Three-dimensional magnetic properties of Bi_2CuO_4

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Abstract. Magnetic susceptibility and neutron diffraction measurements prove the 3D rather than the 2D or 1D character of magnetic interactions in Bi_2CuO_4. It has been shown that, at $T_N = 44.6 \pm 0.3$ K, Bi_2CuO_4 undergoes a transition to an antiferromagnetic state. The magnetic unit cell coincides with the chemical cell ($k = 0$) and is of type I. The value of magnetic moment is either $(0.53 \pm 0.1)\,\mu_B$ or $(0.75 \pm 0.1)\,\mu_B$ depending on whether the magnetic moments are oriented parallel or perpendicular, respectively, to the c axis. The effective magnetic moment of the Cu^{2+} ion is $(1.80 \pm 0.2)\,\mu_B$. The results of theoretical susceptibility calculations for the BCT lattice model and for the SQ lattice model together with the molecular-field interactions have been presented and compared with the experiment.

1. Introduction

With respect to high-T_c materials based on Cu oxides, Bi_2CuO_4 is of interest. This compound has a structure similar to that of $K_2Pt(CN)_4$ which is a well known one-dimensional (1D) system showing Peierls instability when the platinum chain is partially oxidised. However, the details of the crystal structure of Bi_2CuO_4 do not seem to have been unambiguously resolved and some doubts concerning the space group symmetry still remain.

   According to Arpe and Muller-Buschbaum (1976), Bi_2CuO_4 has I4 group symmetry in which there are two distinguishable Cu sites. Another type of structure having $P4/ncc$ group symmetry with one unique Cu site has been proposed by Boivin *et al* (1976). Interestingly, although numerous ionic Cu^{2+} compounds have been found which closely approximate the $s = \frac{1}{2}$ antiferromagnetic Heisenberg chain, none of them show a spin-Peierls (SP) transition. It must be mentioned that, once a three-dimensionally ordered magnetic structure is established, the SP transition can no longer occur. On the basis of susceptibility measurements of Bi_2CuO_4, Sreedhar *et al* (1988) have concluded that the possibility of a SP transition in this compound cannot be ruled out and have suggested that this system may exhibit 1D magnetic properties. The present bulk magnetic measurements and neutron diffraction experiments have been undertaken with the aim of elucidating the crystal structure and magnetic properties of this compound.

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2. Experimental details

Samples of Bi_2CuO_4 were synthesised by solid state reaction of Bi_2O_3 with CuO, both with 99.9% purity. The well ground mixture with a molar ratio of 1 : 1 of the components was first heated in open air at 800 °C for 48 h and then this heating was repeated twice with intermittent grinding. X-ray analysis was carried out on a Stoe powder diffractometer using Cu $K\alpha$ radiation. The single-phase samples obtained with the lattice parameters $a = 8.505(1)$ Å and $c = 5.820(1)$ Å were then divided into two portions and the first portion subjected to an additional annealing at the same temperature, while the other was quenched in air by placing it on a thick copper plate. Determination of the average valency of copper was performed by an iodometric titration method described by Horyń *et al* (1989). It was found that the average valencies of copper are identical in both the slowly cooled and the quenched samples and are equal to 2.

Magnetic susceptibility measurements were made over the temperature range 4.2–300 K, using an RH Cahn electrobalance, whereas in the temperature range 300–700 K an Obuszko microbalance method was applied.

