Magnetic structure of lanthanum copper oxide $La_2Cu_2O_5$

1999 J. Phys.: Condens. Matter 11 6959

(http://iopscience.iop.org/0953-8984/11/36/312)

J. Phys.: Condens. Matter **11** (1999) 6959–6967. Printed in the UK PII: S0953-8984(99)04205-8

Magnetic structure of lanthanum copper oxide $La_2Cu_2O_5$

I V Golosovsky†, A G Gukasov‡‖, V A Polyakov†, D I Zhigunov§ and I A Zobkalo†

† St Petersburg Nuclear Physics Institute, 188350 Gatchina, St Petersburg, Russia
‡ Leon Brillouin Laboratory, CEA Saclay, 91191 Gif-sur-Yvette Cédex, France
§ Institute of Physics of Solids and Semiconductors, Academy of Sciences of Belarus, 220726 Minsk, Belarus

E-mail: gukasov@bali.saclay.cea.fr

Received 11 May 1999

Abstract. A noncollinear antiferromagnetic structure with the propagation vector $\boldsymbol{k} = [0\ \frac{1}{2}\ 0]$ and the transition temperature of ≈130 K was found in the monoclinic compound $La_2Cu_2O_5$ by single-crystal neutron diffraction. The crystal structure parameters and the values and directions of the magnetic moments have been obtained by least-squares refinement. Similar to rare-earth cuprates R_2CuO_4 the compound $La_2Cu_2O_5$ shows a low-dimensional magnetic behaviour with critical index $\beta = 0.228(8)$.

1. Introduction

After the discovery of high-temperature superconductivity in a search for new super-conducting materials a homologous series of copper oxide-based compounds was synthesized [1, 2]. These compounds do not occur in the La_2O_3–CuO chemical system and are based on a different structural principle—the insertion of La_2CuO_4 type ribbons of different widths between CuO planes of complex geometry.

Electron and x-ray diffraction studies have shown that the new compounds have a monoclinic C-centred unit cell. Their crystal structure consists of thin, skew planes of La_2CuO_4 octahedra sandwiched between highly distorted copper–oxygen chains (figure 1). The number of inserted layers of octahedra corresponds to the number n in the general formula $La_{4+4n}Cu_{8+2n}O_{14+8n}$. Single crystals of two members of the series with $n = 2$ and $n = 3$ and formulas $La_2Cu_2O_5$ and $La_8Cu_7O_{19}$, respectively, are stable and can be synthesized.

Magnetic interactions in the related rare-earth cuprates R_2CuO_4 have been the subject of extensive studies in recent years in connection with high-temperature superconductivity. Therefore the magnetic ordering in the compounds, constructed from the same structural units as R_2CuO_4, is of fundamental interest. Very little information about the magnetic properties of the new materials is available, apart from susceptibility measurements on powder samples [1] and some preliminary studies on a single crystal of $La_8Cu_7O_{19}$ by polarized neutron scattering [3].

Here we present the results of a detailed investigation of the magnetic structure of $La_2Cu_2O_5$ by single-crystal neutron diffraction.

‖ Address for correspondence: Laboratoire Leon Brillouin, CE-de Saclay, F-91191 Gif-sur-Yvette Cédex, France.

