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CRYSTAL AND MAGNETIC STRUCTURE OF Li_2CuO_2

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The crystal structure of Li_2CuO_2 has been reinvestigated and its magnetic structure solved by neutron powder diffraction. The crystal structure, according to an earlier work, is adequately described in the space group Immm. The copper atoms constituting the structural chains are coupled ferromagnetically, giving rise to ferromagnetic layers perpendicular to the c axis. The layers are coupled antiferromagnetically. The magnetic structure has a propagation vector k=[001] and is colinear with spin directions along the a axis and well described by the magnetic mode A_x (Shubnikov group: $I_pmm'm'$). The magnetic moment of copper atoms at 1.5 K is $0.96(4)\mu_B$, which is very close to the saturation moment of spin only Cu^{+2} (d^9). Contrary to the antiferromagnetic parents of high T_c superconductors, the small zero-point reduction of the magnetic moment in Li_2CuO_2 supports a 3D behaviour of the magnetic interactions.

1.Introduction

There is currently a renewed interest in the study of the electronic and magnetic properties of ternary copper oxides [1]. Indeed, rationalizing the behaviour of these relatively simple systems could provide us with a useful tool to approach the understanding of the more complex behaviour displayed by the related high T_c superconductors. In particular, the study of the magnetic properties acquires relevance in the light of the claim of some theories about a pairing superconductivity mechanism of magnetic origin [2].

In this context, we have recently described the magnetic structure of Bi_2CuO_4 [3]. As a continuation of this work, we have carried out new neutron diffraction experiments (1.5 and 290 K) involving the oxides Sr_2CuO_3, Ca_2CuO_3, $SrCuO_2$ and Li_2CuO_2. All these oxides contain also square-planar [CuO_4] structural units which share corners (Sr_2CuO_3 and Ca_2CuO_3), edges (Li_2CuO_2) or corners and edges ($SrCuO_2$) [4]. Previous results on these materials include magnetic [2], EPR [5a] and 290K neutron diffraction data [5b].

The magnetic behaviour of Sr_2CuO_3, Ca_2CuO_3 and $SrCuO_2$ is quite similar [2]. They all have very low temperature-independent susceptibilities, suggesting a high antiferromagnetic ordering temperature. Otherwise, the susceptibility of Li_2CuO_2 shows a Curie-Weiss behaviour with a negative value of Θ, which is indicative of antiferromagnetic interactions.

As far as we have progressed in the analysis of our neutron diffraction experiments, there is no clear evidence of peaks of magnetic origin for Sr_2CuO_3, Ca_2CuO_3 and $SrCuO_2$. However in the case of Li_2CuO_2 we observe the appearance at 1.5 K of peaks due to reflections of magnetic origin. Thus, in this work we report the magnetic structure of Li_2CuO_2.

2. Experimental

Polycrystalline samples of Li_2CuO_2 were prepared from stoichiometric amounts of $Li(OH).H_2O$ and CuO. Powdered solids were thoroughly mixed by centrifugal milling in a Fritch-Pulverisette for 30 min. using isopropanol as dispersive medium. The homogenized powder was fired in an alumina boat at 420°C for 8 hours and then at 700°C during 4 days. The X-ray powder diffraction pattern of the resulting brown product was obtained by means of a Kristalloflex 810 Siemens diffractometer using CuK_α radiation. This experimental pattern corresponds to single-phased Li_2CuO_2.

Magnetic susceptibility has been also measured in an AC susceptometer and a preliminary analysis of the results gives a paramagnetic Curie temperature Θ=-41.1K and T_N=8.3K. The Néel temperature was taken as the point at which $d\chi/dT$ changed sign on the low temperature side of the peak.

Neutron powder diffraction experiments were performed with the D2B high resolution powder diffractometer at the I.L.L in Grenoble. About 10g of powdered Li_2CuO_2 sample were used for the experiment. The sample was put into a cylindrical vanadium can (D = 8 mm, h = 5 cm) and inserted into a helium cryostat. Temperature was computer -controlled and its stability during the measurements was better than 0.1 K.Two diffraction patterns were collected at 1.5 K and 290 K.

