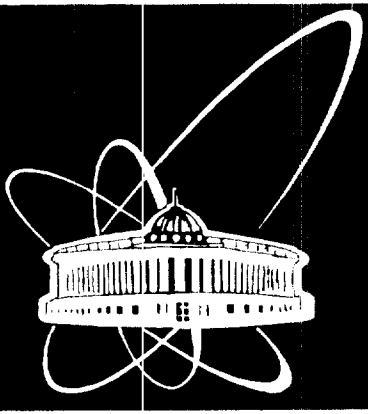

ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ

Дубна

E14-98-10

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MICROSCOPIC PHASE SEPARATION IN La_2CuO_{4+x} INDUCED BY THE SUPERCONDUCTING TRANSITION

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Although the phenomenon of macroscopic phase separation (PS) in La_2CuO_{4+x}, was discovered in 1988 [1], it has no generally accepted explanation yet and the driving force of PS is still the subject of discussion. Recently, it was found that repeatedly published (e.g., [2]) phase diagram of La_2CuO_{4+x}, containing the so-called miscibility gap region $0.01<x<0.06$, is not universal. It has been unambiguously shown in papers of A.Zakharov et al. [3] and A.Balagurov et al. [4] that along with the "usual" La_2CuO_{4+x} single crystals demonstrating the phase separation onto oxygen rich and oxygen poor regions, it is possible to prepare crystals that are inside the miscibility gap and which possess superconductivity without macroscopical phase separation. Combined analysis of neutron and μSR data has shown that the phase separation phenomenon has an even more complicated character, namely, a macroscopically homogeneous superconducting crystal can be inhomogeneous on the microlevel [5]. Finally, we tentatively suggested in [6] that phase separation occurs at microscopic scales in La_2CuO_{4+x} at a temperature close to the superconducting transition temperature and, hence, can be connected with the formation of the superconducting state.

In this paper, we present new experimental data on La_2CuO_{4+x} single crystals, obtained by μSR and neutron diffraction, which allow us to clarify the problem. The most intriguing of the results is that in all of the studied crystals, we observed a coexistence of superconductivity and an ordered magnetic state without macroscopic phase separation with coinciding or very close temperatures for the transitions to the AFM and SC states. This is a strong argument in favor of the existence of the so-called electronic phase separation in these crystals which is theoretically discussed in [7,8].

Two different kinds of La_2CuO_{4+x} superconducting crystals were studied: macroscopically homogeneous and phase separated. The crystals were prepared the by molten solution method under thermodynamic equilibrium conditions. Details of crystal growth, oxygenating procedure and high-resolution neutron diffraction analysis are presented elsewhere [3,4]. Specific feature of this series of crystals is the low oxygen mobility which resulting in the absence of a macroscopic phase separation connected with oxygen diffusion for the crystals in the $x\leq0.03$ region of miscibility gap.

Below, we present the experimental data for two representative crystals: $x=0.02$ for the non-phase separated series of samples (hereinafter, the A crystal) with a superconducting transition temperature $T_c=15$ K, and $x=0.04$ for the phase separated samples (hereinafter, the B crystal) with $T_c=25$ K. The B sample has been studied before by high resolution neutron diffraction [4]. The data on other crystals from these series differs from each other in specific details, but support the main statements of the present work.

The μSR measurements were made using the General Purpose Spectrometer (GPS) on the πM3 surface muon beam line at PSI (Villigen). The neutron diffraction experiments were performed at the IBR-2 pulsed reactor of JINR (Dubna) with the high resolution Fourier diffractometer (HRFD) [9] and the DN-2 instrument equipped with a 2D position-sensitive detector. The magnetization measurements were performed using a custom-made SQUID magnetometer [10].