Neutron diffraction experiments were performed at 10, 60 and 300 K, using the DMC multidetector powder diffractometer installed at the SAPHIR reactor of the Paul Scherrer Institute, Würenlingen, Switzerland (liquid-nitrogen-cooled Si filter; vertically focussing Ge(311) monochromator; $\lambda = 1.7045$ Å). The Bi_2CuO_4 powder sample volume of about 1 cm^3 was sealed under He gas into a cylindrical vanadium container of 8 mm diameter and 50 mm length. The sample was cooled to 10 K using a CTI closed-cycle helium refrigerator. In addition, neutron intensities were collected as a function of temperature on the two-axis diffractometer at the SAPHIR reactor (C(002) monochromator; 60 mm pyrolitic graphite filter; $\lambda = 2.334$ Å). To improve the peak-to-background ratio, all vanadium shields in the CTI refrigerator were replaced by aluminium. The diffraction patterns were analysed by the Rietveld (1969) profile method modified by Hewat (1973). Neutron scattering lengths were taken from Sears (1986) and the magnetic form factor of Cu was adopted from Akimitsu and Ito (1976). Absorption corrections were made according to transmission measurements.

3. Experimental results

3.1. Magnetic susceptibility

In figure 1 we show the reciprocal susceptibility as a function of temperature. The enlarged inset in figure 1 displays experimental data obtained at low temperatures. There is a marked but somewhat broad maximum in the susceptibility at around 50 K and a small rise in this quantity below 10 K. For some of our samples of Bi_2CuO_4 this rise was even more pronounced and occurred at higher temperatures. A similar effect has been reported by Sreedhar *et al* (1988). Their results are also shown in figure 1 for comparison (indicated by crosses). Most probably, the small increase in the susceptibility at low temperatures is caused by impurities, the concentration of which varies from sample to sample. As seen from figure 1, the Curie–Weiss law is obeyed well above about 200 K. Below this temperature there is an upturn in the χ^{-1} versus T curve in accordance with the results of Sreedhar *et al* (1988). Also the value of 1.8 μ_B for the effective magnetic moment of Cu^{2+} calculated from the slope of the χ^{-1} versus T curve above 200 K is very close to that given by these workers, although the values of the
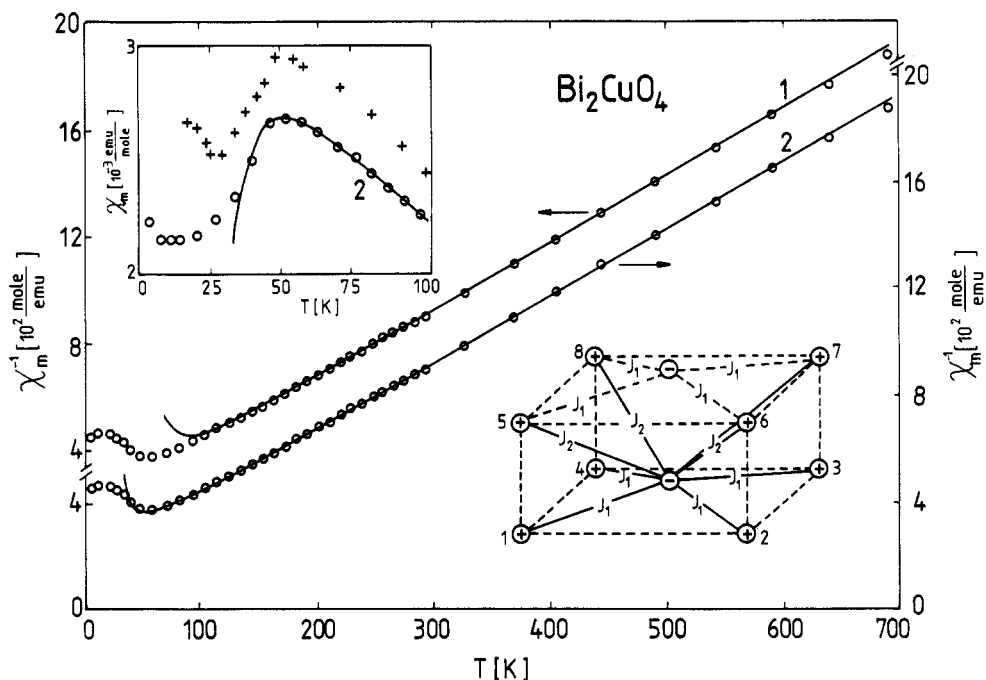
Figure 1. Inverse magnetic susceptibility versus temperature of Bi_2CuO_4 measured in the temperature range 4.2–700 K. The full curves 1 and 2 represent the theoretical results (see text). The upper inset shows the susceptibility of Bi_2CuO_4 at low temperatures measured by Sreedhar *et al* (1988) (crosses) and in the present study (open circles). The full curve represents the theoretical susceptibility calculated from equation (9) as described in the text. The lower inset illustrates the schematic arrangement of Cu^{2+} ions in the lattice. The full lines indicate the superexchange interactions J_1 and J_2.

