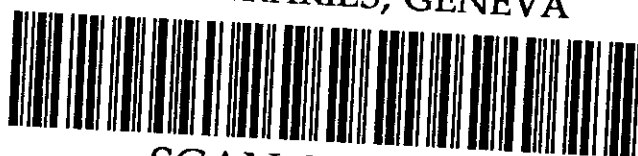


ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ

Дубна

CERN LIBRARIES, GENEVA



SCAN-0001067

E14-99-82

D.V. Sheptyakov, V.Yu. Pomjakushin, A.M. Balagurov,
A.A. Zakharov¹, C. Chaillout-Bougerol², G.J. McIntyre³

STRUCTURE

OF NON-PHASE-SEPARATED $\text{La}_2\text{CuO}_{4.03}$ STUDIED
BY SINGLE-CRYSTAL NEUTRON DIFFRACTION

Submitted to «Physica C»

¹RSC «Kurchatov Institute», Kurchatov sq. 1, 123182, Moscow, Russia

²CNRS Laboratoire de Cristallographie, BP 166,
38042 Grenoble Cedex 9, France

³Institut Max von Laue — Paul Langevin, BP 156,
38042 Grenoble Cedex 9, France

1999

It is well known that $\text{La}_2\text{CuO}_{4+y}$ possesses superconducting properties at low temperatures, with T_c up to 40 K, the non-stoichiometric (extra) oxygen being the doping element. The phase diagram in the coordinates “extra oxygen content – temperature” [1] includes the so-called “miscibility gap”, $0.01 < y < 0.06$, within which the separation of the crystal into regions with low and high extra oxygen content occurs. As was shown for the first time by Jorgensen et al. [2] by powder neutron diffraction, one region is the almost-stoichiometric antiferromagnetic La_2CuO_4 phase, and the other is oxygen-rich and superconducting. Both phases possess orthorhombic symmetry and are almost identical structurally. Chaillout et al. [3] have determined the structure of $\text{La}_2\text{CuO}_{4+y}$ with $y=0.032$ using much more extensive single-crystal data. Structural refinement carried out in the two-phase model has shown that both phases have $Cmca$ symmetry, the extra oxygen being located between two LaO layers with coordinates close to $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.

It has been shown by X-ray [4] and neutron diffraction [5] that, along with the “usual” $\text{La}_2\text{CuO}_{4+y}$ single crystals demonstrating both phase separation and superconductivity, it is possible to prepare crystals with $y=0.02 - 0.03$ (i.e. well inside the “miscibility gap”) which possess superconducting properties without macroscopic separation into two phases. The phase diagram of these homogeneous crystals is completely different from that obtained in the samples revealing phase separation: the Néel temperature can be as low as 15 K (Ref. [6]), and at higher doping levels the antiferromagnetic order is changed to a spin-glass-like one [7]. Combined analysis of neutron and muon spin-resonance data has shown that the phase-separation phenomenon has an even more complicated character, namely, that a macroscopically homogeneous superconducting crystal can be inhomogeneous on the microscopic level [6].

Here we report the results of a low-temperature structure determination on a single crystal of $\text{La}_2\text{CuO}_{4+y}$ with $y \approx 0.03$ (crystal L1 of Ref. [4], [5], further in the text – L1 crystal) which has not undergone the macroscopic separation into oxygen-rich and oxygen-poor phases on cooling. Structure analysis of such a crystal could clarify the reasons for the presence or absence of the phase separation. In addition, a crystal without macroscopic phase separation is a better candidate for the low temperature structure refinement, since it can be carried out in the one-phase approximation.

