Neutron diffraction investigation of phase separation in La$_2$CuO$_{4+y}$ single crystals

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La$_2$CuO$_{4+y}$ single crystals with $y = 0.03$ and 0.04 are investigated with a high-resolution neutron diffractometer in the temperature range $10 < T < 293 \, \text{K}$. Although the excess oxygen concentration $y$ falls in the range of the dissolution gap, the crystal with $y = 0.03$ does not undergo phase separation (PS)—the oxygen distribution in this crystal remains uniform over the entire experimental temperature interval. Macroscopic PS is observed in the crystal with $y = 0.04$. An analysis of the dependence of the widths of the reflection orders on the interplanar separation gives the sizes of the coherent regions of the two coexisting phases: $970 \pm 30 \, \text{Å}$ in the direction of the tetragonal axis $c$ and $1460 \pm 45 \, \text{Å}$ in the basal plane. © 1996 American Institute of Physics.

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It is known$^1$ that there exists in the $(T,y)$ phase diagram of the compound La$_2$CuO$_{4+y}$ a region of temperatures and concentrations where the compound becomes unstable with respect to separation into stoichiometric phases and that this separation occurs on account of the high mobility of the excess oxygen in the initial state. It has been found$^2$–$^4$ that the phase diagram of high-quality La$_2$CuO$_{4+y}$ single crystals is substantially different from diagrams proposed previously, for example, in Ref. 5. According to electron microscopy data$^6$ separation in La$_2$CuO$_{4+y}$ occurs by the spinodal mechanism, i.e., without the formation of nuclei of a new phase in the initial stage. However, according to the theory of the decomposition of solid solutions, besides such a region of absolute instability of the system there exists an interval of temperatures and concentrations where separation occurs by a nucleation mechanism and the kinetics of the process becomes important. In this case the phase diagram should depend on the quality of the crystals studied and the mobility of excess oxygen in them. In Refs. 2 and 4, samples La$_2$CuO$_{4+y}$ from a series of single crystals grown under thermodynamically equilibrium conditions by the flux method were studied. The crystals were doped with superstoichiometric oxygen in a high-pressure chamber and had $y = 0.030(5)$ (crystal L1) and $y = 0.040(5)$ (crystal L2). Both crystals exhibited superconductivity, with $T_c = 12$ and 26 K, respectively, but macroscopic phase separation (PS) with decreasing temperature was observed only in the L2 crystal and not in the L1 crystal. According to magnetic
susceptibility data, the Néel temperature of the $L2$ crystal is $T_N = 250$ K and, according to μSR-measurements, below a “freezing” point $T_x = 8$ K the $L1$ crystal passes into a spin-glass state in which the electronic angular momentum of copper is frozen. In Ref. 2 the decomposition of the $L2$ crystal into regions with different phase compositions and the absence of decomposition in the $L1$ crystal were detected only in x-ray measurements of the splitting of the diffraction peaks and in the temperature dependence of the unit cell parameters. The neutron-diffraction study of these crystals undertaken in the present work enabled us to conclude that the observed effects are volume effects and to obtain more detailed information about the phase states of the crystals and the corresponding structure of the presumed phases. Moreover, the high resolution of the diffractometer made it possible to determine directly the dimensions of the domains of the two coexisting phases.

The experiments were performed on a high-resolution Fourier diffractometer (HRFD) in the IBR-2 pulsed reactor in Dubna. The HRFD is a correlation neutron spectrometer using a fast Fourier chopper to modulate the intensity of the neutron beam and the inverse time-of-flight method to record the scattered neutrons. The resolution of the HRFD with respect to the interplanar spacing $d_{hkl}$ is determined by the maximum rotational speed of the chopper and is equal in the present experiment to about 0.15% near $d_{hkl} = 1$ Å. The diffraction spectra were measured at room temperature and at $T = 10$ K in the (001) and (h00) directions in the reciprocal lattice, with $d_{hkl}$ ranging from 0.7 to 3.5 Å. Six orders of reflection from the (001) plane (Fig. 1) and four orders of reflection from the (100) plane were clearly observed. For the $L2$ crystal, spectra were additionally measured at several temperatures ranging from 10 to 293 K.

At temperatures above 400 K the $La_2CuO_4+y$ crystals are in the $I4/mmm$ tetragonal phase. When the crystals are cooled, they undergo a structural phase transition to a low-symmetry $Bmab$ orthorhombic phase in which, on account of the transformational twinning in the $(a,b)$ plane, the crystal breaks up into domains with 90° orientation of the crystallographic axes. Further cooling of the $L2$ crystal leads to the appearance of a two-phase state consisting (according to Ref. 5) of regions with $Bmab$ symmetry and

FIG. 1. Diffraction spectrum from the (001) plane of a $La_2CuO_{4+y}$ crystal. The numbers indicate the reflection orders. The characteristic holes at the bases of the peaks are due to the peculiarities of data acquisition on the Fourier diffractometer.