D2B was used in its high flux mode of operation which gives resolution good enough for our problem and diminishes the difficulties of handling complicated peak shapes due to monochromator defects. The step size for this experiment was 0.05° in 2θ. The explored angular range was 0-160° (2θ) and the preselected monitor counts, for a fixed position of detector bank, was 100000. The total counting time for each diffraction pattern was about 150 minutes. The neutron wavelength used was 1.5945 Å.

The Rietveld method [6] was used to refine the crystal and magnetic structure. The analysis of the data was performed using the STRAP package [7]. An absorption correction was included in the refinements to take into account the non negligible absorption of neutrons by Li nuclei. The empirical formula used for this correction was given by Rouse *et al.* [8]. The effective μR used in the refinements was 0.751. Moreover, a preferred orientation correction using the March model [9], was performed taking the [100] axis as the preferred orientation vector.

3. Results

The main difference between the diffraction patterns at 1.5 K and 290 K is the appearance of additional magnetic diffraction peaks assignable to reflections which are not allowed in the Immm space group. The low angle parts of the diffraction patterns at the two temperatures are shown in Fig.1 (notice that we are representing Log of the intensity).

Crystal Structure

We have refined the crystal structure on the basis of the previously proposed model [10]. Indeed, the structure is correctly described in the space group Immm for both temperatures. The simplicity of the structure and the low number of positional parameters to fit have allowed the refinement of the anisotropic thermal parameters of all the atoms. Nevertheless, the absolute values of the thermal parameters are, perhaps, not exact due to the uncertainty on the absorption correction. Table I shows the relevant crystallographic fitted parameters and the reliability factors of the refinements for each temperature and Table II summarizes the more significant interatomic distance values. The Rietveld refinement performed for the 290 K case is shown in Fig. 2, where the observed, calculated, difference patterns and the Bragg reflection markers have been plotted. Fig. 3 shows a schematic view of the structure. The structure can be described as consisting of edge-sharing $[CuO_4]$ nearly square planar units -lying on the bc plane- which are linked together along the **b** axis. The resulting $[CuO_2]$ chains are stacked in the **a** axis direction in such a way that each chain is surrounded by six other ones which are related to the former through the translations (±1/2, 1/2, ±1/2) and (±1, 0, 0). Joining the chains between them are [LiO] layers in which the local symmetry around the metallic atoms is D_{2d}. No particular distortion or structural phase transition is detected with the temperature variation.

Magnetic Structure

Given that the magnetic reflections can be indexed using the crystallographic unit cell, the reduced propagation vector of the magnetic structure can be taken as **k**=[000]. In this case, the application of the Macroscopic Theory of Bertaut to obtain the possible magnetic structures is straightforward. Having two magnetic atoms in the unit cell the only magnetic modes are :

$$F = S_1 + S_2 \qquad A = S_1 - S_2$$

The magnetic atoms are numbered according to :