The magnetic susceptibility measured in an external magnetic field of 0.1-30 Oe is presented in **Fig. 1**. The superconducting diamagnetic response in sample A with an onset transition temperature $T_c=15$ K is low and is suppressed by a small external field. The superconducting fraction is much larger in sample B and less sensitive to the applied magnetic field. We found that the diamagnetic response in sample A strongly depends on the cooling rate. Quenching the sample to helium temperatures completely suppresses the dia-

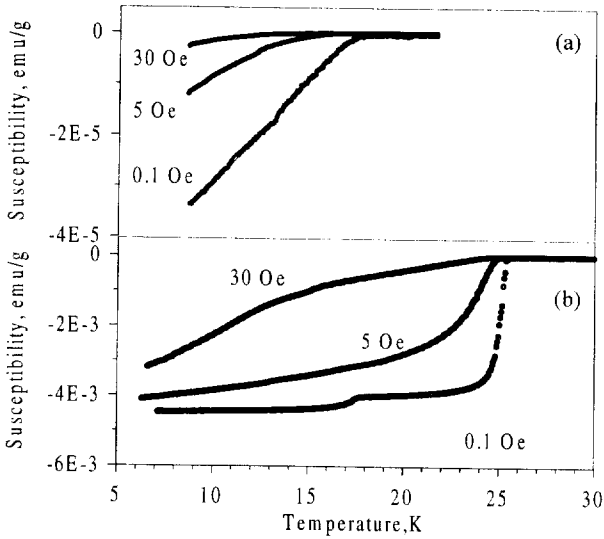

Fig.1: *The temperature dependence of the magnetic susceptibility for the $La_2CuO_{4.02}$ (a) and $La_2CuO_{4.04}$ (b) crystals in different magnetic fields. The magnetic field is parallel to the c-axis of the crystal.*

magnetism. This finding is evidence of the important role of oxygen diffusion and gives an indirect confirmation that the system consists of small grains separated from each other by weak links which can be easily destroyed by a small magnetic field. The situation with quenching is quite different in sample B. The diamagnetic susceptibility is practically independent on the cooling rate (the fastest cooling we used was 200 K/min). Similar effects for single crystal samples of La_2CuO_{4+x} were observed earlier [2,11].

High resolution neutron diffraction (with $\Delta d/d \approx 0.9 \cdot 10^{-3}$) revealed no trace of phase separation in sample A; neither splitting nor broadening of the neutron diffraction peaks were observed. giving evidence that at macroscopic scales, the homogeneous excess oxygen concentration in the crystal is preserved down to the lowest measured temperature (9 K.) In the B sample, the phase separation into oxygen-rich and oxygen-poor phases was observed clearly at cooling [4]. The relative difference in the elementary lattice parameters of these two phases amounted to about $2 \cdot 10^{-3}$, which corresponds well to the data obtained for "usual" La_2CuO_{4+x} crystals [1]. In the B crystal, we observed the specific effects of diffraction peak broadening, an analysis of which allowed us to conclude that the average dimensions of the coherent regions of the coexisting phases coincide and amount to: 100 nm along the c-axis and 150 nm within the plane. The phase separation process starts at T=250 K and is complete at T=200 K. It is worth mentioning that the two-step shape of the superconducting transition **(Fig. 1b)** is possibly connected with a network of coupled superconducting droplets of macroscopic size, as mentioned above.

The magnetic state of the A crystal was identified by the presence of a muon spin precession signal detected in zero external magnetic field (ZF-μSR) below 15 K. Correlated precession of the muon spins is possible only if the surrounding Cu moments are ordered on the scales of several coordination spheres. The time dependence of the muon spin polarization projection P(t) can be described by a function given by

$$P(t) = a_1 \exp(-\lambda t) \cos(2\pi f_\mu t + \varphi) + a_0 \exp(-\lambda_0 t), \qquad (1)$$

where the precession frequency $f_\mu = \gamma_\mu B_\mu$ is given by the local magnetic field acting on the muon $\mathbf{B}_\mu$, which is proportional to the staggered magnetization of the copper magnetic moments; the precession amplitude a_1 is determined by the magnetically ordered volume fraction of the crystal and the direction of $\mathbf{B}_\mu$. The second component is the sum of the non-oscillating part of the muon polarization inside the AFM regions of the crystal and a contribution from the remaining paramagnetic volume. Typical ZF-μSR signals observed in the A sample are shown in **Fig. 2**, where the difference between paramagnetic (T=30 and 20 K) and AFM (T=4 K) states of the crystals can be clearly seen. The amplitude a_1, shown in **Fig.3** had a constant value below 15 K, demonstrating that the magnetic transi-