The single crystal of $\text{La}_2\text{CuO}_{4.03}$ had been grown under thermodynamical equilibrium by the molten-solution method and was doped by oxygen in a high-pressure cell. Details of the crystal preparation and characterisation are given in Refs. [4], [5], [8], where several $\text{La}_2\text{CuO}_{4+y}$ single crystals with y from 0.02 to 0.04 were

investigated. The absolute value of the oxygen content was defined by several methods: (i) weight gain, (ii) X-ray measurement of the orthorhombicity parameter, (iii) using the structural tetragonal – orthorhombic high temperature transition, and amounted to $y=0.030\pm 0.005$ (Ref. [4]). Absolute values of the unit cell parameters of the crystals with $y=0.02$, 0.03 (L1 crystal) and 0.04, measured with the High-Resolution Fourier Diffractometer ($\Delta d/d\approx 0.0009$) (Ref. [8]), are presented in the Table 1.

Fig. 1 shows the dependencies of the b lattice parameter and of the orthorhombic strain on the extra oxygen content. One can see that $y=0.03$ is in good accordance with the concentration dependencies of the lattice parameters.

Table 1. The unit cell parameters and the orthorhombic distortion parameter r of the $\text{La}_2\text{CuO}_{4+y}$ crystals ($T=293$ K, sp.gr. Cmca) measured at the HRFD (Ref. [8]).

Crystal	M4, $y=0.02$	L1, $y=0.03$	L2, $y=0.04$
a , Å	5.3525 (2)	5.3618 (2)	5.3597 (1)
b , Å	13.1519 (2)	13.1688 (3)	13.1823 (2)
c , Å	5.3959 (2)	5.4001 (2)	5.3907 (2)
$r=200(c-b)/(c+a)$	0.808 (5)	0.712 (5)	0.577 (5)

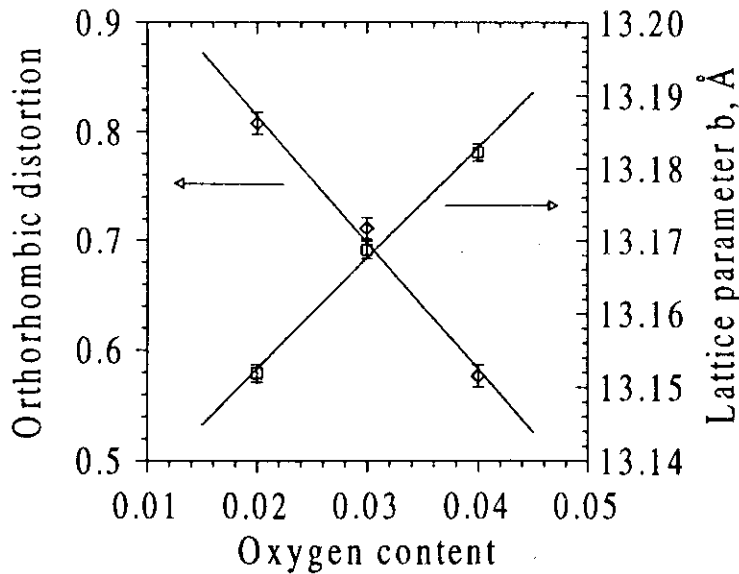


Fig. 1. Lattice parameter b and orthorhombic distortion parameter $200(c-a)/(c+a)$ vs. extra oxygen content in $\text{La}_2\text{CuO}_{4+y}$ (at $T=293$ K, for the Cmca space group).

At the structural transition from the high-temperature tetragonal $I4/mmm$ to the orthorhombic Bmab phase ($T_c \approx 450$ K), the crystals of $\text{La}_2\text{CuO}_{4+y}$ undergo transformational twinning, as a result of which the crystal is splitted to the ferroelastic domains in general with four different orientations [9]. The presence of twins hardens the structural analysis and should be necessarily taken into account in the process of the data treatment. For obtaining the information on the twinning microstructure of the $\text{La}_2\text{CuO}_{4.03}$, the special investigation was carried out (Ref. [8]). This investigation has shown that in this crystal, the peculiar twinning mechanism is realised, which leads to the formation of only three (instead of four) domain types, connected with each other only via the coherent boundaries. The analysis of the two-dimensional

distributions of intensity in the reciprocal lattice nodes has shown that nearly 80 % of the crystal volume was occupied by two types of domains with opposite signs of the shear deformation (A and B in the Fig. 2); these domains were connected to each other by coherent twin boundaries. Nearly 15 % of the crystal volume was filled with the third component (C in the Fig. 2), and nearly 5 % - with transitional regions (intensity between B and C components). The twinning angle corresponded to the orthorhombic distortion of the lattice and was close to 25 min. of arc.