paramagnetic Curie temperatures Θ_p differ, owing to the lower susceptibilities of our samples, from those of Sreedhar *et al* (1988) The values of Θ_p are -65 K and -40 K, respectively. It should be emphasised here that we and probably the above-cited workers have not corrected the susceptibility data on the diamagnetism of the ions forming the compound.

3.2. Neutron diffraction

In contrast to the electron diffraction patterns obtained by Sreedhar *et al* (1988) (where some peaks allowed in P4/*ncc* symmetry but not in I4 symmetry and vice versa were observed), the powder neutron diagrams recorded at room temperature and 60 K could be completely indexed in the P4/*ncc* space group. There was no evidence of impurity phases in the diffraction pattern. Comparing the reliability factors R_I for integrated intensities $R_I = 28.7\%$ and 5.8% for the I4 and P4/*ncc* space groups, respectively, it is clearly seen that the P4/*ncc* space group yields much better agreement than does the I4 space group. Our results therefore support strongly the earlier x-ray study of this compound performed by Boivin *et al* (1976). In the P4/*ncc* space group (we choose the centrosymmetrical setting) four Cu atoms occupy positions 4(c), $\pm(\frac{1}{4}, \frac{1}{4}, z)$, eight Bi sites 8(f), $\pm(-x, x, \frac{1}{4})$ and 16 oxygen atoms the positions 16 (g), $\pm(x, y, z)$. Refined values of

Table 1. Structural parameters of Bi_2CuO_4 (space group, P4/ncc), compared with earlier x-ray measurements (Boivin et al 1976). For refined parameters the number in parentheses represents the ESD of the last significant digit.

Atom	Site	x	y	z	B (Å²)
		X-rays (non-centrosymmetrical setting), 293 K			
Bi	8(f)	0.1685(2)	0.1685(2)	0.2500	0.61(7)
Cu	4(c)	0	0.5000	0.080(4)	0.5(2)
O	16(g)	0.295(4)	0.114(4)	−0.097(4)	1.2(9)
		Neutrons (centrosymmetrical setting), 293 K			
Bi	8(f)	−0.0814(2)	0.0814(2)	0.2500	0.51(1)
Cu	4(c)	0.2500	0.2500	0.0784(5)	0.38(1)
O	16(g)	0.0493(2)	0.3581(2)	0.0914(4)	0.79(2)
		Neutrons (centrosymmetrical setting), 60 K			
Bi	8(f)	−0.0817(1)	0.0817(1)	0.2500	0.0(1)
Cu	4(c)	0.2500	0.2500	0.0779(4)	0.0(1)
O	16(g)	0.0495(2)	0.3581(2)	0.0910(3)	0.2(1)
		Neutrons (centrosymmetrical setting), 10 K			
Bi	8(f)	−0.0817(2)	0.0817(2)	0.2500	0.0(1)
Cu	4(c)	0.2500	0.2500	0.0781(5)	0.0(1)
O	16(g)	0.0502	0.3585(3)	0.0906(3)	0.3(1)

Table 2. Lattice constants and agreement values R, compared with earlier x-ray measurements (Boivin et al 1976). R_I and R_p are the reliability factors of the integrated and profile intensities, respectively. R_{exp} is the expected value, based on counting statistics.