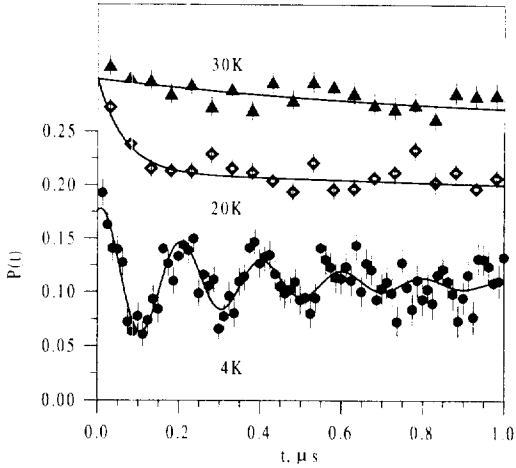

Fig.2: Time dependence of the muon spin polarization P(t) in zero external field above and below the magnetic transition (T_N=15 K) for $La_2CuO_{4.02}$. The data for T=20K and 30K are shifted up along the y-axis.

tion is completely established. The spontaneous muon spin precession frequency f_μ is shown in **Fig.3** as a function of temperature. Its temperature dependence and low temperature value f_μ=5 MHz are typical for the AFM state of stociometric La_2CuO_4 [12], implying that the A sample is ordered in the same AFM structure. No precession signal was observed above 15 K; however, the polarization function possesses a fast decaying component up to 30 K which steadily decreases with increasing temperature. The origin of this fast depolarization is the slowing down of the Cu-spin fluctuations near the phase transition. Thus, the ZF-μSR data unambiguously proves the presence of static antiferromagnetic order in part of the crystal volume. The volume fraction occupied by the AFM phase amounts to ≥50% of crystal volume. This was determined from the data measured in a transverse external field of 4 kOe in the temperature range of 3-280 K.

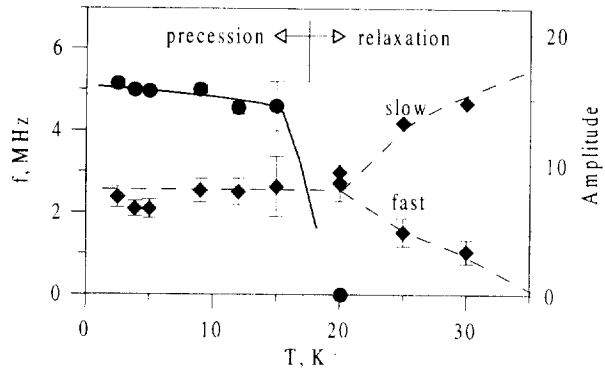

Fig.3: *The spontaneous muon spin precession frequency as a function of temperature in the $La_2CuO_{4.02}$ crystal (left axis). Amplitude of the muon spin polarization (right axis, dashed line). Below 15K it is the amplitude of AFM precession, above 15 K the polarization has no oscillations, but consists of fast and slow damping components.*

Unlike the A sample, there are two characteristic magnetic temperatures for the B sample. Below T_{N1}≈230 K, the AFM phase appears only in 10% of the crystal volume. Then, under cooling to T_{N2}≈25 K, a sharp increase in the AFM fraction occurs, which reaches 40% at low temperatures (**Fig.4**, the left axis). The spontaneous muon spin precession frequency detected below T_{N1} has, again, typical values of about 5 MHz, as was expected for AFM La_2CuO_4. The precession frequency smoothly increases with decreasing the temperature, without any peculiarity at T_{N2}.