0953-8984/99/366959+09$30.00

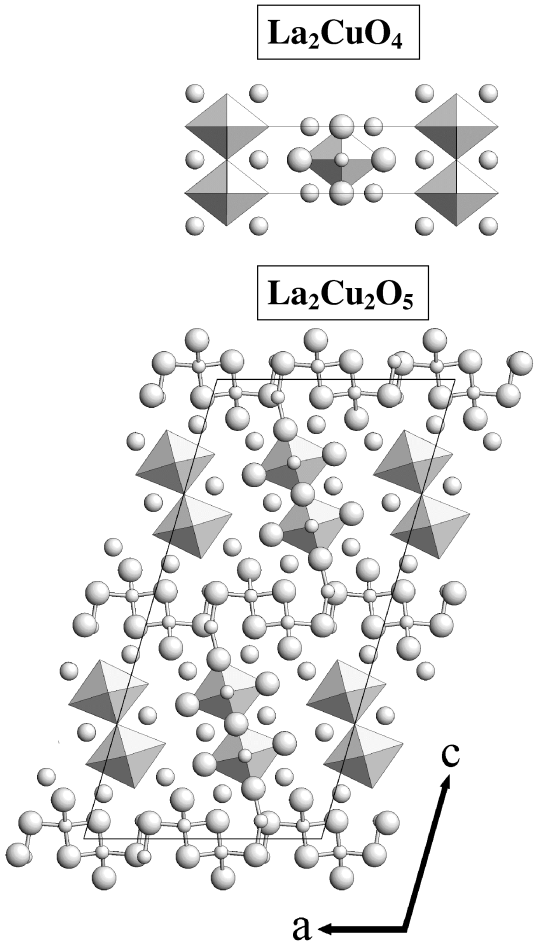

Figure 1. The projection of the nuclear structure of $La_2Cu_2O_5$ on the ac-plane. Largest, medium and small spheres correspond to O, La and Cu atoms respectively. At the top of the figure, the corresponding projection of the La_2CuO_4 structure is shown for comparison.

2. Experiment

Single crystals of $La_2Cu_2O_5$ in the form of elongated prisms were grown by controlled crystallization of the stoichiometric mixture [2]. The unit cell parameters determined by x-ray powder diffraction were $a = 13.86(1)$ Å, $b = 3.74(2)$ Å, $c = 27.99(1)$ Å and $\beta = 106.3(1)^\circ$, in agreement with results reported earlier [1].

Neutron diffraction studies were carried out at the Orphée reactor, Leon Brillouin Laboratory in Saclay. Integrated intensities were measured on the four-circle diffractometer 6T2 in a Displex refrigerator using neutrons of wavelengths 1.5 and 0.9 Å. Pyrolitic graphite and erbium filters were used to suppress higher-order contamination for these wavelengths respectively.

Refinement based on the measured squares of structure factors was performed using programs of the Cambridge Crystallography Subroutine Library (CCSL) [4]. For the magnetic calculations the series expansion form-factor of Cu^{2+} in an analytical approximation was used [5].

3. Crystal structure of $La_2Cu_2O_5$

The unit cell of $La_2Cu_2O_5$ contains 24 symmetry related Cu^{2+} ions in three general crystallographic positions 8e of monoclinic space group $C2/c$ (C_{2h}^6). There are two structural subunits in the crystal structure (figure 1). The first subunit is a double layer of distorted CuO_6 octahedra, constructed from the blocks of La_2CuO_4. The copper atoms in this layer belong to one crystallographic position and will be labelled below as Cu1. The second subunit is a complex copper–oxygen plane, with two types of CuO diamond in double puckered chains, inserted between the layers of octahedra. The copper atoms of this subunit occupy two different crystallographic positions. Below, copper atoms in the CuO diamonds lying in the $\boldsymbol{b}$–$\boldsymbol{c}$-plane are labelled as Cu2 and copper atoms corresponding to the diamonds lying in the $\boldsymbol{a}$–$\boldsymbol{c}$-plane are labelled as Cu3.

First data collection was performed at ambient temperature to check the sample stoichiometry. Only reflections permitted in the space group $C2/c$ were detected, in accordance with [1]. Since the susceptibility measurements, that will be discussed below, showed that the system is still paramagnetic at 150 K, an extensive data set was collected at this temperature.

Table 1. Results of the least-squares refinement of $La_2Cu_2O_5$ at 150 K. F_{obs}^2 and F_{calc}^2 are observed and calculated squares of structure factors; $w = 1/\sigma^2$, where σ is an experimental error.

