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Preliminary Communication

Possible Superconducting State up to 210 K in the new Composition of Y—Ba—Cu—O

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We have observed the zero resistance state up to 210 K in the mixed system of nominal composition $Y_{1.2}Ba_{0.8}CuO_{4-\delta}$ prepared under simultaneous action of pulsed electric field up to 30 kV/cm and uniaxial force of 180 kN. The onset of the decrease of the resistance at 281 K in the repeated cycles and preliminary data diamagnetism are understood by us as a possible superconductivity event related to a particular composition.

Since the discovery of Bednorz and Müller[1] that the perovskite oxide ceramic Ba—La—Cu—O exhibits the superconducting state up to 35 K new compounds of similar type were synthesized. In the mixed system (green phase) $Y_2BaCuO_5 + Ba_2YCu_3O_{9-\delta}$, Chu and coworkers[2] observed an »extremely unstable phase« displaying superconducting properties far above 100 K. Cava *et al.*[3] extracted the superconducting single phase (black) $Ba_2YCu_3O_{9-\delta}$ and succeeded in producing, by an additional oxygen treatment, a reproducible superconductivity in a rather narrow temperature interval of 1.5 K. In the meantime, from different part of the world the occurence of unstable superconductivity in the temperature range 100—350 K was announced. We have observed an unstable supression of resistance by different treatments in more than a dozen of experiments starting from different batches of mixed ($Y_2BaCuO_5 + Ba_2YCu_3O_{9-\delta}$) and single ($Ba_2YCu_3O_{9-\delta}$) phases.

In the course of time it became clear that many more additional experimental data are needed for elucidation of physical properties of these rather exotic ceramics. It is well known that materials[4] of Ba—La—Cu—O family (K_2NiF_4) exhibit ferroelectricity. Further, in the superconducting oxygen-defficient phase of the composition $(Y_{1-x}Ba_x)_2Cu_mO_n$ the presence of oxygen vacancies and their distribution among the lattice sites are of particular importance. Hervieu *et al.*[5] proposed oxygen framework in the perovskite $A_nM_nO_{3n-1}$ with the possibility of existence of oriented domains in various configurations of oxygen vacancies. This motivated us to treat our samples in the electric field. In addition, an injection of oxygen vacancies from the grain or phase boundaries may be stimulated by electric field[6]. Considering the possibility of several vacancy lattices[7] the electric field can possibly transform a particular vacancy distribution into another one.

In this letter, we report a stable and reproducible onset of the decrease of resistance (R) at 281 K obtained in the samples prepared by the following procedure. The powder of the mixed phase was prepared by the reaction of appropriate amounts of Y_2O_3, CuO and Ba_2CO_3 necessary for obtaining the nominal composition $Y_{1.2}Ba_{0.8}CuO_{4-\delta}$. Pellets of 12 mm in diameter and 1 mm thickness were pressed with a pressure of 0.2 GPa. Then the small parts (mass (5—10 mg) were cut from the pellets with a razor blade, and granules were subjected to the press in a steel anvil having the configuration shown in the insert into Figure 1. The position of electrodes used