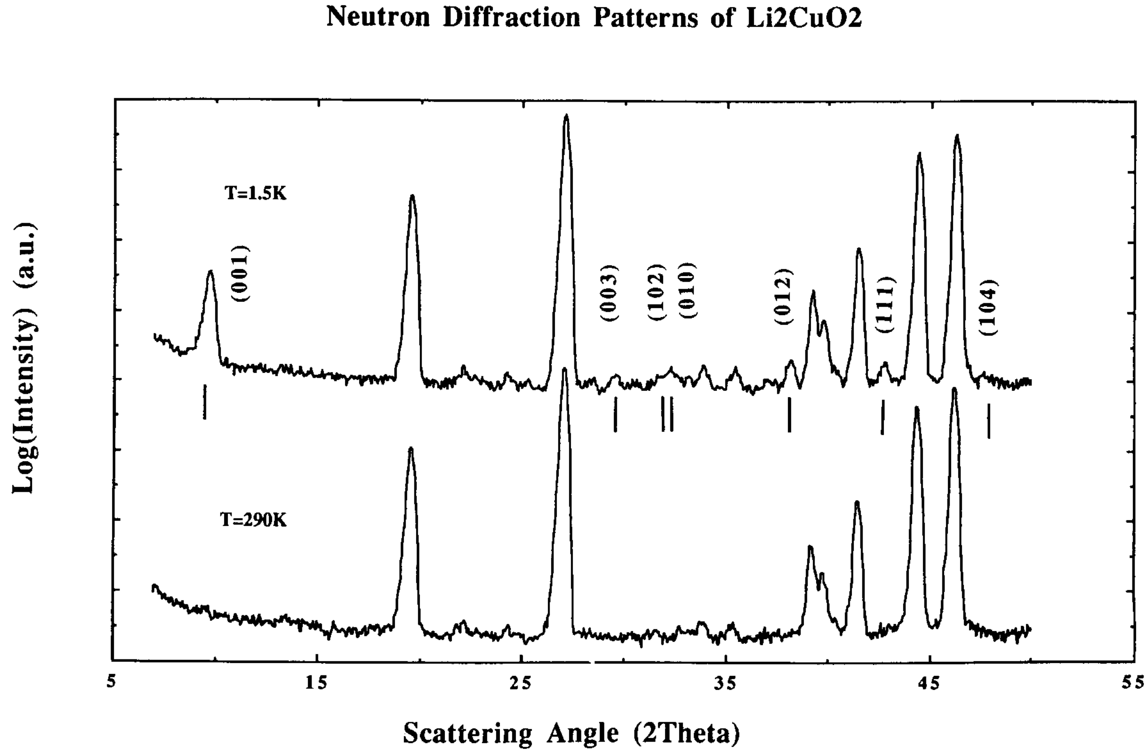

Fig.1. Low angle part of the neutron diffraction patterns of Li_2CuO_2 at 1.5 and 290 K.

Table I

		1.5 K	290 K
	Cell parameters in Å.		
	a	3.65447(5)	3.66153(5)
	b	2.86022(3)	2.86277(2)
	c	9.3774(1)	9.39258(9)
	Li (4j) .mm : (1/2,0,z)		
	z(Li)	0.2869(3)	0.2869(3)
(a)	β_{11}	20(19)	75(19)
	β_{22}	138(25)	198(22)
	β_{33}	16(3)	24(3)
	B_{eq}(Å^2)	0.224	0.736
	Cu (2b) mmm : (0,1/2,1/2)		
	β_{11}	22(8)	102(8)
	β_{22}	25(11)	69(10)
	β_{33}	8(1)	18(1)
	B_{eq}(Å^2)	0.305	0.675
	O (4i) .mmm : (0,0,z)		
	z(O)	0.3577(1)	0.3578(1)
	β_{11}	54(8)	130(8)
	β_{22}	76(11)	125(10)
	β_{33}	6(1)	12(1)
	B_{eq}(Å^2)	0.331	0.730
	Number of reflections	57	63
(b)	r	1.065(3)	1.069(3)
(c)	Reliability Factors		
	R_{wp}	8.90	8.00
	R_E	3.13	3.49
	R_{Bragg}	3.93	3.88

(a)Thermal parameters (β_{ij}x10^4, β_{ij}=0 if i≠j) according to the expression: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$
(b)Preferred orientation parameter (see ref. 9), (c) for a definition of the reliability factors see ref.7.

Table II

Relevant distances (in Å.) and angles (in degrees) for Li_2CuO_2.