	X-rays (Boivin et al 1976) 293 K	Neutron diffraction (present studies)		
		293 K	60 K	10 K
a (Å)	8.510(1)	8.5076(3)	8.5018(2)	8.5009(4)
c (Å)	5.814(1)	5.8225(2)	5.7998(2)	5.7972(3)
R_I (%)	9.7	5.8	4.2	4.6
R_p (%)	—	9.1	7.5	7.2
R_{exp} (%)	—	3.6	3.2	2.0

the structure parameters are summarised in tables 1 and 2 and are compared with the previous results of Boivin et al (1976).

The existence of long-range antiferromagnetic ordering at low temperatures in Bi_2CuO_4 may be inferred from the neutron diffraction pattern taken at 10 K (figure 2 and inset of figure 3). It reveals two very weak peaks arising from the magnetic order of copper ions. They could be readily indexed on the basis of the chemical unit cell as M(100) and M(120). Their magnetic origin has been confirmed by the temperature variation of M(100) (figure 3). This implies an antiferromagnetic structure, in which the magnetic moments of the copper ions, related by the centre of symmetry, are aligned oppositely. Thus the magnetic unit cell coincides with the chemical cell ($a_m = a$, $c_m = c$, $k = 0$). The magnetic ordering is of type I. With the magnetic structure (cf figure 1) in mind, an attempt has been made to draw some conclusions concerning the magnetic
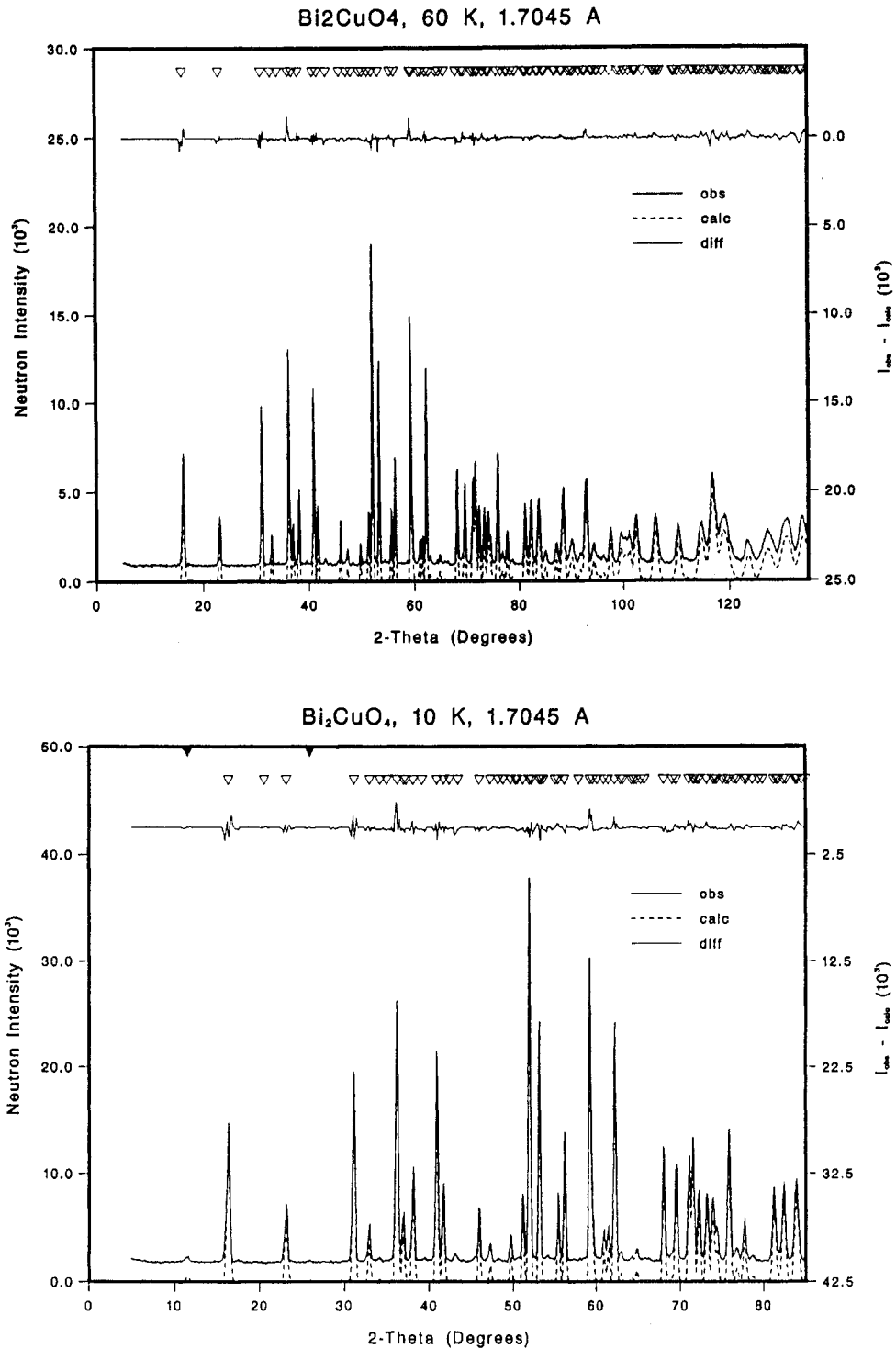
Figure 2. A comparison of neutron diffraction patterns measured at 60 and 10 K. The full and open triangles represent the positions of magnetic and nuclear reflections, respectively. The broken curves indicate the calculated profiles resulting from the Rietveld fit.
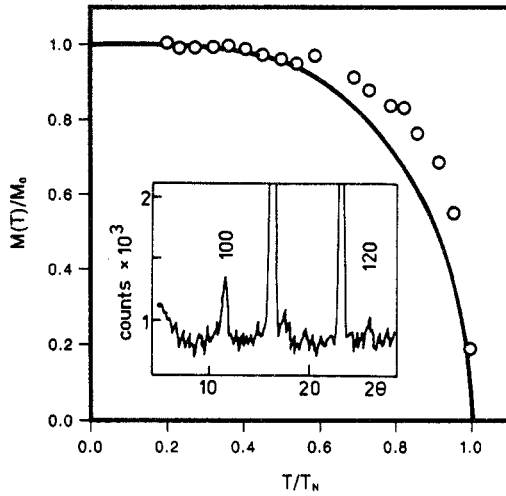
Figure 3. Temperature dependence of the reduced sublattice magnetisation of Cu^{2+} in Bi_2CuO_4 as determined from the neutron intensity of the M(100) reflection. The full curve represents the calculated molecular field result for $s = \frac{1}{2}$. The inset shows on an enlarged scale the small-angle part of the neutron diagram with the positions of the magnetic peaks 100 and 120.

