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Exchange striction and exchange constants in Bi_2CuO_4

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Abstract. The crystal and magnetic structures of Bi_2CuO_4 have been refined between 18 and 113 K in 1 K intervals. Long-range antiferromagnetic order occurs below $T_N = 41.9 \pm 0.5$ K and an exchange striction that shows hysteresis behaviour is observed. A method for estimating the magnetic exchange constants from the exchange striction is presented and applied to the Bi_2CuO_4 data. The resulting values show that strong ferromagnetic exchange takes place between Cu^{2+} spins in infinite stacks of CuO_4 square planes, and weaker antiferromagnetic interactions occur between neighbouring stacks.

1. Introduction

The discovery of high-temperature superconductivity in lanthanum barium copper oxide [1] has given impetus to the study of the magnetic and electronic properties of ternary copper oxides [2] and the relationship between the thermal evolution of these properties and crystal structure [3, 4].

Bi_2CuO_4 is of interest as it has a structure similar to that of the one-dimensional material $\text{K}_2\text{Pt}(\text{CN})_4$ [5] and contains stacks of isolated CuO_4 square planes [6] (see figures 1 and 2). The magnetic susceptibility data for this compound have been interpreted in terms of an antiferromagnetic spin chain that breaks into dimers or charge-disproportionates at low temperatures [2, 7]. This study of the crystal and magnetic structures of Bi_2CuO_4 by low-temperature neutron diffraction was undertaken to investigate these possibilities.

2. Experimental details

Polycrystalline Bi_2CuO_4 was prepared by firing a pelleted 1:1 mixture of Bi_2O_3 and CuO at 700 °C in air. The sample was reground and repelleted several times during a total heating time of three days. The x-ray powder diffraction pattern agreed with that reported [8], and a trace of Bi_2O_3 was also observed.

Neutron diffraction data were collected on diffractometer D1b at the ILL, Grenoble. 10 g of Bi_2CuO_4 were sealed in an 8 mm diameter cylindrical vanadium can and cooled from room temperature to 18 K at about 5 K min^{-1} in a helium cryostat. Diffraction patterns were recorded every 180 s during cooling in order to locate approximately any phase transitions. The sample was held at 18 K for 15 min and then heated to 113 K at 0.002 K s^{-1} while a diffraction pattern was collected every 500 s. The pattern was re-

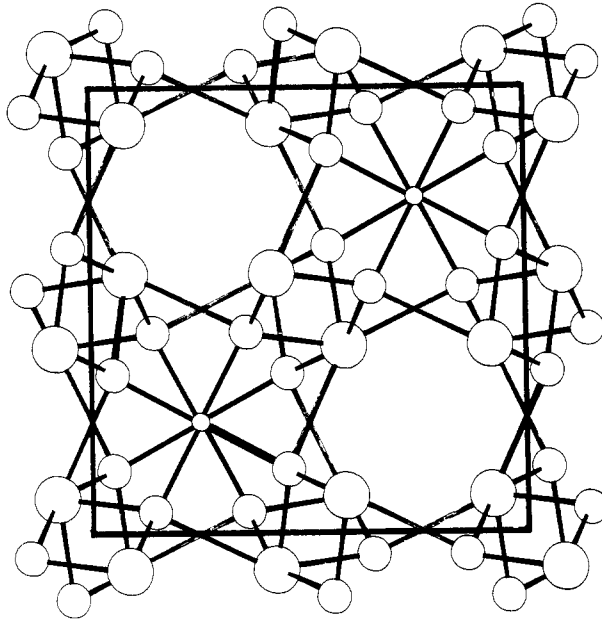


Figure 1. The structure of Bi_2CuO_4 projected onto the (001) plane (Bi/O/Cu are large/medium/small circles).