		1.5 K	290 K
Cu-O	[x4]	1.9560(6)	1.9577(6)
Li-O	[x2]	1.944(1)	1.948(1)
	[x2]	1.971(2)	1.974(2)
O-O	[x1]	2.8602(0)	2.8628(0)
	[x2]	2.669(1)	2.671(1)
Cu-Cu		2.8602(0)	2.8628(0)
Cu-O-Cu		93.97(3)	93.96(3)

Cu_1(0,1/2,1/2) and Cu_2 (1/2,0,0). The generators (modulo lattice translations) of the Immm space group are (2_z, 2_y, T_I, -1), where the notations stand for the binary axis along **c** and **b**, the body centered translation [1/2 1/2 1/2] and the inversion center at the origin, respectively. The one dimensional representations of Immm for **k**=[000] can be labelled by the characters corresponding to the generators. As the spin configuration is invariant under the inversion center, only the even (gerade) representations are relevant. Therefore, only the first three generators are needed to label the representations. In Table III we give the invariant spin configurations which transform according to the 8 even representations of Immm. A simple calculation of the magnetic intensities for these models shows unambiguously that the solution corresponds to the representation Γ_{8g} (---), then to the mode A_x. This mode corresponds to the presence of ferromagnetic layers coupled antiferromagnetically, as shown in Fig. 3. An alternative description of the magnetic structure is to say that the propagation vector is **k**=[001], so the spin at lattice translation site **t** is related to the spin at the origin by $S_t=S_o\exp(ikt)$, S_o being perpendicular to **k**.

To obtain the magnetic moment of copper atoms, a Rietveld refinement of the magnetic structure was done using a locally modified version of the original Rietveld program. Only a restricted angular range (2θ =5-60°) was used due to the weakness of the magnetic reflections. For this reason, the crystallographic parameters were fixed to the values obtained with the "nuclear only" full pattern refinement. The form factor for Cu^{2+} was taken from [11]. The only relevant refined parameter was the magnetic moment of copper atoms. The result was $\mu(Cu)=0.96(4)\mu_B$ at 1.5 K (R_{mag}=12.7). In Table IV we give the observed and calculated magnetic integrated intensities for this refinement.

4. Discussion

In previous work, Sreedhar *et al.*[1] suggested that Li_2CuO_2 should be an ideal candidate to exhibit 1D ferromagnetic behaviour because of the topology of the magnetic chains: the sharing of edges between [CuO_4] units would lead to 90° Cu-O-Cu superexchange pathways (the actual angle is 94°). Nevertheless, their own magnetic susceptibility data, which fit in well with a Curie-Weis law having $\Theta \approx -35$ K, show that the prevailing magnetic interactions at high temperatures are antiferromagnetic. To explain this experimental behaviour, Sreedhar *et al.* invoked the existence of direct copper-to-copper interactions involving the $d_{x^2-y^2}$ orbitals. The possible interchain interactions through the O-Li-O network were implicitly neglected in their arguments.

On the contrary, our results show unequivocally that the interchain interactions are not negligible at all. Further, they are antiferromagnetic and justly lead to the magnetic behaviour observed above the critical temperature. This result is similar to that found for Bi_2CuO_4 [3]. In this last case, the magnetic structure can only be explained by assuming the operability of exchange pathways involving interchain [BiO_2] units. In the same way, it seems very likely that the understanding of the magnetic behaviour of other mixed copper oxides has to be approached taking into account exchange pathways other than the Cu-O-Cu ones.

Thus, in compounds such as Sr_2CuO_3 and Ca_2CuO_3 (built up of [CuO_3] chains linked through [MO] units) or $SrCuO_2$ (double [CuO_2] chains linked by [SrO] units) it is very likely that a strong antiferromagnetic coupling occurs

