

## Ordering of Sr atoms and loss of superconductivity in $(\text{La,Sr})_2\text{CuO}_{4-\delta}$ crystals

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It has been established on the basis of x-ray diffraction data that the statistical replacement of lanthanum by Sr atoms in  $(\text{La}_{0.88}, \text{Sr}_{0.12})_2\text{CuO}_{3.92}$  single crystals occurs among only half of the positions of the La atoms. The reason the  $T_c$  values of ceramic samples are higher than those of single crystals in the lanthanum phases may be because of a different arrangement of Sr atoms and an associated loss of some of the oxygen from the single crystals.

Because of the short time interval which elapsed between the discoveries of superconductivity in  $(\text{La,Sr})_2\text{CuO}_{4-\delta}$  (Ref. 1) and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Ref. 2), with  $T_c$  values measured in the liquid-nitrogen range in the second compound, more-detailed structural studies have presently been carried out on the Y phases. The overwhelming majority of the structural determinations of La phases have been carried out for ceramic samples. While a value  $T_c = 37$  K can be achieved stably in ceramics, we have yet to see a single reliable report of single crystals with such  $T_c$  values. As a rule, large single crystals of La phases do have this property, but with values  $T_c \approx 5\text{--}10$  K, i.e., well below 37 K.

The atomic structure of the initial phase,  $\text{La}_2\text{CuO}_4$ , without the strontium impurity is orthorhombic at room temperature: space group *Abma*,  $a = 5.346$ ,  $b = 6.427$ ,  $c = 13.190$  Å (Ref. 3). Above 590 K, the crystals go into a tetragonal phase: space group *14/mmm*,  $a = 3.782$ ,  $c = 13.225$  Å (Ref. 4). In the literature it is generally assumed that the replacement of some of the La atoms by strontium stabilizes the tetragonal phase at lower temperatures, right up to room temperature. A further lowering of the temperature results in a transition of the crystals to the orthorhombic phase. The various papers, however, disagree even regarding the symmetry of this orthorhombic phase: *Abma* (Ref. 5), *Ammm* (Ref. 6), *Pccn* (Ref. 7), etc.

We have carried out a high-precision x-ray structural study of a crystal of the  $(\text{La,Sr})_2\text{CuO}_{4-\delta}$  phase, produced by pulling a seed crystal from a nonstoichiometric melt.<sup>8</sup> A sample crystal of diffraction quality was machined into a ball 0.45 (1) mm in diameter. To maximize the volume of diffraction data, we used short-wavelength Ag  $K\alpha$  radiation, with  $\lambda = 0.5609$  Å. A detailed analysis of the profiles of reflections, remote in terms of  $\sin \theta / \lambda$ , revealed a splitting of these reflections, which was unambiguous evidence of a microtwinning in the sample by a pseudomerohedral law with (110) plane as a twinning element. The symmetry of the crystal thus turned out to be orthorhombic, and the microtwinning, with twin components roughly equal in volume, imitated a pseudotetragonal symmetry of the sample. Taking the splitting of the remote reflections into account, we determined the dimensions of the orthorhombic

unit cell of the crystal:  $a = 5.363$  (1),  $b = 5.338$  (1),  $c = 13.167$  (4) Å.

An RĒD-4 automatic x-ray diffractometer was used to measure 1265 nonvanishing diffraction reflections in a reciprocal-space hemisphere for  $\sin \theta / \lambda \leq 0.7$  Å<sup>-1</sup>. Taking an average over reflections of equivalent symmetry (Laue class *mmm*), we obtained a set of 340 independent structure amplitudes with  $R_{av}(I) = 3.7\%$ . Analysis of the experimental data, with allowance for the twinning, led us to two possible Fedorov symmetry groups for the crystal: *Pbma* and *Pbmn*, which are subgroups of the *Abma* group of the original La<sub>2</sub>CuO<sub>4</sub> structure. A refinement of the atomic model of our (La,Sr)<sub>2</sub>CuO<sub>4-δ</sub> crystal on the basis of either of these two symmetry groups unambiguously leads to the existence of an ordering in the arrangement of Sr atoms among lanthanum positions. Comparison of the final divergence factors of the experimental and calculated structure amplitudes and an analysis of the difference maps of the electron density distribution make it possible to give preference to the symmetry group *Pbma*. A refinement of the atomic-structure model by the method of least squares on the basis of this symmetry group led to the final divergence factors  $R = 2.21\%$  and  $R_w = 2.32\%$ . The chemical composition of the sample was refined in the course of the study on the basis of the diffraction data; it turned out to be (La<sub>0.88</sub>,Sr<sub>0.12</sub>)<sub>2</sub>CuO<sub>3.92</sub> or, in more detail, La(La<sub>0.76</sub>,Sr<sub>0.24</sub>)CuO<sub>3.92</sub>. The oxygen deficiency occurs in the crystallographic position occupied by the O(22) atoms. These atoms are in double layers of