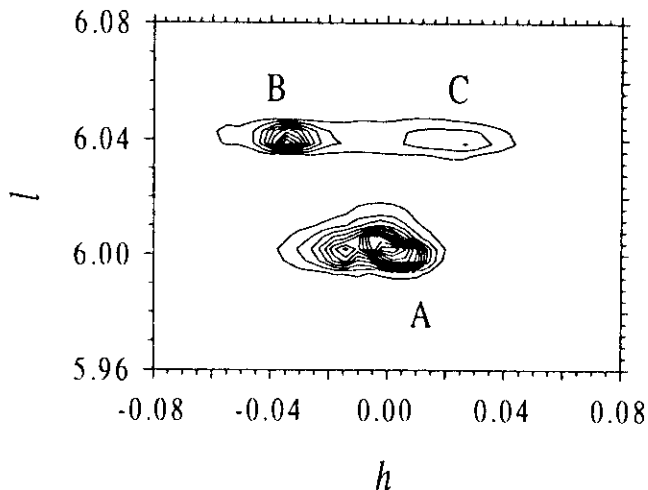


Fig. 2. Example of the two-dimensional intensity distribution in the neighbourhood of the (006) reciprocal-lattice node obtained by high-resolution X-ray diffraction. The three main maxima (A, B and C) correspond to the three types of the transformational twin domains observed in this crystal. The B and C maxima are connected by the continuous intensity distribution due to the scattering from the transitional regions.

The crystal had a rectangular pyramidal shape with dimensions $2 \times 1 \times 5 \text{ mm}^3$. The conventional single-crystal diffraction experiment has been carried out on the four-circle single-crystal diffractometer D9 on the hot neutron source of the high-flux reactor at the Institut Max von Laue - Paul Langevin using the neutron wavelength $\lambda = 0.843 \text{ \AA}$. This diffractometer is equipped with a small two-dimensional position-sensitive detector which allows observation of the local three-dimensional count distribution around each reflection [10]. A complete set of Bragg reflections in the space group $Cmca$ (with allowance for twinning) was measured at $T = 13 \text{ K}$ in a half sphere of reciprocal space to $\sin(\theta)/\lambda = 0.91 \text{ \AA}^{-1}$. 1051 independent reflections were used in the refinement. The correctness of the space group choice was additionally examined by transmission electron microscopy. It was confirmed that the cell is really C-centered.

The integration of the scattered neutron intensities was done with the *RACER* program based on the algorithm from Ref. [11]. For a conventional untwined crystal this program uses the observed three-dimensional shapes of nearby strong reflections to optimise the precision of the integration of the weak ones. This method is inappropriate for our data since the twinning causes large local variations in the extent of the peak. The weak peaks were therefore integrated simply by summing the counts within the ellipsoid, which was observed to enclose all the peak counts for the strong peaks.

Table 2. Structural parameters for the non-phase-separated single crystal L1 of $\text{La}_2\text{CuO}_{4+y}$ in space group Cmca compared with the data on the two-phase crystal with the same average oxygen content [3].