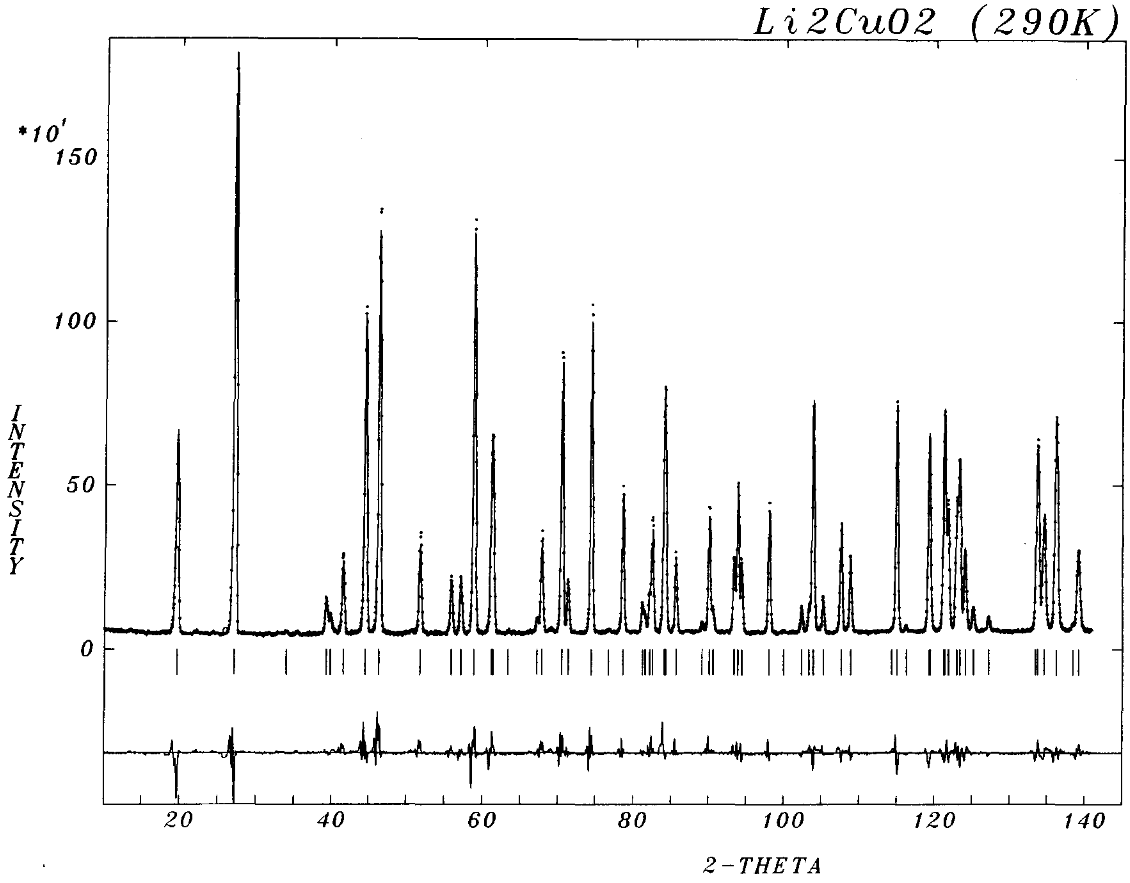

Fig.2. Observed and calculated pattern of Li_2CuO_2 at 290 K. Crosses are observed counts, continuous line is the calculated pattern. Curve at the bottom is the difference pattern y_{obs}-y_{calc}, small bars indicate the angular positions of the allowed Bragg reflections.

among the copper atoms in the chains owing to the 180° Cu-O-Cu array. However, interchain interactions (involving O-M-O paths) significant enough to lead to high antiferromagnetic ordering temperature must be operative in order to explain the magnetic susceptibility and EPR data [5a].

The failure of our neutron powder diffraction experiments to show clearly magnetic peaks at 1.5 K, however, may be attributed to small values of the magnetic structure factors in relation to the nuclear ones.

Let us establish the conditions to be satisfied by the exchange integrals in order to get the mode A_x as the ground state. We shall restrict ourselves to the classical Heisenberg isotropic exchange, the anisotropy responsible for the particular direction of the spins along **a** will not be taken into account in the following discussion.