To check whether the observed transitions in the A and B samples lead to a true long-range AFM order, we measured the neutron diffraction spectra along the [100] direction with the DN-2 instrument (**Fig.5**). According to the μSR data, we expected to find the (100) magnetic peak below the magnetic transition below T_N=15 K in the A sample and below T_{N1}=230 K in the B sample. Indeed, in the B sample, this peak was well pronounced, whereas in the A sample, neutron diffraction revealed no traces of this reflection (insert in **Fig.5**). Temperature dependence of the (100) peak area in the sample B is shown in **Fig.4** (right axis). Since the copper magnetic moment does not change at T_{N2}, according to the temperature dependence of the muon spin precession frequency, one would expect to have an increase in the (100) peak area below T_{N2} similar to the increase in AFM fraction detected by μSR. However, neutrons do not see any peculiarity below T_{N2}=25 K, whereas the muons see a four fold increase in the AFM fraction. Similar to sample A, we have a coincidence of the transition temperature to an ordered state seen only by μSR and of the temperature where the superconducting transition starts to set in.

Thus, the main experimental result concerning the A crystal (x=0.02) is the appearance of correlated muon spin precession below T_N=15 K, which coincides with the superconducting transition T_c. Moreover, the crystal fraction occupied by the AFM phase is close to 50%. However, the magnetic state at low temperature does not possess any long

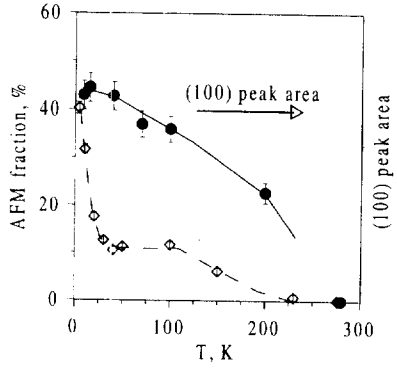

Fig.4: The AFM volume fraction of the $La_2CuO_{4.04}$ crystal seen by μSR (the diamonds, left axis). The area of the (100) AFM peak as a function of temperature measured by neutron diffraction (circles, right axis) is also shown.

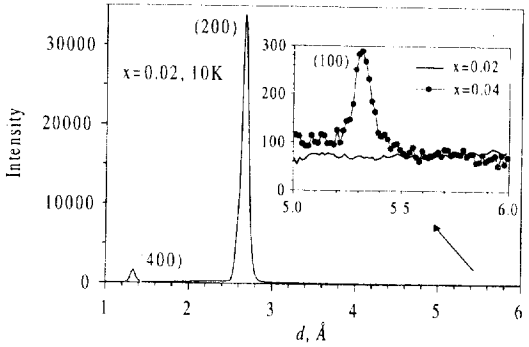

Fig.5: The diffraction pattern from the [100] plane for $La_2CuO_{4.02}$ measured at T=10 K. The insert shows fragments of the diffraction patterns for both $La_2CuO_{4.02}$ and $La_2CuO_{4.04}$ near the (100) AFM peak. The position and intensity of (200) and (400) peaks are the same for both crystals.

range magnetic order since the neutron diffraction study failed to observe the (100) magnetic peak. In the B crystal (x=0.04), the ordered magnetic state appears at T_{N1}≈230 K,which can be seen from both the μSR and neutron data. Down to the superconducting transition temperature coinciding with T_{N2}=25 K, the volume fraction of the AFM phase is only ~10%, which increases to ~40% upon further cooling. At the same time, the fraction of the sample volume occupied by the AFM phase with the correlation range sufficient for the formation of the magnetic Bragg peak remains at the level of ~10% in the whole temperature range.

We will start our discussion of the experimental results with a brief sketch of the "temperature-concentration" phase diagram of La_2CuO_{4+x}. An earlier experimental study showed the presence of miscibility gap in a rather wide concentration region. However, when a solid solution decomposes into two phases, two routes for the decay are possible: *the nucleation and growth* mechanism and/or the *spinodal* mechanism. Because there is an activation barrier in the former case, the process may be completely quenched in crystals with low mobility of the dopants. The spinodal decay does not need an activation process and, hence, inevitably proceeds to the creation of a spatial fluctuation of the composition in the sample. We believe that the decay mechanism is the main difference in our crystals: the x=0.02 crystal does not have a high enough oxygen index to be in the spinodal region and

has to be split via nucleation mechanism — which is not effective at low mobility. The oxygen index in the x=0.04 crystal, on the other hand, situates the sample in the spinodal region and the decay takes place independently of the oxygen mobility.