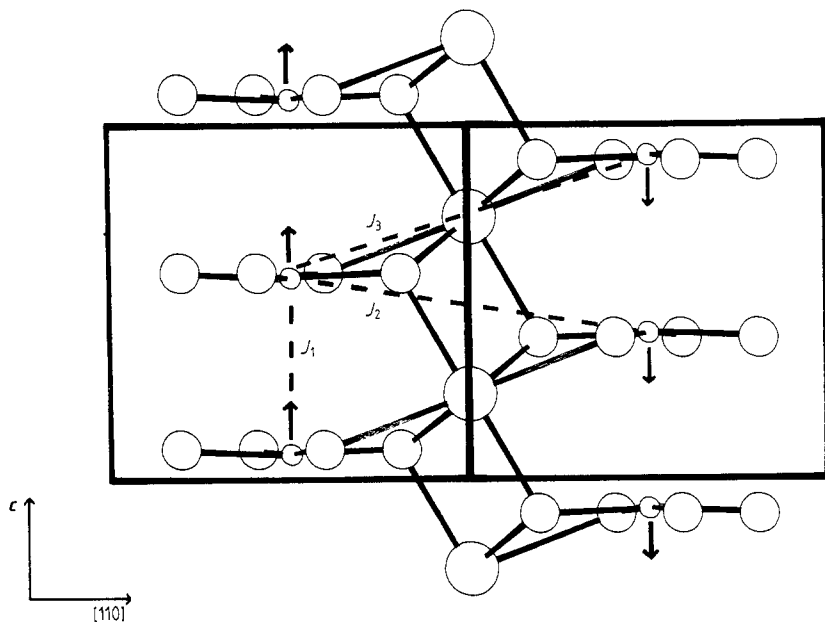


Figure 2. A $\bar{1}10$ view of the unit cell of Bi_2CuO_4 showing the linking of the stacks of CuO_4 units by Bi^{3+} cations. The spin directions in the ordered magnetic structure are shown and the exchange interactions referred to in the text are labelled.

corded by a stationary, 400-element, position-sensitive detector covering the range $2\theta = 10\text{--}90^\circ$ with a 0.2° spacing between elements. The neutron wavelength was 2.522 \AA .

3. Structure refinements

Inspection of the diffraction patterns revealed no gross structural changes between 18 and 113 K. Magnetic diffraction peaks were evident below an ordering temperature of $T_N = 41.9 \pm 0.5 \text{ K}$ and no other magnetic transitions were observed.

The diffraction profiles were fitted by the Rietveld method [9]. A standard program [10] was modified so as to perform sequential refinements in order of ascending or descending temperature, using the refined parameters from one pattern as a starting model for the next. This enabled all of the profiles to be fitted automatically, as the changes from one pattern to the next are very small. A diffraction pattern recorded while the sample had cooled from 33 to 19 K was also fitted.

The nuclear diffraction peaks were fitted using the structure in tetragonal space group $P4/ncc$ given by Boivan *et al* [6]. (The $I4$ symmetry reported elsewhere [11] is erroneous.) During the early part of this work, the antiferromagnetic structure of Bi_2CuO_4 was communicated by Rodriguez-Carvajal [12], and this model was used to fit the magnetic peaks. Neutron scattering lengths [13] and the magnetic form factor for Cu^{2+} [14] were taken from standard works.

The temperature variations of the magnetic moment, cell parameters a and c , and volume V are shown in figure 3. The refined atomic coordinates did not change significantly over the temperature range of the experiment and average values are given in table 1 with other details of the fits. Typical observed, calculated, and difference profiles are shown in figure 4.

4. Calculation of exchange parameters

The discontinuities in the cell parameters and volume seen around T_N in figure 3 are due to an exchange striction: a slight deformation of the structure due to the magnetic exchange interactions in the antiferromagnetically ordered phase. Exchange strictions are well known in simple antiferromagnets such as MnO [15], and can be related to the magnetic exchange constants if the elastic constants are known. As such lattice dynamic properties can be calculated from experimentally derived interatomic potentials [16], the following method has been devised to estimate exchange constants from observed discontinuities in the structural parameters x_i (cell constants and fractional atomic coordinates).