	L1 crystal	crystal from [3]	
	one phase $\text{La}_2\text{CuO}_{4.03}$	oxygen-poor La_2CuO_4	oxygen-rich $\text{La}_2\text{CuO}_{4.048}$
y (La)	0.36113 (3)	0.3616 (2)	0.36088 (6)
z (La)	0.0077 (1)	0.0096 (5)	0.0053 (2)
y (O1)	0.18316 (7)	0.1843 (2)	0.1823 (1)
z (O1)	-0.0369 (3)	-0.048 (1)	-0.0261 (5)
y (O2)	-0.00771 (6)	-0.0112 (5)	-0.0031 (2)
x (O3)	0 (*)		0.033 (5)
y (O3)	0.170 (3)		0.185 (2)
z (O3)	0.131 (7)		0.105 (4)
y (O4)	0.249 (5)		0.242 (4)
n (O1)	1.924 (7)	1.98 (2)	1.844 (16)
n (O2)	2 (*)	1.98 (2)	1.998 (10)
n (O3)	0.080 (8)		0.160 (16)
n (O4)	0.028 (4)		0.048 (8)
U11 (La)	0.0027 (2)	-0.002 (1)	0.011 (1)
U22 (La)	0.0022 (1)	0.0056 (7)	0.0018 (2)
U33 (La)	0.0033 (2)	0.004 (1)	0.0008 (7)
U23 (La)	0.0001 (2)	0.0004 (4)	-0.0005 (4)
U11 (Cu)	0.0021 (3)	0.001 (2)	0.005 (2)
U22 (Cu)	0.0042 (2)	0.0043 (9)	0.0051 (4)
U33 (Cu)	0.0014 (3)	0.001 (2)	0.000 (1)
U23 (Cu)	0.0004 (2)	-0.0002 (6)	-0.0003 (6)
U11 (O1)	0.0091 (4)	0.005 (1)	0.015 (2)
U22 (O1)	0.0046 (3)	0.0018 (8)	0.0051 (4)
U33 (O1)	0.0087 (3)	0.006 (2)	0.0087 (7)
U23 (O1)	0.0004 (2)	-0.0003 (8)	0.0000 (8)
U11 (O2)	0.0033 (3)	0.001 (1)	0.011 (1)
U22 (O2)	0.0078 (2)	0.003 (1)	0.0127 (5)
U33 (O2)	0.0039 (3)	0.003 (1)	0.000 (1)
U13 (O2)	0.0000 (2)	0.0008 (6)	0.0006 (4)
U (O3)	0.005 (*)		0.005 (*)
U (O4)	0.005 (*)		0.005 (*)
p (phase)			0.69 (3)
1-p (phase)		0.31 (3)	
R _w (%)	4.7	4.45	
R _{uw} (%)	2.8	3.1	
χ^2	4.21	4.18	
the parameters were fixed in the refinements			

The structure refinement was done with the MXD refinement program [12]. The model used for the final refinement was taken from Ref. [3], where the extra oxygen is located at $(\frac{1}{4}, y, \frac{1}{4})$ and every extra oxygen atom inserted causes the displacement of some of the O1 atoms to the O3 site. The presence of twinning in the crystal was taken into account in the refinement by comparing the observed structure amplitude to the domain-averaged calculated amplitude $F_c'(hkl)$, which is given in terms of the calculated amplitudes for one domain, $F_c(hkl)$, by $[F_c'(hkl)]^2 = [pF_c^2(hkl) + (1-p)F_c^2(lkh)]$, where p is the sum of the fractional populations of the domains that contribute hkl and $\bar{h}\bar{k}\bar{l}$.

