Superconductivity and phase separation in La_2CuO_{4+x}

A. A. Zakharov and A. A. Nikonov
Kurchatov Institute Russian Science Center, 123182 Moscow, Russia

(Submitted 13 July 1994)
Pis'ma Zh. Eksp. Teor. Fiz. **60**, No. 5, 340–344 (10 September 1994)

It has been observed that the superconducting properties of the La_2CuO_{4+x} ($x \leqslant 0.04$) system depend substantially on how the excess oxygen is distributed in the sample: uniformly or in a manner which results in the formation of a new phase. Precise measurements of the magnetic susceptibility of oxygenated La_2CuO_{4+x} crystals, combined with data found previously, lead to a revision of the phase diagram of this system. © *American Institute of Physics.*

The onset of a superconducting state in La_2CuO_{4+x} upon doping with oxygen is now generally believed to be directly related to the formation of a new phase as the result of phase separation in the system at temperatures $200 < T < 300$ K (Refs. 1–3, for example). The phase transition to the spatially inhomogeneous system is a first-order transition, as has been demonstrated repeatedly by the observation of hysteresis.[3,4] The very fact that phase separation occurs is of a thermodynamic nature. Working from existing estimates of the first Bohr radius of a carrier localized at an impurity in La_2CuO_{4+x}, i.e., $a_b \simeq 8$ Å (Ref. 5), we conclude that in this case the overlap of hole orbitals occurs at impurity concentrations close to atomic values. This circumstance apparently explains why the critical concentration for the insulator–metal transition is very large (for semiconductors) in all known cuprates: ~5 at. %. At such high concentrations, however, we can no longer ignore the interaction between defect regions which form as a result of the incorporation of impurities. A thermodynamic consequence of this interaction is an instability of the system with respect to an arbitrary defect distribution. The decrease in entropy with decreasing temperature may occur because of a separation of the original phase into phases which are near certain stoichiometric compositions.

Although a separation into different phases upon the dissolution of oxygen is a consequence of the thermodynamics, the spatial redistribution of oxygen at such low temperatures is due to only the kinetics, i.e., the high mobility of oxygen. In this case, defects of the crystal structure play a fundamental role. The use of higher-quality single crystals in experiments may thus lead to qualitative changes in the phase diagram and in the picture of the onset of the superconducting state.

The crystals used in the present experiments were grown by the molten-solution method at various temperatures[6] ($1150 < T_g < 1050$ °C). The as-grown crystals produced at the highest temperature (1150 °C) are very good insulators, making it possible to record good optical reflection spectra and to observe all dipole-active phonon modes.[7,8] Furthermore, there is a monotonic decrease in the Néel temperature in these crystals at excess-oxygen concentrations $x < 0.01$, without any traces of a phase separation or superconductivity at low temperatures.[9] Oxygenation of these initially good insulators was carried out in a special vessel at $T = 650$–700 °C and $p = 3$ kbar for 72 h. For compari-

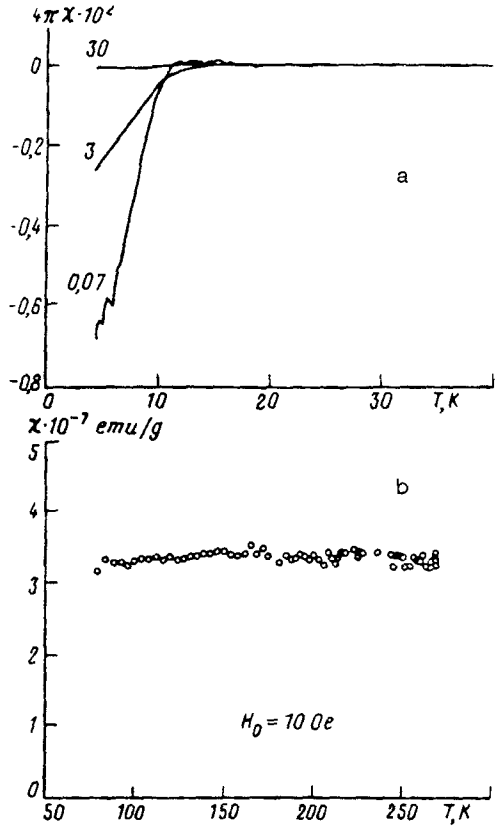

FIG. 1. Temperature dependence of the magnetic susceptibility of $La_2CuO_{4.03}$. a—Diamagnetic response for various amplitudes (in oersteds) of the modulating field; b—in the paramagnetic state at $H_0 = 10$ Oe. In both cases, the magnetic field is in the orientation $\mathbf{H} \perp ab$ plane.

son, samples grown at low temperatures (1050 °C), with considerably poorer insulating properties,[10] were placed in the vessel along with these crystals. The oxygen solubility limits turned out to be different for the two lots of samples: $x = 0.03$ for the good insulators and $x = 0.04$ for the comparison samples. Our purposes in the present study were to learn about the superconductivity and magnetic properties of $La_2CuO_{4.03}$ and $La_2CuO_{4.04}$ crystals and to construct a phase diagram of La_2CuO_{4+x}.

