Crystal structure of the superconducting compound $LaBa_2Cu_3O_7$

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Neutron diffraction is used to determine the crystal structure of the superconducting oxide $LaBa_2Cu_3O_7$ (space group D^1_{4h}). The structures of $LaBa_2Cu_3O_7$ and $LaBa_2Cu_3O_{7-y}$ are compared. The connection between the structure properties and the superconductivity of the oxides $RBa_2Cu_3O_x$ is discussed.

It was shown in Refs. 1–3 that the lanthanum analog of the compound $YBa_2Cu_3O_7$ is a superconductor having a high critical temperature. The crystal structure of this compound is of interest. The structure of the oxide $La_{1.5}Ba_{1.5}Cu_3O_{7+y}$ close to it in composition has, according to neutron-diffraction data,[4] is an oxygen-defective tetragonal superstructure based on perovskite with a cell $a_t \approx a_c\sqrt{2}$, $c_t \approx 3a_c$ (a_c is the period of the perovskite cubic cell); the ordering in metal has not been reliably established in view of the proximity of the atomic numbers of La (57) and Ba (56). We investigate in the present paper the $LaBa_2Cu_3O_7$ structure by powder neutron and x-ray diffraction methods.

The sample was synthesized at the Crystallography Institute of the USSR Academy of Sciences by standard ceramic technology. A stoichiometric mixture of the initial components La_2O_3, $BaCO_3$ and CuO was annealed in air at 1223 K for 24 h, with intermediate regrinding after 12 hours of annealing. The oxygen content in $LaBa_2Cu_3O_x$ was determined by thermogravimetric analysis (with a *Q*-1500*D* "derivatograph") of the initial mixture and of the synthesized oxide; the value of x at room temperature reached 6.95 (Fig. 1). The $LaBa_2Cu_3O_7$ powder was pressed into pellets, sintered in an oxygen atmosphere at 1223 K for 10 h, and cooled to room temperature at an approximate rate of 100 K/h. Measurement of the electric resistance have shown that the resultant sample is a superconductor with a superconducting transition onset $T_c = 67$ K and a width $\Delta T_c = 20$ K (according to Refs. 5 and 6, T_c of $LaBa_2Cu_3O_x$ can range from 27 to 90 K).

The diffraction experiments were performed at room temperature with a DRON-3.0 x-ray diffractometer (CuK_α radiation) and with a DISK-7 neutron diffractometer[7] ($\lambda = 1.730$ Å) at the Kurchatov Atomic Energy Institute. The lines on the diffraction pattern were indexed in an $a_t = 3.921$ Å, $c_t = 11.768$ Å $\approx 3a_t$ tetragonal cell, in which case the reflections (002), (101), (102), (004), (111), (112), (005, 104), (105, 114) and others, which are superstructural relative to the perovskite cubic cell ($a_c \sim 3.921$ Å), were stronger on the neutron-diffraction than on the x-ray diffraction patterns. The reason is that the neutron-scattering abilities of La and Ba atoms differ noticeably, and the neutrons are scattered by oxygen atoms more strongly than by x-rays. The diffraction patterns reveal also weak lines of $BaCuO_2$ (Refs. 4 and 8). The reflections of type $\{h/2\,k/2\,l\}$, needed to increase the cell to $a_t' = a_t\sqrt{2}$, $c' = c_t$, were not observed (in Ref. 4 the cell was chosen to be enlarged on the basis of a single and very weak reflection). The absence of the superstructure lines $\{h/2\,k/2\,l\}$ notwithstanding, we have verified the ordering-by-oxygen model proposed in Ref. 4. For this model, the agreement between the experimental and calculated intensities of the neutron-diffraction peaks turned out to be unsatisfactory: the R-factor from the integral intensities was 19%.

The basis used to determine the $LaBa_2Cu_3O_7$ structure was the structure of the rhombic phase of $YBa_2Cu_3O_7$ (Ref. 9), in which the atoms O4 and O5 were totally disordered, so that the symmetry of the atoms became tetragonal. The calculations were performed in the space group D^1_{4h}, with variation of the position parameters of the atom and of the composition relative to oxygen. Minimization of the R-factor with respect to the integrated intensities of the neutron-diffraction peaks led to good agreement with experiment ($R = 4.4\%$) for the composition $LaBa_2Cu_3O_{7.0\pm0.1}$ and for the parameters listed in Table I. The metal ordering in the $LaBa_2Cu_3O_7$ structure is analogous to that in $YBa_2Cu_3O_7$. Calculations carried out assuming disordered La and Ba positions worsened the R-factor to 12%, considerably in excess of the experimental error (about 4%). A similar tetragonal structure with a fully disordered arrangement of the O4 and O5 atoms was observed by us in $YBa_2Cu_3O_{6.4}$ obtained by quenching $YBa_2Cu_3O_{7-y}$ from a temperature 1070 K (higher than the order-disorder transition temperature).[10]

