that the copper sites are no longer connected by a centre of symmetry, i.e. half of them bear a magnetic moment opposite to that on the other half.

Bi_2CuO_4 has four copper ions in its unit cell located on sites (4c) as displayed in table 1. Assuming a collinear array of magnetic moments of the same length, the magnetic

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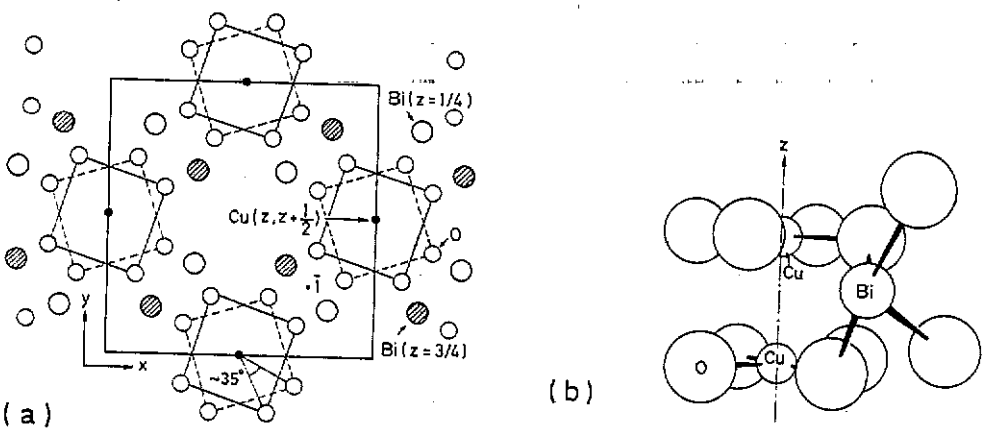

Figure 1. (*a*) Projection of the unit cell of Bi_2CuO_4 on the (001) plane. (*b*) Neighbourhood of the copper ion. Reproduced from Popovic *et al* [3] and Boivin *et al* [4].

Table 1. Position of copper ions in the non-centrosymmetrical unit cell [4].

	x	y	z	Magnetic moment	
Cu (1)	0	$\frac{1}{2}$	z_{Cu}	m_1	+
Cu (2)	0	$\frac{1}{2}$	$\frac{1}{2} + z_{Cu}$	m_2	+
Cu (3)	$\frac{1}{2}$	0	$\frac{1}{2} - z_{Cu}$	m_3	−
Cu (4)	$\frac{1}{2}$	0	$-z_{Cu}$	m_4	−

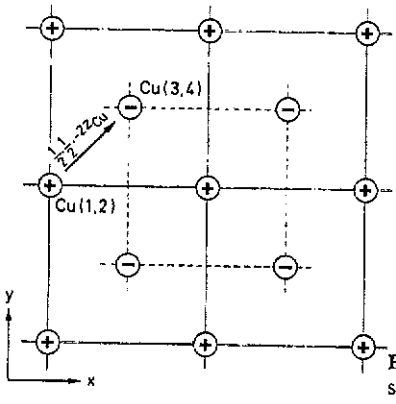

Figure 2. Projection of the antiferromagnetic structure on the (001) plane.

structure factor for peaks (100) and (210), disregarding the sign, is reduced to: $|F| = |(m_1 + m_2) - (m_3 + m_4)|$ where $|m_1| = |m_2| = |m_3| = |m_4|$; $m_1 = -m_3$; $m_2 = -m_4$; and m_i is the magnetic moment on copper site *i*. This expression differs from zero when $m_1 = m_2$ (i.e. $m_3 = m_4$) for instance. This leads to the proposed antiferromagnetic structure sketched in figure 2. It divides into two opposite sublattices shifted by a non-elementary translation of $(\frac{1}{2}, \frac{1}{2}, -2z_{Cu})$. The foregoing analysis is compatible with the presence of the two magnetic peaks. Magnetic peak (002) is not observable, being too far into reciprocal space, and this prevents us from deciding whether the magnetic moment is along the *c*-axis or in the *a*–*b*-plane.

Table 2. Structural parameters of Bi_2CuO_4 in the non-centrosymmetrical unit cell.