Let X_p be the set of parameters that would describe the structure at some temperature below T_N if no magnetic order occurred. These values can be determined by extrapolation from the paramagnetic region. The set of observed values, X_m , is obtained from the refinement of the magnetically ordered structure at this temperature. The former values describe the minimum energy structure when only the total lattice energy (E_L) is considered, i.e.

$$\partial E_L(X_p)/\partial x_i = 0 \quad (1)$$

while the latter describe the minimum energy configuration taking both the lattice and magnetic energies (E_M) into account:

$$\partial [E_L(X_m) + E_M(X_m)]/\partial x_i = 0. \quad (2)$$

Both ionic and short-range interactions are considered in calculating the derivatives

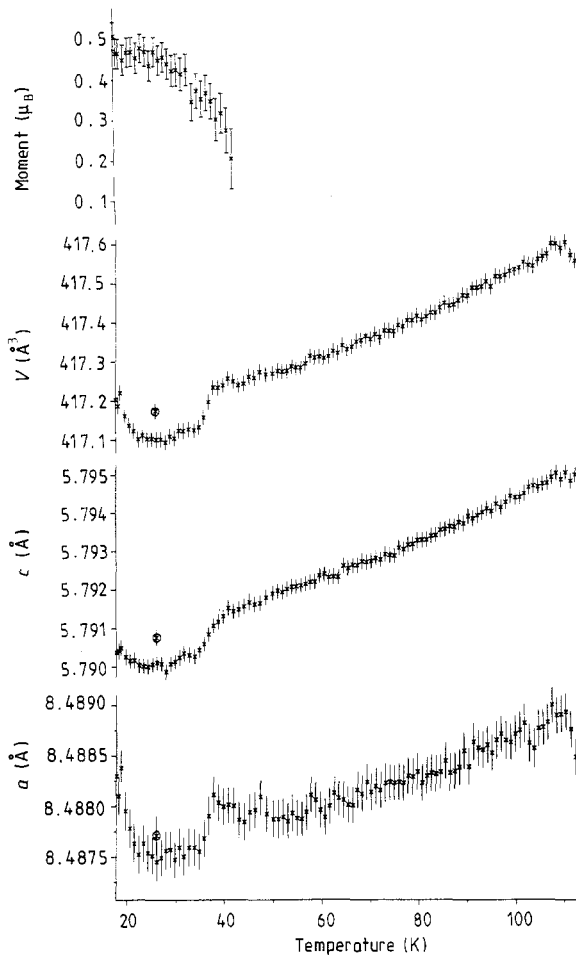


Figure 3. The temperature variations of (from top to bottom) the magnetic moment, cell volume, and tetragonal c and a cell parameters from the refinements of the magnetic and crystal structures of Bi_2CuO_4 . The error bars correspond to one ESD. The circled points are derived from the profile collected while cooling the sample from 33 to 19 K; all others come from the slow warming of the sample from 18 to 113 K in 1 K intervals.

Table 1. Details and results of the refinements of Bi_2CuO_4 with ESDs in parentheses. The parameters and R -factors are defined in [9].

Range of 2θ 10–90°

Number of profile points 364

Number of nuclear hkl 21

Refined atomic parameters: scale, overall B_{ISO} , 5 (x, y, z), μ_z^a

Refined profile parameters^b: a, c, U, V, W , 1 background variable

Typical R -factors:

$R_{\text{WP}} = 3.0\%$ $R_{\text{P}} = 2.3\%$ $R_1 = 1.0\%$ $R_{\text{EX}} = 1.1\%$

Average fractional coordinates in P4/ncc (space group No 130)

Atom	Symmetry position	x	y	z
Bi	8(f)	0.4183(1)	0.9183(1)	$\frac{1}{4}$
Cu	4(c)	$\frac{1}{4}$	$\frac{1}{4}$	0.0771(2)
O	16(g)	0.5493(1)	0.8575(1)	−0.0909(2)

^a μ_z , the z -component of the magnetic moment, was varied only for patterns below 42 K.