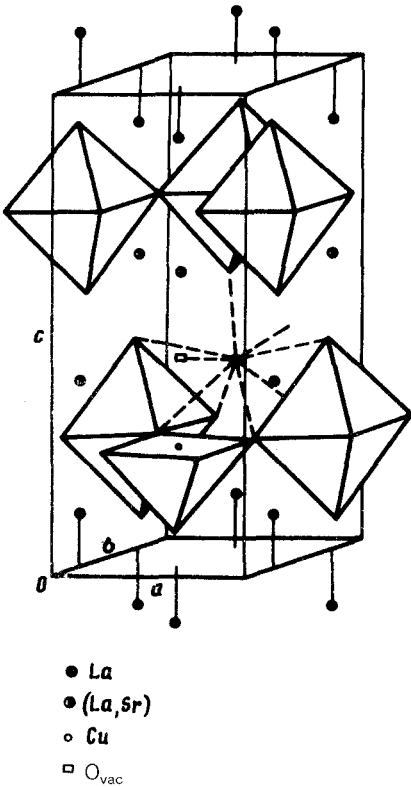


FIG. 1. Atomic model of the structure of the La(La<sub>0.76</sub>,Sr<sub>0.24</sub>)CuO<sub>3.92</sub> crystal. Shown here are CuO<sub>6</sub> octahedra. One of these octahedra has an oxygen vacancy: An O(22) atom is missing. For one of the atoms (La,Sr), the dashed lines show the nearest O atoms.

TABLE I.

Atom	$q$	$x/a$	$y/b$	$z/c$	$B, \text{\AA}^{-2}$
La	1.00	0.0058 (1)	0.25	0.11108 (5)	0.73 (2)
(La, Sr)	0.76 (2) 0.24	0.0041 (1)	0.75	0.61119 (5)	0.70 (2)
Cu	1.00	0.0002 (5)	0.25	0.7530 (4)	0.72 (2)
O(11)	1.00	0.25	0.50	0.755 (1)	0.9 (1)
O(12)	1.00	0.25	0.00	0.255 (1)	0.9 (1)
O(21)	1.00	-0.024 (2)	0.25	0.9337 (8)	1.3 (2)
O(22)	0.92 (3)	-0.025 (2)	0.75	0.4345 (8)	1.2 (2)

atoms (La,Sr); in the Cu octahedra they are the vertices farthest from the copper (Fig. 1).

The coordinates of the basal atoms of the structure, the factors describing the filling by atoms of their own positions ( $q$ ), and the isotropic thermal-vibration factors of the atoms ( $B$ ) are summarized in Table I. The corresponding standard deviations are given in parentheses.

Figure 1 shows an atomic model of the structure, in which there is a regular alternation of layers along the crystallographic  $c$  axis: -La-La-Cu-(La,Sr)-(La, Sr)-Cu-La-La-, etc. Strontium atoms are concentrated in the corresponding double layers of the structure; the replacement of trivalent lanthanum by divalent strontium has the consequence that the "extra" oxygen leaves these layers. With increasing number of Sr atoms, these atoms begin to interact in the structure, activating the process by which oxygen is lost. The difference between the superconducting transition temperatures of ceramics and single crystals of the lanthanum phases—a difference which has been noted in the literature—can naturally be linked with the circumstance that there is an ordering in the arrangement of strontium in the single crystals, as we have just established, and that some of the O(22) oxygen is lost. The process by which single crystals are grown differs from that by which ceramics are produced in that the system remains close to equilibrium. In order to raise the values of  $T_c$  of the single crystals of lanthanum phases, it will be necessary to prevent the strontium (the activating impurity) from assuming an ordered distribution during the growth and to prevent the associated loss of oxygen.

The O(22) vacancies have the consequence that the Cu octahedra lose only one of their vertices. The Cu atom turns out to be in a semioctahedron and is displaced from the equatorial plane of the octahedron into the polyhedron. We have objectively detected this displacement in the course of refining the atomic model on the basis of the diffraction data.

In concluding this analysis of the atomic structure of  $(\text{La,Sr})_2\text{CuO}_{4-\delta}$  crystals,

we wish to emphasize a fundamental difference between the structural features which lead to the superconductivity of the lanthanum and yttrium phases. While increasing  $T_c$  in the Y-phase crystals requires seven O atoms per formula unit and an *ordered* arrangement of these atoms in the structure,<sup>9</sup> in the La phases, with four O atoms, we need a *uniform* distribution of the Sr atoms among all crystallographic positions of lanthanum in the structure.

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