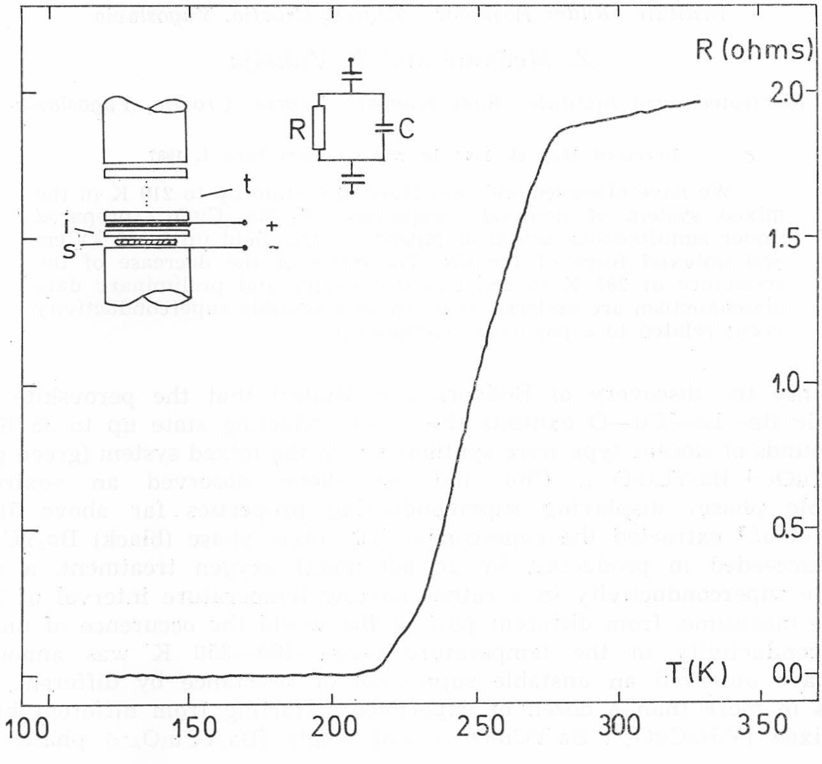

Figure 1. Temperature dependence of the electrical resistance of treated sample (definition in text). In the insert the tool for uniaxial pressure is shown: Teflon sheets (t), insulation (i) consisting of Teflon sheet plus 10 foils of polystyrene and sample (s). The equivalent scheme of the sample (RC) compacted between the insulation sheets is also given.

for generation of pulsed electric field with a peak value up to 1000 V is also shown. The pulses result from a half wave rectified AC voltage modified by a cascade of fast thyristors[8] in order to obtain rise time of pulses in the range 10^{-2} s to 5×10^{-7} s. The upper electrode was made of beryllium bronze foil, 80 μm thick. The lower part of the anvil was in direct contact with the sample and served as a ground electrode. For the measurements sensitive to the presence of iron (X-ray and magnetic susceptibility measurements) the sample was separated from the ground electrode by 10 μm polyester foil. The equivalent scheme of the sample and the insulating sheets is also shown in the insert into Figure 1. The typical resistance of the sample in the pressed state was 2 MΩ which corresponds to the resistivity of $\sim 10^6$ Ωm. The measured time constant of the sample itself is RC $\sim 2 \times 10^{-4}$ s. The voltage drop on two faces on the sample was measured in a separate experiment with 5 μm aluminium foils and is estimated to be $\sim$ 80 per cent of the applied voltage at the frequency of 1 kHz. We have detected no current flowing in the described circuit and hence there were no traces of voltage leakage. The dimensions of thin laminae obtained in such a way were 40—60 μm thick, having a front area of 0.5—0.7 cm^2. Sintering was undertaken in atmosphere by heating up to 965 °C.[7]

Measurements of electrical resistance were performed on the samples of typical cross-section 1×0.04 mm^2 by four-probe method using usual silver paint and 30 μm gold wire. In forthcoming text the samples subjected to the electric field and uniaxial pressure will be refferred to as »treated«, and samples sintered in the same temperature cycle (with no use of electric field or pressure) will be termed »nontreated«.

In the samples prepared with pulsations (rise time 10^{-2} s, first batch) the measuring current was 1 mA and the measured resistivities at room temperature (RT) were 7×10^{-4} Ω cm. The accuracy of the measurement of electrical resistance is limited by the noise level to $\sim$ 5 mΩ. The resolution of the measurement of R was 0.06 mΩ. The »zero resistance« state was achieved below 210 K (Figure 1). We have increased the measuring current in order to test the possible superconducting state. Up to 12 mA measuring current, when the contacts failed, no shift from the low resistance state was observed.