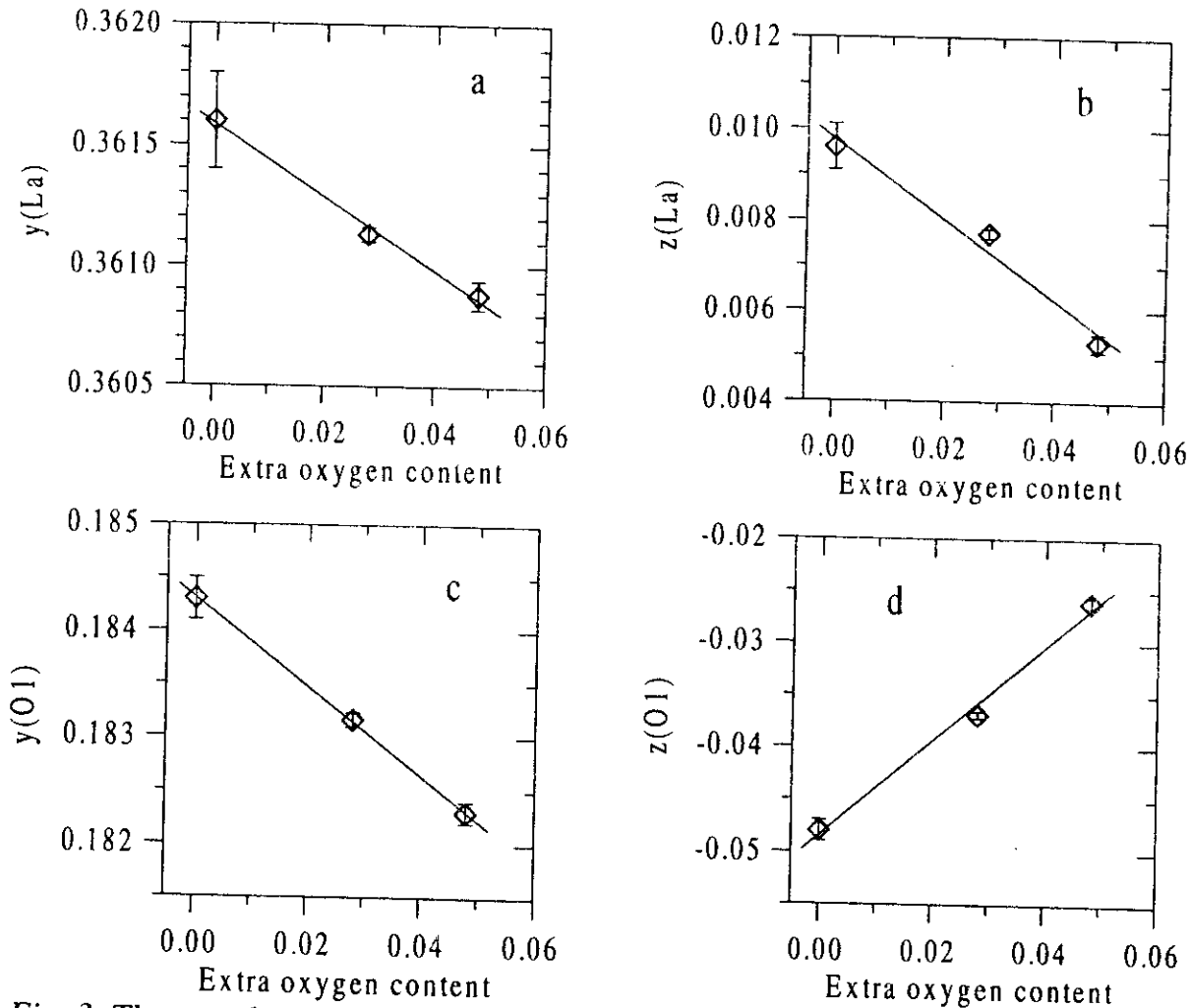


Fig. 3. The coordinates of La and O1 atoms vs. extra oxygen content for our crystal ($y=0.03$) and for the oxygen-poor ($y=0.00$) and oxygen-rich ($y=0.048$) phases of the phase-separated crystal with the same average oxygen content (Ref. [3]). The lines are the least-squares linear fits to the data.