Table 3. The $a_n^{(k)}$ coefficients in HTSE of the susceptibility for the BCT lattice.

n	$a_n^{(k)}$
0	$a_0^{(0)} = 1$
1	$a_1^{(0)} = 4$
	$a_1^{(1)} = 0$
2	$a_2^{(0)} = 12$
	$a_2^{(1)} = 0$
	$a_2^{(2)} = -4$
3	$a_3^{(0)} = 34.67$
	$a_3^{(1)} = 0$
	$a_3^{(2)} = -24$
	$a_3^{(3)} = 0$

moment magnitude of the Cu^{2+} ions and the moment orientation with respect to the unit-cell axes.

In uniaxial structures, the powder diffractometry allows for the determination of only an angle between the unique axis and the direction of magnetic moment. In the case under discussion this is a c axis. In Bi_2CuO_4 the problem is complicated by the fact that only two weak, purely magnetic peaks M(100) and M(120) were observed. They do not allow us to distinguish between the parallel and perpendicular alignment of the magnetic moments with respect to the c axis. Both configurations result in identical neutron powder intensities except for different magnitudes of the magnetic moments, namely $(0.75 \pm 0.1)\mu_B$ and $(0.53 \pm 0.1)\mu_B$ for perpendicular and parallel orientations, respectively, leaving the problem of their spatial orientation unresolved. M(101) and M(111) coincide with very large 102 and 112 nuclear reflections and cannot be used for the analysis. Similarly, the M(001) reflection (overlapping with the 002 nuclear peak), for which the calculated intensity for perpendicular alignment yields a negligible contribution (about 3% of the M(100) intensity) renders such an analysis unfeasible. The model of the spin configuration of Bi_2CuO_4 as determined from the present neutron
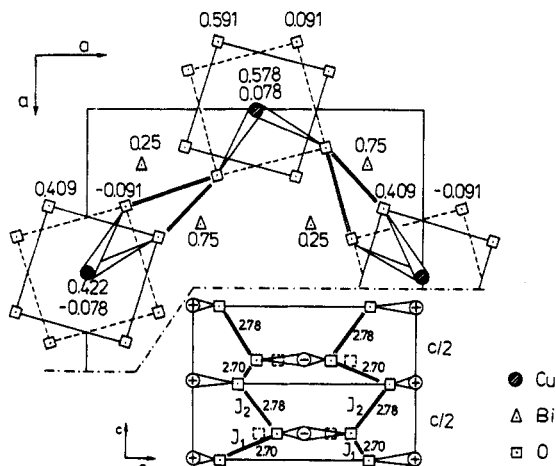
Figure 4. A part of the crystal structure of Bi_2CuO_4 projected onto the a–b plane as well as the full structure projected onto the c–a plane (the numbers are either the z parameters of atoms or the O^{2-}–O^{2-} distances). The latter projection shows schematically the Cu^{2+}–O^{2-}–O^{2-}–Cu^{2+} superexchange interactions paths labelled by J_1 and J_2. The opposite alignment of Cu spins is indicated by + and − signs.

diffraction study is sketched in figure 1. The temperature variation of the M(100) peak intensity yields the Néel temperature $T_N = 44.6 \pm 0.3$ K, which is only slightly lower than that derived from the maximum of the magnetic susceptibility—$T_N \simeq 50$ K— observed also by Sreedhar *et al* (1988).

4. Analysis of results

The main features of the crystal structure of Bi_2CuO_4 are the CuO_4 square planar units (cf figure 4) with the Cu–O distances of 2.04 Å, which are stacked along the z axis in a staggered manner. The successive square planes of oxygen atoms are rotated by an angle of about 35°. In such a coordination, the $d_{x^2-y^2}$ orbitals of Cu^{2+} d^9 ions, directed towards the oxygen anions, are expected to be half filled, whereas those along the z axis, i.e. d_{z^2} orbitals, should be filled. The direct cation–cation interactions in the Bi_2CuO_4 structure seem to be negligible. Also the simple cation–anion–cation superexchange interactions are not possible in this structure. Only the superexchange via two oxygen atoms between Cu^{2+} ions can be considered (see figure 4). In this process, two holes are excited virtually from Cu to the neighbouring O sites and result in antiferromagnetic coupling after interchanging their position on oxygen atoms. In view of these considerations it seems reasonable to assume that the type of magnetic ordering in Bi_2CuO_4 will be mainly determined by the interactions between the near neighbours lying in the closest sheets perpendicular to the C axis. Each Cu ion has eight such Cu neighbours, four of which lie in a plane below and four are situated in a plane above the Cu ion. The interactions between them are labelled in figure 4 and in the lower inset in figure 1 by J_1 and J_2, respectively. Both interactions are negative owing to the antiparallel alignment of the corresponding Cu moments.