^b The zero-point error in counter position was fixed at a predetermined value.

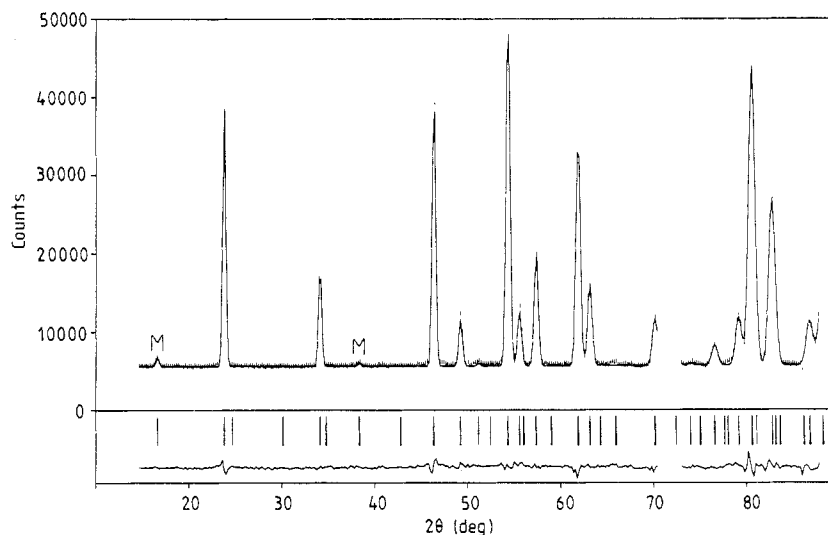


Figure 4. Typical (20 K) observed (points), calculated (full curve) and difference neutron diffraction profiles for Bi_2CuO_4 , with reflection positions marked and prominent magnetic peaks labelled 'M'. A weak Bi_2O_3 reflection at $72^\circ 2\theta$ was excluded from the refinement.

of E_L [16]. The ionic parts are calculated from a formal point-charge model using Ewald's method [17, 18] and the short-range interactions are described by two-body Buckingham potentials:

$$V(r) = Ae^{-r/\rho} - Cr^{-6} \quad (3)$$

where r is the interatomic distance. Values of A , C and ρ that satisfy equations (1) are found by least-squares fitting or other procedures and are then used to calculate the appropriate terms in equations (2), giving the derivatives of E_M .

In magnetic insulators, the dominant contributions to E_M are the Heisenberg interactions between spins S_i and S_j characterised by the exchange parameter J_{ij} :

$$E_M = -2\sum J_{ij}S_i \cdot S_j. \quad (4)$$

J is commonly assumed to have the form

$$J = J_0 r^{-n} \quad (5)$$

giving

$$dJ/dr = -(n/r)J. \quad (6)$$

Hence

$$\partial E_M / \partial x_i = 2\sum (n/r_{ij})J_{ij}(\partial r_{ij} / \partial x_i)S_i \cdot S_j. \quad (7)$$

Equations (7) enable the exchange parameters to be estimated if the exponent n is known. Experimental measures of n have been made for 180° M–X–M super-exchange interactions. De Jongh and Block found $n = 12$ from the variation of J with M^{2+} – M^{2+} distance in some manganese, cobalt, and nickel fluorides [19]. The values of ε for the linear Mn–X–Mn interactions in MnO and MnS have been reported as 12.4 and 12.2, respectively [15], where

$$\varepsilon = -r(d(\ln J)/dr). \quad (8)$$

If J varies as equation (5) then $\varepsilon = n$. Hence we have assumed $n = 12$ in calculating the exchange interactions in Bi_2CuO_4 .

Table 2. Potential parameters for Bi_2CuO_4 .