Table 2 contains the results of the refinement including the refined atom coordinates, the thermal parameters and the occupancy factors. The refined oxygen content is 4.03 ± 0.01 . The relation between the absolute quantities of additional O4 and displaced O3 oxygen atoms is $n(\text{O4})/n(\text{O3}) \approx 1/3$, which means that every inserted extra oxygen causes the displacement of approximately three oxygen atoms from O1 to O3 sites. This value is very close to that obtained in Ref. [3]. Inspection of the results in Table 2 shows that the majority of the structural parameters (atom coordinates, site occupancies and even thermal parameters) lay between the corresponding values obtained in Ref. [3] for the oxygen-rich and oxygen-poor phases of the crystal with close average oxygen content (Fig. 3). Since the refinement is on a single phase, the errors of the structural parameters in our structure determination are on average three times lower than that of Ref. [3] for the two-phase crystal.

That the refined occupation of extra oxygen amounted to 0.03, and that the refined low-temperature structure parameters for the composition we studied are given by values laying between those obtained for the compositions representing the edges of the miscibility gap, provide unambiguous evidence that this crystal at low temperatures does lie in the previously inaccessible region with extra oxygen concentration $y=0.03$.

As suggested in Ref. [6], in such type of $\text{La}_2\text{CuO}_{4+y}$ single crystals a microscopic phase separation takes place at low temperature, which is very likely driven by the parallel formation of superconducting and antiferromagnetic states.

Acknowledgements

The authors would like to thank Dr. P.G. Radaelli for help in the experiments and for useful discussions. One of us (D.V.S.) is grateful to Dr. J.-J. Capponi for travel support. The work has been carried out with the support of the grants: SNSF (7SUPJ048473), INTAS-RFBR (95-639) and the RFBR (96-02-17823).

References

- [1] P.G. Radaelli, J.D. Jorgensen, R. Kleb *et al.*, Phys. Rev. **B49**, 6239, (1994).
- [2] J.D. Jorgensen, B. Dabrowski, S. Pei *et al.*, Phys. Rev. **B38**, 11337, (1988).
- [3] C. Chaillout, J. Chenavas, S.W. Cheong, Z. Fisk, M. Marezio, B. Morosin and J.E. Schirber, Physica C **170**, 87, (1990).
- [4] A.A. Zakharov A.A. Nikonov, O.E. Parfenov *et al.*, Physica C, **223**, 157, (1994).
- [5] A.M. Balagurov, V.Yu. Pomjakushin, V.G. Simkin and A.A. Zakharov, Physica C, **272**, 277, (1996).
- [6] V.Yu. Pomjakushin, A.A. Zakharov, A.M. Balagurov, F.N. Gygax, A. Schenck, A. Amato, D. Herlach, A.I. Beskrovny, V.N. Duginov, Yu.V. Obukhov, A.N. Ponomarev and S.N. Barilo, Physica C, **282-287**, 1353, (1997); Phys. Rev. **B58**, 12350, (1998).
- [7] V.Yu. Pomjakushin, A.A. Zakharov, A. Amato, V.N. Duginov, F.N. Gygax, D. Herlach, A.N. Ponomarev and A. Schenck, Physica C **272**, 250, (1996).

- [8] A.M. Balagurov, A.I. Beskrovnyi, V.Yu. Pomjakushin et al., Accepted for publication in *Kristallografiya* **44** (1998) (in Russian).
- [9] M. Braden, G. Heger, P. Schweiss, Z. Fisk, K. Gamayunov, I. Tanaka and H. Kojima, *Physica C* **191**, 455, (1992).
- [10] M.S. Lehmann, W.F. Kuhs, G.J. McIntyre, C. Wilkinson and J.R. Allibon, *J. Appl. Cryst.*, **22**, 562, (1989).
- [11] C. Wilkinson, H. Khamis, R.F.D. Stansfield and G.J. McIntyre, *D. J. Appl. Cryst.*, **21**, 471, (1988).
- [12] P. Wolfers, MXD Refinement program, *J. Appl. Cryst.*, **23**, 554, (1990).

Received by Publishing Department
on April 1, 1999.