Atom	x	y	z	B (Å^2)
La1	0.6183(1)	−0.0194(6)	0.231 86(5)	0.64(2)
La2	0.2325(1)	−0.0329(6)	0.134 77(5)	0.64(2)
La3	0.4719(1)	0.0063(6)	0.098 43(5)	0.64(2)
Cu1	0.0766(1)	0.0137(7)	0.819 18(6)	0.72(2)
Cu2	0.2238(1)	0.0049(7)	0.460 68(6)	0.72(2)
Cu3	0.0939(1)	0.1223(6)	0.029 00(7)	0.72(2)
O1	0.00000	−0.014(1)	0.250 00	0.82(5)
O2	0.8474(2)	−0.005(1)	0.109 92(8)	0.78(4)
O3	0.9232(2)	0.483(1)	0.180 90(8)	0.76(4)
O4	0.2438(2)	0.008(1)	0.034 72(8)	1.08(4)
O5	0.2722(2)	0.471(1)	0.208 16(8)	0.91(4)
O6	0.1336(2)	0.450(1)	0.085 06(8)	0.82(4)
O7	0.9597(2)	0.025(1)	0.038 62(8)	0.96(4)
O8	0.5827(2)	0.465(1)	0.161 96(8)	0.89(4)
$a = 13.86(1)$ Å, $b = 3.74(2)$ Å, $c = 27.99(1)$ Å, $\beta = 106.3(1)^\circ$				
mosaic spread			$0.118(6) \times 10^{-4}$ radian	
domain radius			100 μm (fixed)	
Space group			$C2/c$ (C_{2h}^6)	
Number of independent reflections N_{obs}			900	
Number of variables N_{var}			52	
$\sin\Theta/\lambda$			<0.63 Å^{-1}	
$R = \Sigma\lvert F_{obs}^2 - F_{calc}^2\rvert/\Sigma F_{obs}^2$			7.55%	
$\chi^2 = \Sigma w^2(F_{obs}^2 - F_{calc}^2)^2/(N_{obs} - N_{var})$			3.20	

The refinement of the crystal structure was performed on 900 independent observations, using the Becker–Coppens Gaussian model of secondary extinction [6]. A fit of occupancy factors has shown that the sample is perfectly stoichiometric. The crystal structure parameters and the details of the refinement are given in table 1. The refined atomic positions agree well with those obtained earlier by single-crystal x-ray diffraction [1]. Because of the absence of data at high scattering angles only isotropic temperature factors were varied.

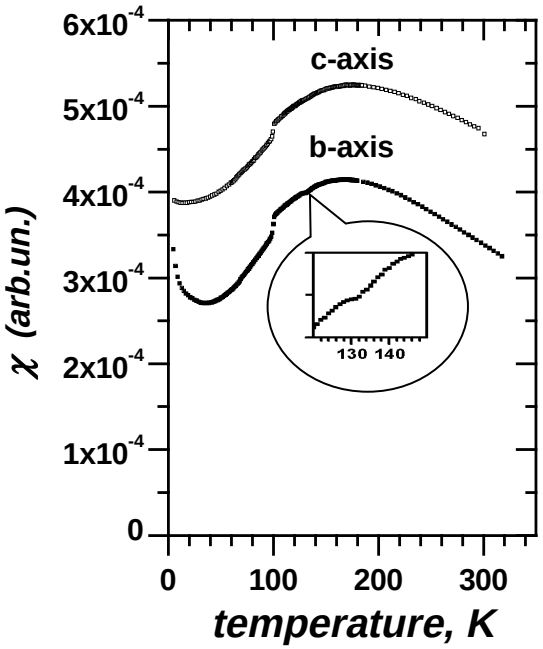

Figure 2. The temperature dependencies of single-crystal susceptibility χ for $La_2Cu_2O_5$ measured along the ***c***- (open squares) and the ***b***-axis (solid squares) by SQUID magnetometer in a magnetic field of 10 kOe. In the inset the enlarged part of the plot with a peculiarity is shown.

4. Magnetic ordering of $La_2Cu_2O_5$

The magnetic susceptibility measurements were performed on a single crystal using the SQUID magnetometer of CENG (Grenoble) in a magnetic field of 10 kOe. The temperature dependencies of susceptibility measured along the ***c***- and the ***b***-axes are presented in figure 2. The general features of these dependencies are consistent with those reported for a powder sample [1]. However, in the single-crystal measurements some additional peculiarities are clearly seen. First, both curves show an anomaly at about 100 K. Second, a small kink at $\approx$130 K is seen on the curve of susceptibility measured along the ***b***-axis (inset in figure 2). A search for magnetic reflections performed at 20 K, using a neutron wavelength of 2.35 Å, revealed the presence of a set of super-structure reflections with half-integer k-indices. From the temperature dependence of the magnetic reflection $(1\ \frac{1}{2}\ 2)$ shown in figure 3 the Néel temperature T_N was evaluated to be 130 K, which coincides with the temperature of the second anomaly. If this anomaly corresponded well to the onset of long-range magnetic ordering, the origin of an anomaly at about 100 K remain unclear. In an attempt to clarify this problem a search for superstructure reflections was undertaken at 110 K. No additional reflections apart from those with half-integer k-indices was observed and a set of 50 magnetic reflections was measured at 110 K and used in the refinement.