Interaction	A (eV)	ρ (Å)	C eV Å ⁻⁶	Reference
$\text{Bi}^{3+}\text{-O}^{2-}$ ^a	1644.98	0.33644 ^b	0	[20]
$\text{Cu}^{2+}\text{-O}^{2-}$	294.15	0.44778 ^b	0	[20]
$\text{O}^{2-}\text{-O}^{2-}$	22764.3	0.1490	27.88	[16]

^a The values derived for the $\text{La}^{3+}\text{-O}^{2-}$ potential were used as La^{3+} and Bi^{3+} have equal ionic radii.

^b This value adjusted to satisfy equations (1).

The refinements of Bi_2CuO_4 show that only the cell parameters a and c display a significant discontinuity around T_N , and so two equations result from expressions (1), (2), and (7). The exchange parameters were calculated from the refined results at 27 K, which we assume to be the lowest temperature at which the full exchange striction was observed during the heating experiment. The estimated cell parameters if magnetic order were absent at 27 K are $a_p = 8.4879(1)$ Å and $c_p = 5.7910(1)$ Å, the observed parameters are $a_m = 8.4875(1)$ Å and $c_m = 5.7901(1)$ Å, and the refined magnetic moment is $0.46(4)$ μ_B . The parameters for the Buckingham potentials were taken from the literature [16, 20] and are shown in table 2; the ρ -values for the Bi–O and Cu–O interactions were adjusted to satisfy equations (1). The derivatives were calculated several times with slightly different sets of potential parameters to determine their sensitivity to these values. It was found that the derivatives were insensitive to these variations provided that the set of parameters satisfied equations (1). The resulting derivatives of E_M were found to be $\partial E_M/\partial a = 17(2)$ meV Å⁻¹ and $\partial E_M/\partial c = 16(1)$ meV Å⁻¹.

Significant magnetic exchange interactions occur within and between the chains of stacked CuO_4 units in Bi_2CuO_4 . There is one intra-chain (J_1) and two inequivalent inter-chain (J_2 and J_3) exchange interactions, as shown in figure 2. As it is not possible to estimate all three parameters from the two derivatives of E_M , J_2 and J_3 were assumed to be equal, giving $J_1/k = 193(4)$ K and $J_2/k = -90(5)$ K from equations (7).

5. Discussion

Although diffractometer D1b gives low-resolution neutron diffraction patterns over a limited 2θ -range, these data are sufficient to give a precise description of simple structures such as that of Bi_2CuO_4 . The advantage of such an instrument is that the sample and detectors are stationary throughout the experiment, which results in very high relative accuracy between parameters derived from successive patterns, enabling subtle structural changes to be detected [4].

The refinements of Bi_2CuO_4 over the range 18–113 K show that long-range antiferromagnetic order occurs below $T_N = 41.9 \pm 0.5$ K and there is no change in the spin arrangement between 18 K and T_N . The magnetic structure agrees with that reported [12] (figure 2) in which each spin is parallel to those in the same stack of CuO_4 units along the z axis, but is antiparallel to those in the four neighbouring stacks. The spins lie parallel to c and the magnetic unit cell is identical to the structural one. At 18 K the ordered moment of 0.5 μ_B is significantly less than the limit of $0.8\text{--}1.0$ μ_B expected for a Cu^{2+} spin. This value, which is similar to those in other copper oxides such as $\text{La}_2\text{CuO}_{4-y}$ [21] and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [22], may be lowered by covalency effects, although the moment

may also not be fully saturated at 18 K. The decrease in the moment from 18 K to T_N follows a typical Brillouin curve.