In Table V we give the full network of exchange pathways between a copper atom and its neighbours.

The magnetic structure can be described as consisting of [CuO_2] slabs stacked in the **c** axis direction. The ex-

Table III

One dimensional representations for **k**=[000] of space group Imm and basis functions corresponding to magnetic atoms situated in positions (2b). The + and - symbols correspond to the characters 1 or -1 of the generators 2_z, 2_y and T_I (see text).

	x	y	z
Γ_{1g}(+++)	-	-	-
Γ_{2g}(++-)	-	-	-
Γ_{3g}(+-+)	-	-	F_z
Γ_{4g}(-++)	-	F_y	-
Γ_{5g}(+--)	-	-	A_z
Γ_{6g}(-+-)	-	A_y	-
Γ_{7g}(--+)	F_x	-	-
Γ_{8g}(---)	A_x	-	-

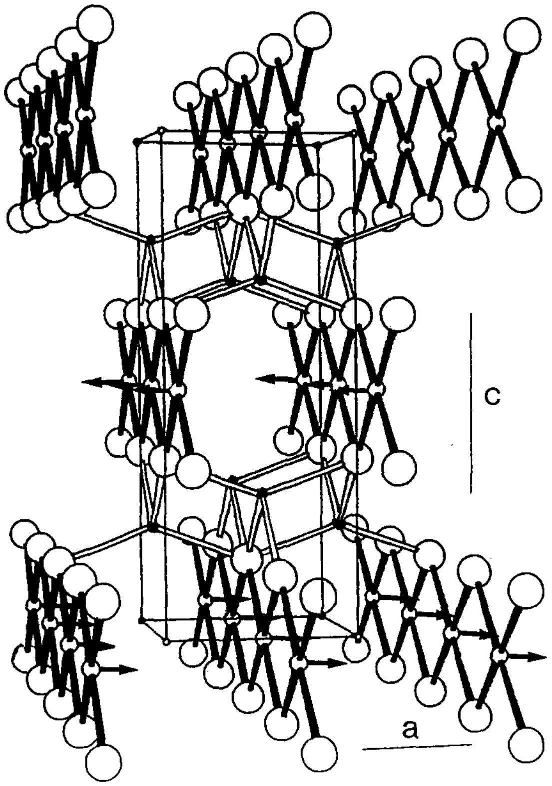

Fig.3. Crystal and magnetic structure of Li_2CuO_2. Small full circles are the Li atoms, small open circles are the Cu atoms and the larger open circles are oxygen atoms. The direction of the magnetic moments are indicated only in the Cu-layers with z=0 and z=1/2

change integrals in each slab are J_y (intrachain) and J_x(interchain) The slabs interact among them by an effective coupling J_z through $[LiO_2]$ sheets (see Table V). Thus each copper atom interacts with eight copper neighbours on the plane of its slab and sixteen more on the adjacent slab planes. Applying Bertaut's microscopic theory, we obtain the following expression for the energy, at 0 K, as a function of the exchange integrals and the propagation vector components:

$$H=-4S^2[2J_x\cos2\pi k_x\{1+\cos2\pi k_y\}+J_y\cos2\pi k_y+ +4J_z\cos\pi k_x\cos\pi k_y\cos\pi k_z] \qquad (i)$$

Table IV

Observed and calculated magnetic intensities

(hkl)	I_{obs}	I_{calc}
001	1480	1380
003	119	116
102	89	66
010	86	92
012	187	118
111	120	105
104	44	42
005	87	26
113	68	69
014	51	46
201	0	1

The stability conditions for a propagation vector $k=[k_xk_yk_z]$, are obtained from the condition that the matrix $H_{ij}=\partial^2H/\partial k_i\partial k_j$ must have only positive eigenvalues. It is a simple matter to verify that the energy and stability conditions of the A mode (propagation vector [001]) are given by:

$$H_{[001]}=-4S^2[4J_x+J_y-4J_z] \qquad (ii)$$

$$J_z<0\,; \qquad 4J_x> J_z\,; \qquad 2J_x+J_y>J_z \qquad (iii)$$

From these conditions the sign of the interplane interaction J_z is unambiguously defined as negative. The positivity of both J_x and J_y gives as a result that the mode A is the lowest energy one even considering non-colinear or spiral modes.