4.1. Group theory analysis of the magnetic structure

The observed set of superstructure reflections corresponds to a magnetic unit cell doubled along the ***b***-axis and can be described by propagation vector $\boldsymbol{k} = [0\ \frac{1}{2}\ 0]$. According to the

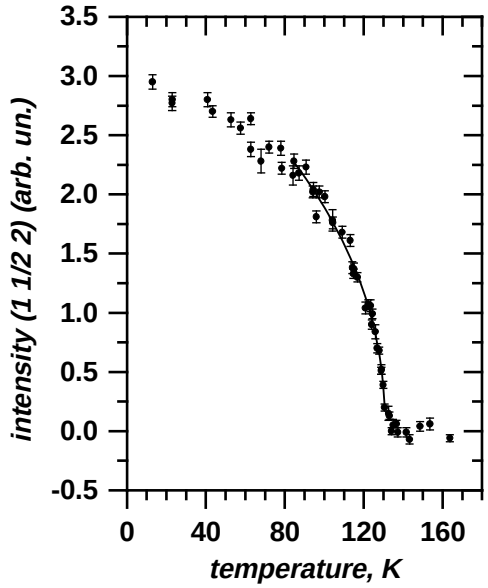

Figure 3. The temperature dependency of the integrated intensity of the magnetic reflection $(1\ \frac{1}{2}\ 2)$. The solid line corresponds to a fit by the function $\sim(1-T/T_N)^{2\beta}$ with refined $T_N = 130.8(2)$ and critical index $\beta = 0.228(8)$.

definition of the propagation vector $\boldsymbol{k}$ the invariance of spin in the lattice leads to a set of equations, describing possible translations (or anti-translations) in the magnetic group:

$$\exp(2\pi k_L t_n) = \pm 1 \tag{1}$$

where t_n denotes the lattice translation and k_L different arms of the star of vector $\boldsymbol{k}$ [7]. It is easy to see that the translation $t_n = (\frac{1}{2}\ \frac{1}{2}\ 0)$ being present in the paramagnetic group C^6_{2h} does not satisfy equation (1) for the propagation vector $\boldsymbol{k} = [0\ \frac{1}{2}\ 0]$. This means that the spins of atoms related by the translation $t_n = (\frac{1}{2}\ \frac{1}{2}\ 0)$ are not connected by a symmetry operation.

Note that the lost of base centring in the magnetic group should lead to crystal structure distortions. In fact, some weak superstructure reflections violating the C-centring extinction rules were observed at 20 K. Unfortunately, the quality of data was not sufficient for a reliable refinement of the structural distortions.

The group theory analysis [7] of possible magnetic modes was performed in the frame of space group C^6_{2h} for the propagation vector $\boldsymbol{k} = [0\ \frac{1}{2}\ 0]$. The magnetic representation d^k_m is composed from four one-dimensional threefold irreducible representations:

$$d^k_m = 3\tau_1 \oplus 3\tau_2 \oplus 3\tau_3 \oplus \tau_4. \tag{2}$$

For each irreducible representation τ_i a basis function (mode) Φ_i can be written as:

$$\begin{aligned}
\Phi_1 &= C_{11}(G_x, 0, 0) + C_{12}(0, F_y, 0) + C_{13}(0, 0, G_z) \\
\Phi_2 &= C_{21}(A_x, 0, 0) + C_{22}(0, C_y, 0) + C_{23}(0, 0, A_z) \\
\Phi_3 &= C_{31}(F_x, 0, 0) + C_{32}(0, G_y, 0) + C_{33}(0, 0, F_z) \\
\Phi_4 &= C_{41}(C_x, 0, 0) + C_{42}(0, A_y, 0) + C_{43}(0, 0, C_z).
\end{aligned} \tag{3}$$

Here, the spin configurations (sequences of signs for the components of the moments) are shown in the brackets and C_{ij} are the mixing coefficients. The letters F, G, A and C denote

the different sequences of signs: F (++++), G (+−+−), A (+−−+), C (++−−) for four atoms with coordinates: (1) x, y, z; (2) $-x$, y, $-z+\frac{1}{2}$; (3) $-x$, $-y$, $-z$; (4) x, $-y$, $z+\frac{1}{2}$ which belong to a primitive cell. The other four atoms at general position 8g of C_{2h}^6 are generated by translation $t_n = (\frac{1}{2}\ \frac{1}{2}\ 0)$. According to definition [7] the translation $t_n = (\frac{1}{2}\ \frac{1}{2}\ 0)$ can be considered as a 'lost translation'. Hence, the spins of two primitive cells described by the same basic functions (3) are not related by symmetry.