Two main experimental results of the present work should be discussed: (i) the appearance (or sharp increase in the volume fraction) of the low temperature AFM phase when the system enters the superconducting state and (ii) why this AFM phase is not seen by neutron diffraction. We should mention that a very similar phenomenon has been observed in the crystal with another oxygen index (x=0.03) [5] where a magnetic transition to the short range spin-glass-like state was set in the vicinity of the superconducting transition.

One natural explanation for the observed behavior is the suggestion that after cooling, the crystals consist of grains of oxygen-rich and oxygen-poor phases of very small size (in the x=0.04 crystal, there are also metallic regions of larger size due to the macroscopic PS which produce a robust superconductivity at low temperatures). Then the transition at low temperature corresponds to the Neel temperature of the oxygen-poor phase. The absence of AFM neutron reflections at the respective temperatures implies that the sizes of the coherent regions of this AFM phase are very small (the order of several dozens angstroms) and, therefore, they cannot be seen as Bragg reflections because of size broadening effect.

The coincidence between the temperatures of the magnetic and superconducting transition in quite different crystals, however, remains surprising. One may have to consider another possibility connected with an electronic phase separation, which causes a charge concentration wave inside the crystal. From the fact that the appearance of a magnetic order for x=0.02 (**fig.2**), T_N=15 K, in x=0.04 (**fig.4**), T_{N2}=25 K and in x=0.03 [5], T_f=8 K, is always close to the onset of the superconducting regime in all crystals, independent of their actual microstructure and critical temperatures we may conclude that the magnetic ordering *is induced* by the superconducting transition. It is worth mentioning in this context the relevant theory [8] where the instability of a homogeneous system was found to result from the existence of different insulating correlations, characterized by long-range or short-range order. There it was also shown that the stability boundary becomes wider in the presence of superconducting pairing. As a result, the superconducting transition may cause a sample which is homogeneously metallic in its normal phase to split into metallic droplets that are separated from each other by weakly coupled insulating interlayers.

In summary μSR and neutron diffraction studies show that a microscopic phase separation (as opposed to macroscopic phase separation) appears in parallel with superconductivity and is very likely driven by the superconducting pairing.

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Помякушин В.Ю. и др.
Индуцированное сверхпроводящим переходом
микроскопическое фазовое разделение в La_2CuO_{4+x}

E14-98-10

Явление фазового разделения в сверхпроводящих монокристаллах La_2CuO_{4+x} ($x \leq 0{,}04$) было исследовано методами μSR-спектроскопии, дифракции нейтронов высокого разрешения и магнитной восприимчивости. Несмотря на то, что все кристаллы находятся внутри щели растворения ($0{,}01 < x < 0{,}06$), макроскопическое фазовое разделение, по данным дифракции нейтронов, испытывают только те кристаллы, которые обладают достаточно высокой концентрацией избыточного кислорода $x \geq 0{,}04$. Тем не менее фазовый переход в магнитоупорядоченное состояние детектируется μSR-методом, причем он происходит одновременно с переходом в сверхпроводящее состояние. Такое неожиданное поведение позволяет предположить, что микроскопическое фазовое разделение индуцируется сверхпроводимостью.

Работа выполнена в Лаборатории нейтронной физики им. И.М.Франка.

Препринт Объединенного института ядерных исследований. Дубна, 1998

Pomjakushin V.Yu. et al.
Microscopic Phase Separation in La_2CuO_{4+x} Induced
by the Superconducting Transition

E14-98-10

The phase separation (PS) effect in superconducting La_2CuO_{4+x} ($x \leq 0.04$) single crystals with low oxygen mobility was studied via μSR spectroscopy, high resolution neutron diffraction and magnetic susceptibility. Despite the fact that all crystals are inside the miscibility gap ($0.01 < x < 0.06$), only crystals with a sufficiently large excess oxygen concentration $x \geq 0.04$ show a macroscopic phase separation according to the neutron diffraction data. However, in all samples a phase transition to an ordered magnetic state was observed by μSR spectroscopy concomitantly with the onset of superconductivity. This unexpected behaviour suggests that the underlying microscopic PS is driven by superconductivity.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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