To interpret the observed susceptibility in terms of exchange interactions, we assume that our system can be described by an isotropic $s = \frac{1}{2}$ Heisenberg model. This assumption

is particularly applicable to Cu^{2+}-containing compounds (de Jongh and Miedema 1974). The corresponding Hamiltonian has the form

$$\mathcal{H} = -\sum_i^N \left(2J_1 \sum_{j_i=1}^4 \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_{j_i} + 2J_2 \sum_{j_i=5}^8 \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_{j_i} + g\mu_B \sigma_i^z H \right) \tag{1}$$

where $\boldsymbol{\sigma}_i = (\sigma_i^x, \sigma_i^y, \sigma_i^z)$ is the vector of Pauli matrices and $N (\equiv n^3)$ is the total number of spins in the system. In the high-temperature series expansion (HTSE) technique (Domb and Green 1974), the susceptibility can be expressed as follows:

$$\chi(T) = \frac{C}{T} \sum_n b_n \left(\frac{J}{k_B T} \right)^n \qquad C = \frac{g^2 \mu_B^2 s(s+1)}{3k_B}. \tag{2}$$

For Bi_2CuO_4,

$$b_n = \sum_k^n a_n^{(k)} \alpha^k \qquad \alpha = \frac{J_1 - J_2}{J_1 + J_2} \qquad J = \frac{J_1 + J_2}{2}. \tag{3}$$

In the expansion of b_n we used the coefficients $a_n^{(0)}$ as for the body-centred cubic (BCC) lattice (see, e.g., Domb and Green 1974) and we have calculated the corrections $a_n^{(k)}$ for the tetragonal lattice up to $n = 3$, relying on the fact that the higher-order terms would affect the lower-temperature results more than higher-temperature results. Note that the case $J_1 = J_2$ corresponds to the BCC lattice while, for J_1 or $J_2 = 0$, expansion (2) corresponds to the two-dimensional (2D) simple quadratic (SQ) lattice. The evaluation of J_1 and J_2 using the two-point non-linear least-squares Levenberg–Marquart method could be performed by fitting $\chi(T)$ to the experimental data only above about 150 K. The theoretical curve 1 together with the experimental data are displayed in figure 1. It may be seen that the fit, especially at the highest temperatures which are the most important for the determination of exchange integrals, is quite good. The increased discrepancy towards the lowest temperature, i.e. below about 150 K, is readily explained by omission of the higher-order terms in expansion (2). For $g = 2.05$, for which the error of fitting is minimal (ESR experiment gives $g = 2.08$ (Sreedhar et al 1988)), the resulting values of the exchange constants J_1 and J_2 are as follows:

$$J_1/k_B = -24.6 \pm 2.9 \text{ K} \qquad J_2/k_B = -5.9 \pm 3.4 \text{ K}.$$

Using the values of J_1 and J_2 obtained above we can roughly estimate the Néel temperature T_N. Namely, from equation (2) the paramagnetic Curie temperature Θ_p is $(J_1 + J_2)a_1^{(0)}/2k_B$. Then combining the mean value $J = (J_1 + J_2)/2$ with the expression $T_N = 2.8|J|/k_B$ for the BCC lattice (Domb and Green 1974, Rushbrooke and Wood 1963) we obtain $T_N = 42.6$ K, which is very close to the experimental value of 44.6 ± 0.3 K, found in the neutron diffraction measurement. As a cross check of the method used above, we have attempted to recalculate these parameters in the mean-field approximation (MFA). This can be done by rewriting the Hamiltonian (1) as follows:

$$\mathcal{H}' = -\sum_{planes}^n \left[\sum_k^{n^2} \left(2J_1 \boldsymbol{\sigma}_k \cdot \sum_{l_k=1}^4 \boldsymbol{\sigma}_{l_k} + 2zJ_2 \sigma_k^z \langle \sigma_{l_k}^z \rangle + g\mu_B \sigma_k^z H \right) \right]$$