The temperature variations of the cell parameters and volume shown in figure 3 reveal an exchange striction around T_N that appears to be reversed between 18 and 23 K. This is ascribable to a hysteresis in the exchange striction due to the rapid cooling of the sample from above T_N to 18 K at the start of the experiment. The refined cell parameters for the profile collected while the sample was cooled from 33 to 19 K confirm this. The c -value is significantly greater than those obtained during the slow warming of the sample over the same temperature range, and lies on a line interpolated between the values above T_N and at 18 K. The trend in the a parameter is less clear, due in part to the greater ESDs in these values. The magnetic moments in figure 3 show no anomalous changes between 18 and 23 K, demonstrating that there is hysteresis only in the exchange striction of the structure, and not in the magnetic order, and that the phenomenon is not due to a lack of thermal equilibrium between the sample and the thermocouple or some other error in the temperature measurement.

The observation of hysteresis in an exchange striction transition is unusual, although such behaviour is known in magnetostrictions. This may be a consequence of domain formation or kinetic factors and shows that exchange striction may be regarded as a structural transition that is caused by, but is not necessarily coincident with, a magnetic ordering transition. This is analogous to the hystereses that have been observed in pressure-induced transformations [23]; the magnetic order gives rise to an 'internal pressure' that causes the slight structural deformation. The width of the hysteresis in this experiment is not clear, as the exchange striction was not first observed when cooling the sample but while slowly warming it from 18 K after rapid cooling from above T_N .

The method described above enables exchange constants to be estimated by calculating the derivatives of E_M from the observed exchange striction. The ESDs quoted in the above values reflect the experimental errors in the cell parameters and the magnetic moment. However, it is more difficult to estimate the uncertainty in the exponent n in equations (7); if $n = 12 \pm 1$ [19] then additional errors of $\pm 8\%$ are introduced into the exchange constants. Hence, an alternative use of the method might be to calculate n when the exchange constants are known.

The estimated magnetic exchange constants show that strong ferromagnetic exchange takes place between neighbouring CuO_4 square planes in the chains parallel to c , and that the inter-chain exchange is weaker and antiferromagnetic. The intra-chain Cu–Cu distance of 2.90 Å and exchange constant of 193(4) K are comparable to the distances and the magnitude of the exchange constants of -220 to -240 K in the hydrated copper acetate dimer and related compounds [24]. In the latter compounds there is antiferromagnetic super-exchange between eclipsed CuO_4 units through the bridging acetate groups, but in Bi_2CuO_4 neighbouring square planes are staggered by 33.6° and ferromagnetic potential exchange dominates the super-exchange interaction. The interactions between chains are mediated by Cu–O–O–Cu and Cu–O–Bi–O–Cu pathways in which mutual overlap of the magnetic orbitals with ligand orbitals occurs and so the exchange is antiferromagnetic. However, the calculated value of $-90(5)$ K for the average inter-chain exchange parameter may be an overestimate as this has twice the magnitude of T_N .

Although the accuracy of exchange constants derived by this method is poorer than that for those determined by conventional spectroscopic or susceptibility methods, there are some potential advantages in this methodology. Most conventional techniques have to assume a model for the dimensionality and sign of the interactions, and can only be

used to estimate two or three independent values. This method determines the sign of the exchange constants directly from the scalar products $S_i \cdot S_j$, as neutron diffraction gives both the direction and magnitude of the magnetic moments. In Bi_2CuO_4 the intra-chain Cu–Cu interaction is shown to be ferromagnetic by this method although exchange constants were previously derived from susceptibility data assuming antiferromagnetic exchange [2, 7]. Another advantage is that as many exchange constants can be estimated as there are independent structural variables that change significantly around T_N . In this study, changes were only observed in the cell parameters, but the method is applicable to changes in fractional atomic coordinates or derived quantities such as bond distances and angles, which will give detailed insight into magneto-structural relationships. Continuing improvements in high-resolution powder diffractometry and profile refinement techniques makes it possible to measure precisely structural parameters even for large or low-symmetry structures. It is notable that an exchange striction was observed in this study although the ordered moment is $\leq 0.5 \mu_B$. As moments of up to $5 \mu_B$ may be found in transition-metal salts, it should be possible to observe much larger effects in other systems.

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