4.2. Least-squares refinements of the magnetic structure

At the first stage of refinement, the only constraints applied were to keep the spin values the same for all copper atoms. However, the refinement showed that none of the modes listed above describes the observed intensities. It turned out that the best fit ($\chi^2 = 4.9$ and R-factor $= 16.9\%$ comparing with $\chi^2 = 20$–30 for other models) corresponds to a spin arrangement with the components (A_x, G_y, A_z) constructed from modes Φ_2 and Φ_3, belonging to two different representations τ_2 and τ_3, respectively. As known, the mixing of magnetic modes from different irreducible representations contradicts the conception of a single irreducible representation [7]. However, as is easy to show, all irreducible representations (2) compose a single exchange multiplet and so if one neglects anisotropy and other weak interactions, the corresponding basic functions will have the same energy.

A much better result with $\chi^2 = 1.53$ and R-factor $= 9.9\%$ was obtained if the spin values were constrained to be equal for the pairs of atoms connected by the translation $(\frac{1}{2}\ \frac{1}{2}\ 0)$. These pairs of crystallographic positions 4g will be labelled below as Cu11–Cu12, Cu21–Cu22 and Cu31–Cu32. The refined moment values are presented in table 2. It is seen that if the moment values in the positions Cu11–Cu12 and Cu21–Cu22 are the same in the limit of two standard errors and are close to the value observed in La_2CuO_4 [8], the values in the positions Cu21–Cu22 (0.51(2) μ_B) and Cu31–Cu32 (0.68(2) μ_B) differ markedly. This difference can be attributed to very different oxygen environment of the spins in two different types of CuO diamond, lying in the $\boldsymbol{b}$–$\boldsymbol{c}$- and $\boldsymbol{a}$–$\boldsymbol{c}$-planes.

Table 2. Results of least-squares refinement of magnetic structure of $La_2Cu_2O_5$ at 20 K.

Atom	Position	m (μ_B)	θ (°)	φ (°)
Cu11	octahedra	0.45(2)	76(2)	116(3)
Cu12		0.45(2)	166(2)	116(3)
Cu21	CuO diamonds	0.51(2)	76(2)	−116(3)
Cu22	in the $\boldsymbol{b}$–$\boldsymbol{c}$-plane	0.51(2)	14(2)	−154(3)
Cu31	CuO diamonds	0.68(2)	76(2)	−116(3)
Cu32	in the $\boldsymbol{a}$–$\boldsymbol{c}$-plane	0.68(2)	166(2)	−26(3)
$R = \Sigma\lvert F_{obs}^2 - F_{calc}^2\rvert / \Sigma F_{obs}^2$			12.3%	
χ^2			2.60	

In the process of the refinement it was found that in the limit of errors the spin directions of atoms connected by the translation $(\frac{1}{2}\ \frac{1}{2}\ 0)$ are perpendicular. Besides, the spins of Cu21 and Cu31 positions are aligned in the same direction, while the spins of Cu11 position are rotated by 180° about the $\boldsymbol{c}$-axis. The results of the spin direction refinement with the relevant constraints, which reduce the number of independent variables to five, are given in table 2. Here, the spin directions are described by the polar angles θ and φ of the moment direction with respect to CCSL orthogonal axes: z is parallel to the $\boldsymbol{c}$-axis, x lies in the $\boldsymbol{a}$–$\boldsymbol{c}$ plane

and is perpendicular to the $\boldsymbol{c}$-axis, (i.e. is parallel to the $\boldsymbol{a}^*$), y makes up a right-handed set.

Similar results were obtained after a refinement performed on 50 independent observations collected at 110 K. The magnetic moment values were found to be 0.33(2) μ_B, 0.34(2) μ_B and 0.43(2) μ_B for positions Cu11–Cu12, Cu21–Cu22 and Cu31–Cu32 respectively. No difference between the magnetic moment directions was detected at 20 K and 110 K within experimental accuracy. Thus the question about the origin of the anomaly in the susceptibility at 100 K remains open.