The magnetic susceptibility was measured by the double-modulation method on a mutual-inductance bridge.[11] In the measurements, the test sample, in an alternating magnetic field $H = H_0 \sin(\omega t)$, oscillates between two pickup coils at a frequency $\Omega = 3$ Hz. A signal with a frequency ω and an amplitude modulation at Ω arises at the output from the bridge. The emf signal proportional to the magnetic susceptibility is found through double synchronous detection of the modulated signal. The absolute error in the susceptibility measurements by this apparatus is 5×10^{-8} emu at a modulating-field amplitude of 0.3 mT. This circumstance is of particular importance in measurements of the small susceptibility of La_2CuO_{4+x} in its normal state and because of the need to use small magnetic-field amplitudes in detecting the diamagnetic response.

Figure 1 shows the temperature dependence of the magnetic susceptibility of a

$La_2CuO_{4.03}$ single crystal at low (a) and high (b) temperatures. A basic result is that the temperature at which the diamagnetic response arises (~ 12 K) is considerably lower than the temperatures usually observed in the La_2Cu_{4+x} system. In this system, according to the phase-separation picture, the temperature T_c is determined by the existence of a metallic phase, and the volume of this phase simply changes with increasing concentration of excess oxygen. That a phase separation does not occur in $La_2CuO_{4.03}$ crystals has been demonstrated by direct structural measurements.[10] The data in Fig. 1b confirm the conclusion that the oxygen distribution in the crystal is uniform. In a case in which a system separates into two phases, we should observe a peak in the magnetic susceptibility at $T=T_N$ at the same time as the diamagnetic response. This peak would be due to the onset of a long-range magnetic order in the oxygen-depleted part of the crystal. The temperature-independent (at $T>T_c$) magnetic susceptibility is evidence that there is no macroscopic inhomogeneity in the system. The absolute value $\chi(T>T_c)\simeq 3.5\times 10^{-7}$ emu/g is slightly larger than in lightly doped samples[9] (2×10^{-7} emu/g). This circumstance is again a consequence of the significant doping; it gives rise to a uniform background of carriers in the sample. The pronounced sensitivity to the magnitude of the modulating magnetic field at $T<T_c$ and the small value ($\sim 1\%$) of the diamagnetic signal (Fig. 1a) can apparently be taken as evidence that pinning centers are playing an important role in this superconductor.

The picture of the onset of the superconducting state is completely different in crystals with a slightly larger oxygen index, $x=0.04$. Figure 2 shows corresponding data for a $La_2CuO_{4.04}$ sample. A superconducting phase (Fig. 2a) and an antiferromagnetic phase (Fig. 2b), with a Néel temperature $T_N\simeq 230$ K, coexist in this sample. In this case (first) we observe a weak dependence on the magnetic-field amplitude in the same interval of magnetic fields as for the $La_2CuO_{4.03}$ sample (Fig. 1a). Second, the large diamagnetic response (50%) indicates that the antiferromagnetic and superconducting phases occupy roughly equal volumes in the $La_2CuO_{4.04}$. This conclusion corresponds well to the phase diagram[12] of La_2CuO_{4+x}, on which the enriched stoichiometric phase has an oxygen index $x=0.08$. The presence of macroscopically large regions of both superconducting and antiferromagnetic phases is evidence of a high mobility of oxygen in $La_2CuO_{4.04}$. It is also evidence that the system is unstable with respect to phase separation. On the temperature–composition phase diagram of supersaturated solid solutions,[13] there may be, depending on the sign of $\partial^2F/\partial x^2$ (F is the free energy, and x the concentration), regions in which the solution is absolutely unstable with respect to phase separation. The supersaturated solution decomposes through the formation of regions of segregation over the entire volume of the crystal simultaneously, without the formation of nucleating regions (a spinodal decomposition mechanism, $\partial^2F/\partial x^2<0$). In the opposite case, $\partial^2F/\partial x^2>0$, a solution of this sort is unstable with respect to only large concentration fluctuations, and the separation involves the formation of nucleation centers. In this case the oxygen mobility becomes the decisive factor for the realization of phase separation. We believe that the oxygen diffusion coefficient in $La_2CuO_{4.03}$ crystals is much smaller because of the higher quality of these crystals, and macroscopically large nucleation centers do not form. We should mention that attempts to raise the concentration of excess oxygen in these crystals through a longer hold in the oxygen bomb under the same conditions ($T=650$ °C, $p=3$ kbar) were unsuccessful: The concentration of excess oxy-