The oxide $LaBa_2Cu_3O_{7-y}$ quenched from 1000 K loses oxygen (Fig. 1) and superconducting properties, becoming semiconducting, viz., the resistivity increases with decrease of temperature. A similar phenomenon was previously observed in $YBa_2Cu_3O_{7-y}$ (Refs. 10 and 11). This means that in the oxides $RBa_2Cu_3O_x$ (R = Y and a rare earth metal) the superconducting phase can be rhombic (oxygen-ordered) as well as tetragonal (disordered), but under the con-

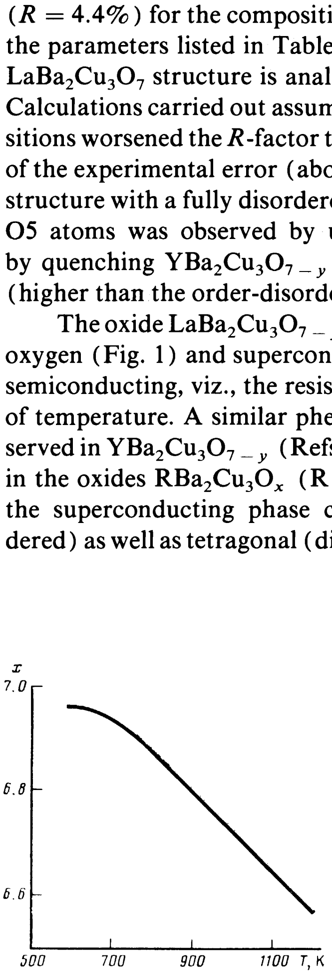

FIG. 1. Temperature dependence of the oxygen content in $LaBa_2Cu_3O_x$.

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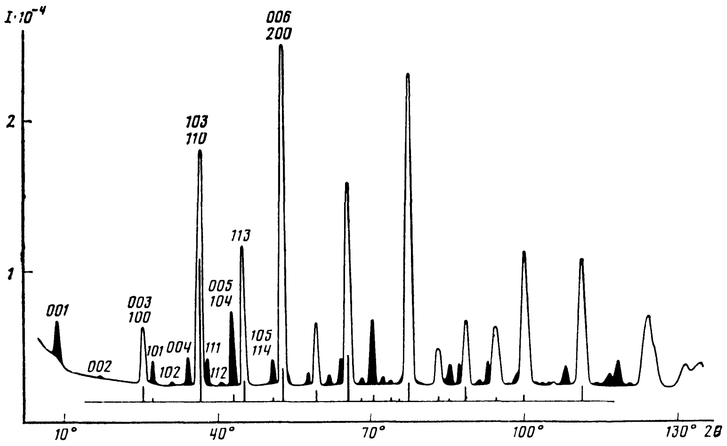

FIG. 2. Neutron-diffraction pattern of $LaBa_2Cu_3O_7$, $T = 300$ K, $\lambda = 1.730$ Å; the blackened lines are superstructural relative to the perovskite cubic cell. Below—line diagram of x-ray diffraction pattern.

TABLE I. Parameters of $LaBa_2Cu_3O_7$ atoms ($T = 300$ K, space group D^1_{4h}).

Atom	Position	Occupation probability	x	y	z	B*, Å^2
La	$1d$	1	$^1/_2$	$^1/_2$	$^1/_2$	0.6
Ba	$2h$	1	$^1/_2$	$^1/_2$	0.1793±0.0003	0.6
Cu1	$1a$	1	0	0	0	0.7
Cu2	$2g$	1	0	0	0.3459±0.0001	0.7
O1	$2g$	1	0	0	0.1558±0.0005	1.5
O2, O3	$4i$	1	$^1/_2$	0	0.3690±0.0010	1.5
O4, O5	$2f$	0.5	$^1/_2$	0	0	1.5

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*B—isotropic thermal factor.

dition that $x \approx 7$. The difference between them is that the rhombic phase contains the atom chains –O4–Cu1–O4–Cu1–, whereas the tetragonal phase contains fully disordered, oxygen-defective O4–O5-Cu1 planes, in which the O4 and O5 positions are occupied with equal probability p. The presence of superconductivity in the $LaBa_2Cu_3O_7$ tetragonal phase ($p = 0.5$) means that the entire O4–O5–Cu1 plane is conducting, and its conductivity is preserved until p becomes smaller than the percolation limit (1/2) for a two-dimensional lattice.

Other tetragonal $RBa_2Cu_3O_x$ oxides can be expected to have a similar structure, and the presence of oxygen-disorder in them raises hopes of obtaining, under suitable conditions, ordered rhombic phases.

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