4.3. Model of the magnetic structure

The model of the magnetic structure is shown in figure 4. As seen from the figure the ordering in the subunit constructed from the distorted blocks of La_2CuO_4 is quite simple. The Cu^{2+} spins lie either in the basal planes of oxygen octahedra or are perpendicular to them (inset in figure 4). This arrangement resembles the noncollinear magnetic ordering proposed for cuprates Nd_2CuO_4, Pr_2CuO_4 and Sm_2CuO_4 [9]. As has been shown recently, this type of noncollinear ordering could be explained assuming the presence of pseudo-dipolar interaction [10].

In the magnetic structure the spins are connected by the following simple transformations. The x- and z-components of spins for the pairs of atoms connected by the inversion operation are opposite, while the y-component does not change sign. Spins of pairs of atoms connected by the two-fold axis are opposite.

In the magnetic structure described by the propagation vector $\boldsymbol{k} = [0\ \frac{1}{2}\ 0]$ the spins of atoms related by the translation along the $\boldsymbol{b}$-axis are antiparallel. Moreover, in figure 4 one can distinguish the antiferromagnetic planes parallel to the [1 0 1] direction and passing through the octahedra. The adjacent planes are very distant and the exchange interaction between these planes is practically absent. In fact they interact only through the CuO diamonds. The existence of these weakly interacting antiferromagnetic planes is responsible for the low-dimensional magnetic behaviour of $La_2Cu_2O_5$.

4.4. Low-dimensional magnetic behaviour

As has been already noted in [1] the susceptibility curves (figure 2) are characteristic of a low-dimensional magnetic behaviour of $La_2Cu_2O_5$. The temperature dependency of the magnetic reflection $(1\ \frac{1}{2}\ 2)$ gives further arguments in favour of this (figure 2). First, this dependency does not follow the Brillouin function with $s = \frac{1}{2}$. Second, the intensity decreases rapidly with increasing temperature, which is typical for low-dimensional magnetic systems. It is known [11] that for the cuprates R_2CuO_4, the staggered magnetization of the Cu^{2+} sublattice $\langle S \rangle$ can be represented as:

$$\langle S \rangle \sim (1 - T/T_N)^{\beta} \tag{4}$$

and the intensity of magnetic reflections as:

$$I \sim (1 - T/T_N)^{2\beta}. \tag{5}$$

In fact the observed temperature dependency of the magnetic reflections can be well fitted by formula (5) with the parameters: $T_N = 130.8(2)$ and $\beta = 0.228(8)$ (solid line in figure 4). The critical index β obtained by fitting is slightly lower than value $\sim$0.25, usually observed for the cuprates R_2CuO_4.