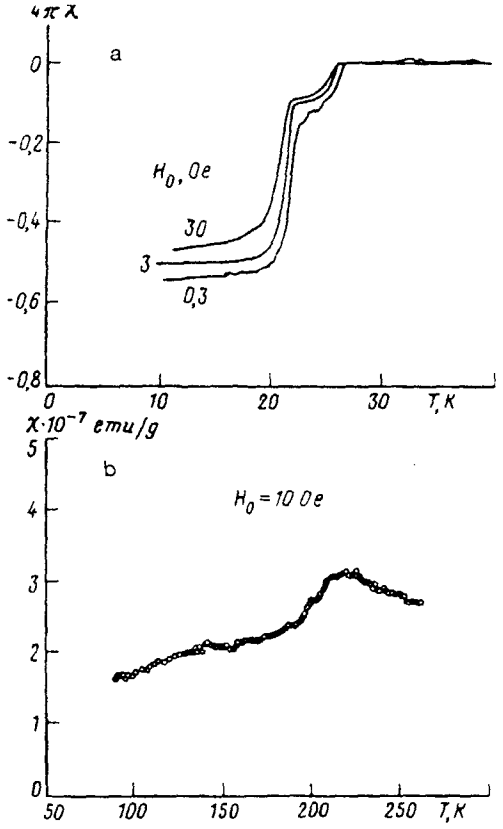

FIG. 2. Temperature dependence of the magnetic susceptibility of $La_2CuO_{0.04}$. The notation is the same as in Fig. 1.

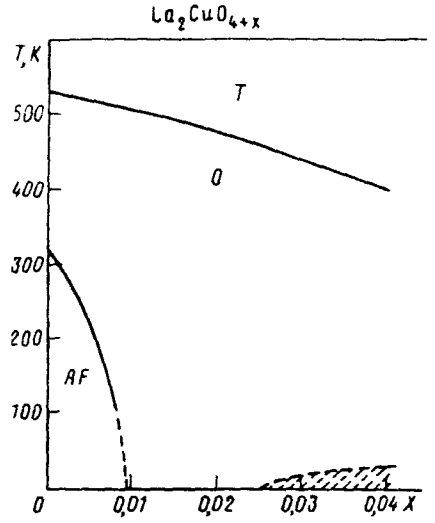

FIG. 3. Initial part of the phase diagram of La_2CuO_{4+x}, constructed from data on high-quality single crystals. Here T and O are the tetragonal and orthorhombic phases, respectively. The hatched region corresponds to the superconducting state; the dashed curves are the presumed $T_N(x)$ and $T_c(x)$ curves.

gen remained at the same level, $x = 0.03$. It may be that the oxygen solubility limit depends on the level of imperfection of the crystal.

It can thus be asserted that the phase diagram of the La_2CuO_{4+x} depends strongly on the quality of the original test samples. Figure 3 shows the initial part of the La_2CuO_{4+x} phase diagram as constructed from the set of results obtained on lightly doped[9] and heavily doped (Ref. 10 and the present study) good insulators. In contrast with the phase diagrams which have been published elsewhere,[14,15] on which the region of a uniform solid solution of oxygen in a La_2CuO_4 matrix is exceedingly narrow, the diagram in Fig. 3 is more reminiscent of the phase diagram of the $La_{2-x}Sr_xCuO_4$ system, in which the superconducting and antiferromagnetic regions are separated by a significant concentration interval of a spin-glass phase. The question of the concentration dependence of T_c in the La_2CuO_{4+x} system remains open and requires further research. It can be concluded from the results found in this study that the superconducting properties of the La_2CuO_{4+x} system depend on the particular way in which the excess oxygen is produced: Higher T_c's are observed in phase-inhomogeneous test samples.

This study is being supported by the State Program on High-Temperature Superconductivity (Project 93019).

[1] J. D. Jorgensen *et al.*, Phys. Rev. B **38**, 11337 (1989).
[2] P. Zolliker *et al.*, Phys. Rev. B **42**, 6332 (1990).
[3] J. Ryder *et al.*, Physica C **173**, 9 (1991).
[4] M. F. Hundley *et al.*, Phys. Rev. B **41**, 4062 (1990).
[5] C. Y. Chen *et al.*, Phys. Rev. B **43**, 392 (1991).
[6] S. N. Barilo *et al.*, *Int. Conf. on HTSC: Material Aspects (ICMC '90)* (Garmisch-Partenkirchen), Vol. 1, p. 107.
[7] A. V. Bazhenov *et al.*, Physica C **208**, 197 (1993).
[8] A. V. Bazhenov *et al.*, Physica C **214**, 45 (1993).
[9] A. A. Zakharov *et al.*, Sverkhprovodimost' (KIAE) **5**(2), 198 (1992) [Superconductivity **5**(2), 207 (1992)].
[10] A. A. Zakharov *et al.*, Physica C **223**, 157 (1994).
[11] A. A. Nikonov, Preprint IAÉ-5467/9, Kurchatov Institute of Atomic Energy, Moscow, 1992.
[12] B. Dabrowski *et al.*, Physica C **162–164**, 99 (1989).
[13] M. I. Zakharova, *Atomic-Crystalline Structure and Properties of Metals and Alloys* [in Russian] (Izd. Mosk. Univ., Moscow, 1972).
[14] J.-C. Grenier *et al.*, Physica C **202, 209** (1992).
[15] P. G. Radaelli *et al.*, Phys. Rev. B **49**, 6239 (1994).

Translated by D. Parsons