Atom	Site	x	y	z	a (Å)	c (Å)
X-rays [4]; $T = 293$ K						
					8.510 (1)	5.814 (1)
Bi	8f	0.1685 (2)	0.1685 (2)	$\frac{1}{4}$		
Cu	4c	0	$\frac{1}{2}$	0.080 (4)		
O	16g	0.295 (4)	0.114 (4)	−0.097 (4)		
Neutrons (present study); $T = 298$ K						
					8.5067 (12)	5.8279 (4)
Bi	8f	0.175(2)	0.175(2)	$\frac{1}{4}$		
Cu	4c	0	$\frac{1}{2}$	0.096 (4)		
O	16g	0.290	0.104	−0.057 (4)		
Neutrons (present study); $T = 19$ K						
Bi	8f	0.169	0.169	$\frac{1}{4}$	8.5101 (7)	5.8044 (3)
Cu	4c	0	$\frac{1}{2}$	0.117		
O	16g	0.292 (1)	0.106 (1)	−0.044 (1)		

Rietveld [5] profile refinements of the spectra were performed, and fourteen parameters were allowed to vary in the treatment of the spectra in the paramagnetic region, i.e. above $T_N = 47.5$ K. It turned out that an anisotropic Debye–Waller factor (DBF) was required for each atom, due to a much larger dilatation along c than along a or b. The DBF of copper and oxygen were coupled according to relation (3) in [6]. The resulting refinement factor for this structure was $R_I = 1.25$ at room temperature. Table 2 lists the structural parameters of the compound for the two limiting temperatures. At room temperature there is fairly good agreement with the x-ray results of Boivin *et al* [4], apart from a slight readjustment of the oxygen position along z, as expected for light elements.

In the ordered region the magnetic moments were assumed to be parallel to the c-axis. The refinement factor rose to $R_I = 4.56$ at $T = 19$ K with a magnetic moment of $m = 0.45 \pm 0.02\ \mu_B$, quite irreconcilable with the estimation of [1], but close to the determination of $m = 0.53 \pm 1\ \mu_B$ given by [2], considering that we have used a different determination for the magnetic form factor of Cu^{++} [7]. Measurements of the amplitude of the magnetic moment in other copper oxides always led to values in the same range: $0.65\ \mu_B$ in CuO [8], $0.48\ \mu_B$ [9] in La_2CuO_4, $0.6\ \mu_B$ in $YBa_2Cu_3O_6$ [10]. It must be noted that the precise knowledge of that amplitude is of prime importance for the characterization of the degree of covalency and hybridization of the Cu–O bond.

In figure 3 (100) and (210) magnetic peaks are shown. Rietveld analysis leads to the variation with temperature of the magnetic moment on the copper ion shown in figure 4. We compared the data with a two-state Brillouin function, and obtained a satisfactory fit with $T_N = 47.5$ and a magnetic moment at saturation of $m = 0.45\ \mu_B$. This suggests that the molecular field theory applies here and $\beta = 0.5$ is expected for the critical exponent of the sublattice magnetization.

In order to ascertain that the direction of the magnetization is indeed along the c-axis, single-crystal experiments are scheduled to search for a magnetic contribution to the (002) peak.

Two of us (GP and MA) thank Dr V Caignaert of CRISMAT/ISMRA, France, for providing us with the Rietveld refinement program package, used in this work and in [6].

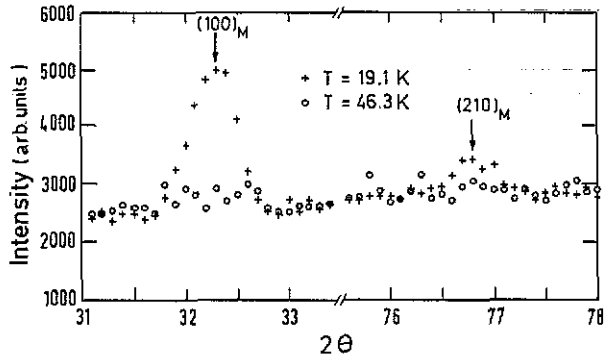

Figure 3. (001) and (210) peaks at $T = 19.1$ K and $T = 46.3$ K. Intensity versus $2\theta_B$. $\lambda = 4.725$ Å.

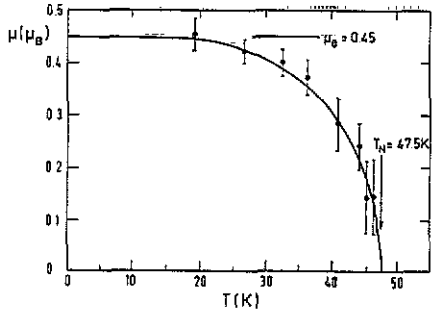

Figure 4. Variation with temperature of the magnetic moment on the copper ions, error bars being as estimated by the Rietveld refinement. The full curve is a Brillouin function best fit.

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