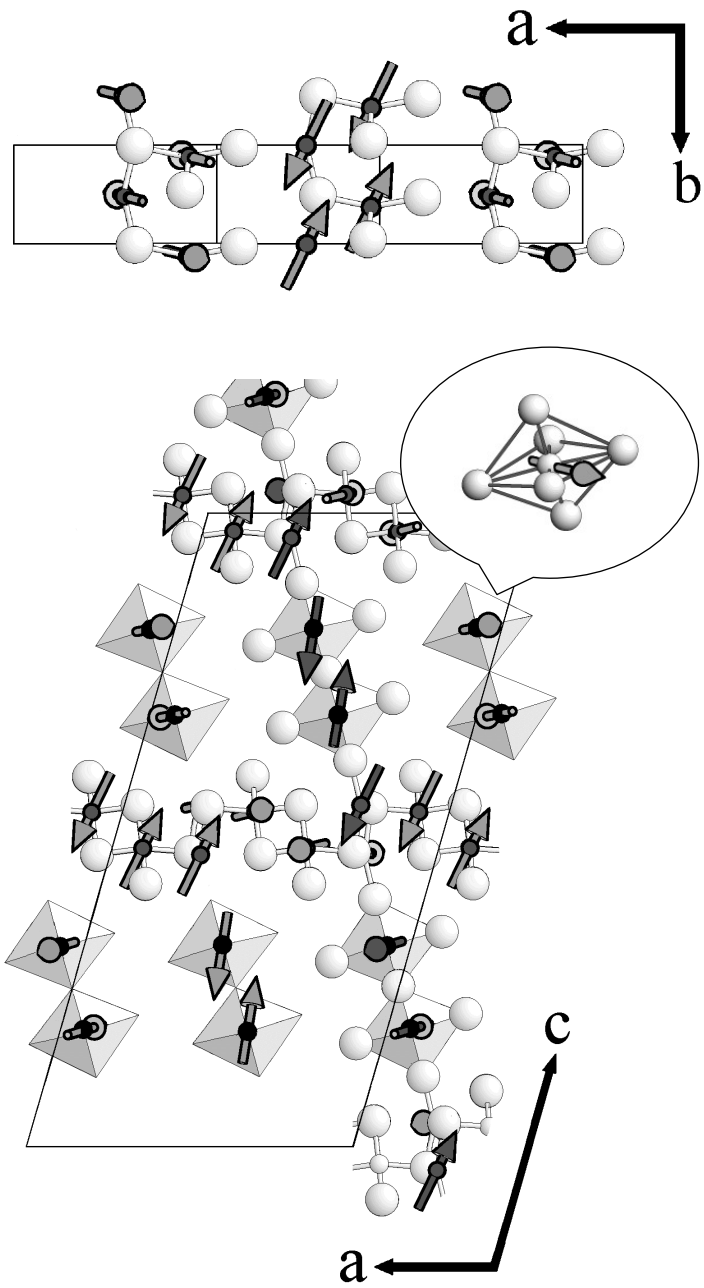

Figure 4. The magnetic structure of Cu^{2+} in the projections on the ***a*–*c***- and ***a*–*b***-planes. The direction of spin in the octahedron is shown in the inset. (Note that for simplicity some of the oxygen atoms are omitted.)

5. Conclusion

A noncollinear antiferromagnetic spin arrangement with the propagation vector $\boldsymbol{k} = [0\ \frac{1}{2}\ 0]$ was found in the monoclinic copper oxide-based compound $La_2Cu_2O_5$ by single-crystal

neutron diffraction. From the least-squares refinement, crystal and magnetic structure parameters have been obtained. In spite of a complex crystal structure, the observed spin arrangement of Cu^{2+} resembles the noncollinear magnetic structures of Cu^{2+} in the rare-earth cuprates Nd_2CuO_4, Pr_2CuO_4 and Sm_2CuO_4, but with essentially the lower transition temperature of $\approx$130 K. The temperature dependency of the susceptibility, as well as that of the magnetic reflection intensity, shows low-dimensional magnetic behaviour with critical index $\beta = 0.228(6)$.

Acknowledgments

Authors thank L V Kurnevich for sample preparation and P J Brown for interesting and helpful discussions.

The work was partially supported by RFBR (Project No 99-02-17273) and the Russian Federal Foundation for Neutron Studies on Condensed Matter.

References

[1] Cava R J, Siegrist T, Hessen B, Krajewsky J J, Peck W F, Batlogg B, Takagi H, Waszczak J V, Schneemeyer L F and Zandbergen H W 1991 *J. Solid State Chem.* **94** 170

[2] Barilo S N, Zhigunov D I, Pushkarev A V, Kurnevich L A, Shiryaev S V, Zakharov A A, Zobkalo I A, Polayakov V A and Smirnov O P 1993 *ICMAS-93 Superconducting Materials* ed Niku-Lari (Paris: HTT International) pp 77–82

[3] Zobkalo I A, Polayakov V A, Smirnov O P, Gavrilov S V, Barilo S N, Zhigunov D I and Bonnet M 1997 *Physica* B **234–236** 734

[4] Brown P J and Matthewman J C 1997 *Cambridge Crystallography Subroutine Library* Mark 4, Rutherford Appleton Laboratory report 93-009

[5] Brown P J 1992 *International Tables for Crystallography* vol C, ed A J C Wilson (Dordrecht: Kluwer) p 391

[6] Becker P J and Coppens P 1974 *Acta Crystallogr.* A **30** 129

[7] Izyumov Yu A, Naish V E and Ozerov R P 1991 *Neutron Diffraction of Magnetic Materials* (New York: Plenum)

[8] Yamada K, Kakurai K, Endoh Y, Thurston T R, Kastner M A, Birgeneau R J, Shirane G, Hidaka Y and Murakami T 1989 *Phys. Rev.* B **40** 4557

[9] Skanthakumar S and Lynn J W 1991 *J. Appl. Phys.* **69** 4866

[10] Pettigrand D, Maleev S V, Bourges Ph and Ivanov A S 1999 *Phys. Rev.* B **59** 1079

[11] Sachidanandam R, Yildirim T, Harris A, Aharony A and Entin-Wohlman O 1997 *Phys. Rev.* B **56** 260