$$= -\sum_{planes}^n \left(\sum_k^{n^2} 2J_1 \boldsymbol{\sigma}_k \cdot \sum_{l_k=1}^4 \boldsymbol{\sigma}_{l_k} + \sum_{k\,odd} g\mu_B \sigma_k^z \lambda M_1 - \sum_{k\,even} g\mu_B \sigma_k^z \lambda M_2 \right.$$

$$\left. + \sum_k^{n^2} g\mu_B \sigma_k^z H \right) = \sum_{planes}^n \mathcal{H}_0' \tag{4}$$

where H is the magnetic field, $z = 4$ is the number of nearest neighbours and λ is the molecular-field constant:

$$\lambda = 2zJ_2/g^2\mu_B^2. \tag{5}$$

The magnetisation M should be determined self-consistently from

$$M_{1,2} = \mp g\mu_B\langle\sigma_k^z\rangle = \mp g\mu_B \, \mathrm{Tr}[\sigma_k^z \exp(-\beta\mathcal{H}_0')]/\mathrm{Tr}[\exp(-\beta\mathcal{H}_0')] \tag{6}$$

where the $-$ and $+$ signs indicate k odd and k even, respectively.

It is worth noting that the above non-linear equation for M arises directly from the conditions necessary for the minimum of the free energy of our system, defined for example by Bogolubov (see Tiablikov 1975).

The first term of the Hamiltonian (4) describes the $s = \frac{1}{2}$ Heisenberg model for the 2D SQ lattice with the exchange parameter J_1, while the next two terms describe interplane interactions in the MFA (see lower inset of figure 1). To calculate the magnetic susceptibility χ for this model (Watanabe 1962) let us consider the response of the system to a small change δH in the external magnetic field:

$$\delta M = \chi \, \delta H. \tag{7}$$

We can also relate δM to a small change in the total field seen by the spins:

$$\delta M = \chi_{SQ}(\delta H + \lambda \, \delta M) \tag{8}$$

where the 'intrinsic' susceptibility χ_{SQ} corresponds to the SQ lattice. Then we obtain

$$\chi = (1 + |\lambda|\chi_{SQ})^{-1}\chi_{SQ}. \tag{9}$$

The values of the coefficients b_n for χ_{SQ} in expansion (2) for $J = J_1$ are well known (Domb and Green 1974). By fitting equation (9) to the high-temperature experimental data, and again using the two-point non-linear least-squares Levenberg–Marquart method, the best fit has been obtained as before for $g = 2.05$, with the following values of parameters J_1 and J_2:

$$J_1/k_B = -25.4 \pm 1.1 \text{ K} \qquad J_2/k_B = -5.5 \pm 0.5 \text{ K}.$$

The results of the fitting procedure is presented in figure 1 as the theoretical curve 2 which follows the experimental points almost down to lowest temperatures. Thus we obtained very good agreement with the calculated parameters of the previous fitting. The above calculation yields the ratio $J_1/J_2 \simeq 4.5$ ($\alpha \simeq \frac{2}{3}$) which is fairly large, but not sufficient to cause 2D behaviour of our system.

The observed values of the ordered magnetic moment are apparently lower than that expected for $s = \frac{1}{2}$ (about $1\mu_B$). It is well known that the zero-point spin deviation effect, especially in 2D systems, is significant (Chakrawerty et al 1988, Horsh and Van den Linden 1988) and leads to a considerable reduction in the value of the ordered Cu^{2+} magnetic moment. Alternatively, the lowering of the moment can be due to covalency effects of the Cu–O bonding. We think that both effects may be important here. On the basis of the present experiment, one may conclude that neither SP behaviour nor quasi-1D character can be attributed to the studied compound. Thus Bi_2CuO_4 manifests itself as a mostly three-dimensional magnetic system (half-spin Heisenberg antiferromagnet). For a better description of its magnetic structure a single-crystal measurement would be required.

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