SUBJECT CATEGORIES OF THE JINR PUBLICATIONS

Index	Subject
1.	High energy experimental physics
2.	High energy theoretical physics
3.	Low energy experimental physics
4.	Low energy theoretical physics
5.	Mathematics
6.	Nuclear spectroscopy and radiochemistry
7.	Heavy ion physics
8.	Cryogenics
9.	Accelerators
10.	Automatization of data processing
11.	Computing mathematics and technique
12.	Chemistry
13.	Experimental techniques and methods
14.	Solid state physics. Liquids
15.	Experimental physics of nuclear reactions at low energies
16.	Health physics. Shieldings
17.	Theory of condensed matter
18.	Applied researches
19.	Biophysics

Шептяков Д.В. и др.

E14-99-82

Нейтронно-дифракционное исследование структуры фазово-неразделенного монокристалла $\text{La}_2\text{CuO}_{4.03}$

Изучена структура монокристалла $\text{La}_2\text{CuO}_{4+y}$ с содержанием допирующего кислорода $y=0,03$ с помощью дифракции нейтронов при $T=13$ К. Несмотря на то, что содержание кислорода $y=0,03$ отвечает состоянию внутри «щели растворения» $\text{La}_2\text{CuO}_{4+y}$ ($0,01 < y < 0,06$), кристалл не разделяется на две фазы при низких температурах. Единственная фаза, образующая вещество, имеет симметрию $Cmca$. Показано, что дополнительный кислород (O4) находится вблизи позиции $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. Структурные параметры всех атомов занимают промежуточные значения между величинами, ранее определенными для обедненной и обогащенной кислородом фазы, представляющими края «щели растворения», $y=0,01$ и $0,06$, соответственно. Результаты позволяют заключить, что фазово-разделяющиеся и неразделяющиеся соединения $\text{La}_2\text{CuO}_{4+y}$ структурно идентичны и кристаллическая структура $\text{La}_2\text{CuO}_{4+y}$ монотонно изменяется при изменении содержания допирующего кислорода от 0 до 0,05.

Работа выполнена в Лаборатории нейтронной физики им. И.М.Франка ОИЯИ и в Институте Лауэ–Ланжевена, Гренобль, Франция.

Препринт Объединенного института ядерных исследований. Дубна, 1999

Sheptyakov D.V. et al.

E14-99-82

Structure of Non-Phase-Separated $\text{La}_2\text{CuO}_{4.03}$ Studied by Single-Crystal Neutron Diffraction

The structure of a $\text{La}_2\text{CuO}_{4+y}$ single crystal with the excess oxygen content $y=0.03$ has been studied by means of neutron diffraction at $T=13$ K. Although the extra oxygen content of $y=0.03$ is inside the miscibility gap of $\text{La}_2\text{CuO}_{4+y}$ ($0.01 < y < 0.06$), the crystal is not phase-separated at low temperatures. The sole phase constituting the sample has $Cmca$ symmetry. It was confirmed that the extra oxygen, O4, is located close to the site $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. The structural parameters for all atoms lay between those previously determined for the oxygen-poor and oxygen-rich phases representing the edges of the miscibility gap, $y=0.01$ and 0.06 respectively. Our data allow us to conclude that, (1) The phase-separated and non-phase-separated $\text{La}_2\text{CuO}_{4+y}$ compounds are structurally identical, and (2) The crystal structure of $\text{La}_2\text{CuO}_{4+y}$ changes monotonically when the extra oxygen content changes from 0 to 0.05.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR and at the Institut Laue–Langevin, Grenoble, France.

Preprint of the Joint Institute for Nuclear Research. Dubna, 1999

Макет Т.Е.Попеко

Подписано в печать 16.04.99

Формат 60 × 90/16. Офсетная печать. Уч.-изд. листов 0,99

Тираж 305. Заказ 51311. Цена 1 р. 18 к.

Издательский отдел Объединенного института ядерных исследований
Дубна Московской области