Another relation, of general validity, that satisfies the exchange integrals is obtained from the high temperature characteristics of the magnetic susceptibility: the Curie-Weiss constant Θ is related to the J's (in kelvin units) by [12]:

$$\Theta=2S(S+1)/3\sum z_iJ_i \qquad (iv)$$

In our case we obtain the equality relation:

$$\Theta= -41.1 = 4J_x+J_y+4J_z \qquad (v)$$

A Molecular Field (MF) treatment of the colinear antiferromagnetism leads and upper-bond value for the critical temperature [see, for instance, ref 12]:

$$T_N= 8.3 \le T_{MF} = 4J_x+J_y-4J_z \qquad (vi)$$

If we apply the condition $T_N=T_{MF}$, we obtain $J_z\approx-6K$, $J_x>-1.5K$ and $J_y > -6-2J_x$ which is inconsistent with (*v*). The lowest value of T_{MF} consistent with (*iii*) and (*v*) is $T_{MF}\approx$ 20K but leads to negative value for all the J's. In that case the magnetic lattice is completely frustrated and a non-colinear mode would have lower energy.

In principle it is not necessary to impose a ferromagnetic character on the ≈90° Cu-O-Cu interaction, given that the ferromagnetic-antiferromagnetic crossover for related systems occurs, depending on the nature of the bridging ligand, in the 90-100° angular range [13].

Although it is impossible to set unequivocally the sign for J_y and J_x, orbital overlap arguments suggest that J_x is associated with an unefficient exchange pathway that yields antiferromagnetic interactions. Therefore, the intrachain J_y must be positive in order to have a stable A mode.

A more detailed study of the magnetic transition on single crystals using a high flux neutron diffractometer, magnetic susceptibility and specific heat experiments is necessary to ascertain the nature of the transition and how the 3D magnetic order is established.

Table V

Exchange interactions between atom Cu_1(0 1/2 1/2) and its neighbours (z). The aproximations indicated in the last column have been taken in order to simplify the stability analysis of the magnetic structure. $J_2 \approx 2J_3$ can be justified from orbital overlap arguments.

z	Coordinates	distance (Å)	J
2	(0 3/2 1/2), (0 -1/2 1/2)	2.86	$J_1 = J_y$
2	(±1 1/2 1/2)	3.65	$J_2 \approx 2J_x$
4	(±1 3/2 1/2), (±1 -1/2 1/2)	4.64	$J_3 = J_x$
8	(±1/2 0 0), (±1/2 1 0), (±1/2 0 1), (±1/2 1 1)	5.23	$J_4 = J_z$
8	(±1/2 2 0), (±1/2 -1 0), (±1/2 2 1), (±1/2 -1 1)	6.61	$J_5 \approx 0$

5. Concluding remarks

The antiferromagnetic parents of superconducting copper oxides, which have CuO_2 planes built up from corner sharing squares [CuO_4] as structural units, present low dimensionality magnetic behaviour. At first glance, a second class of copper oxides would also show a similar behaviour if one looks at their crystal structure: presence of planes, chains or dimers. However, at least for Bi_2CuO_4 and Li_2CuO_2, the short range magnetic interactions are not predominant in any particular direction. This is also supported by the fact that the large zero-point reduction of the magnetic moment, characteristic of low dimensional antiferromagnetism, is not observed for the second class of copper oxides: the magnetic moment for Cu^{+2} in the antiferromagnetic parents of superconductors is about $0.5\mu_B$ below 4K, while in the above mentioned oxides its value is around $0.9\mu_B$.

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