The AC susceptibility measurements were performed in a standard inductance bridge[9] with two opposite secondaries at measuring frequency of 28.4 Hz. The samples were positioned on a copper holder and attached by Teflon tape. A copper-constantan thermocouple served as temperature-sensing element. The maximum AC field was about 10 A m^{-1} (0.13 Oe). In view of the small portion of significant phase (estimated to be less than 5% of total mass in a sample of mass 0.6 mg), the measurement of susceptibility must be taken under extreme care. On Figure 2 is shown the temperature dependence of AC susceptibility signal for the sample used for Figure 1. The highest diamagnetic contribution was nearly three times the noise level. An abrupt decrease of susceptibility (χ_{ac}) is evident at $T < 280$ K, as well as a saturation near 200 K. This saturation is followed by a gradual increase of susceptibility towards lower temperatures. We tested the apparatus by performing the measurement on copper holder without the sample and, separately, with a non-treated sample.

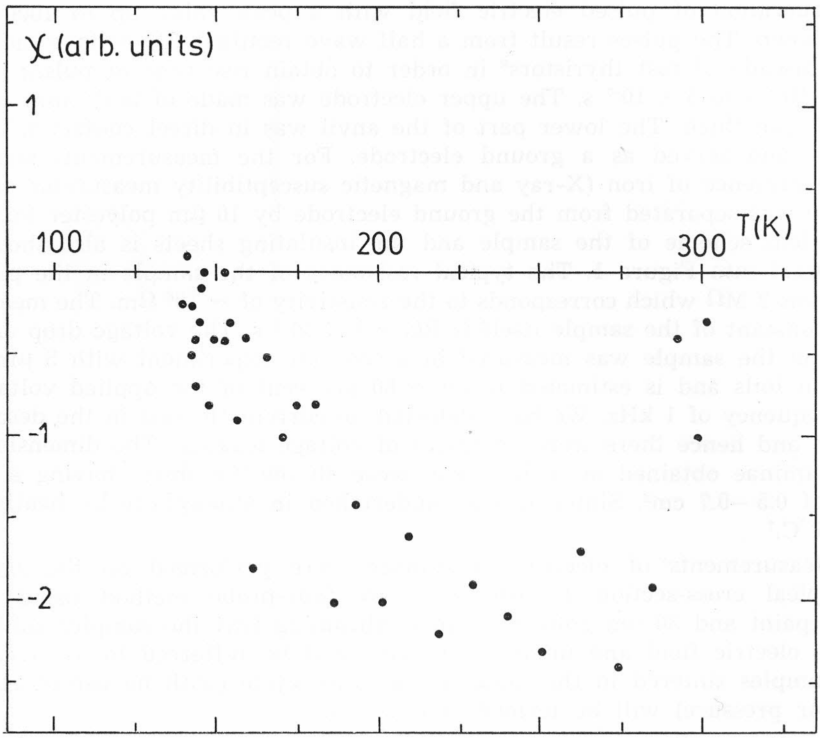

Figure 2. Temperature dependence of the magnetic susceptibility (arbitrary units).

The gradual increase of susceptibility at $T < 200$ K may be due to the paramagnetic contribution coming from the insulating part of the sample[7]. Third, small portion of possible superconducting phase precludes the possibility of determining unambiguously, with the AC technique employed here on bulk samples, whether we are dealing with Meissner effect, »shielding« effect, or both of them[10]. However, our earlier measurements on much greater powdered and bulk $Ba_2YCu_3O_{9-\delta}$ samples revealed that the sudden onset of diamagnetism in bulk samples was always accompanied with the Meissner effect in the powder.

We also examined the Raman spectra excited by COHERENT INNOVA — 100 argon laser operating at 514.5 nm and giving 100 mW to the sample. RT spectra were recorded by DILOR Z — 24 triple spectrometer under 90° scattering geometry and with the near-grazing incidence. The step size was 1 cm^{-1}, slit width 2 cm^{-1} and the sampling time interval 19. Spectra of treated samples (Figure 3a) are significantly less intensive (probably due to more apparent darkness of treated samples) but they contain a new broad feature near 600 cm^{-1}. Although Raman spectra taken at RT must be considered with care for the analysis of high T_c superconducting materials we believe that, in combination with other methods, they can help to elucidate the structure of present material. X-ray powder diffraction data were simultaneously recorded for samples of treated, non-treated and single phase $YBa_2Cu_3O_{9-\delta}$

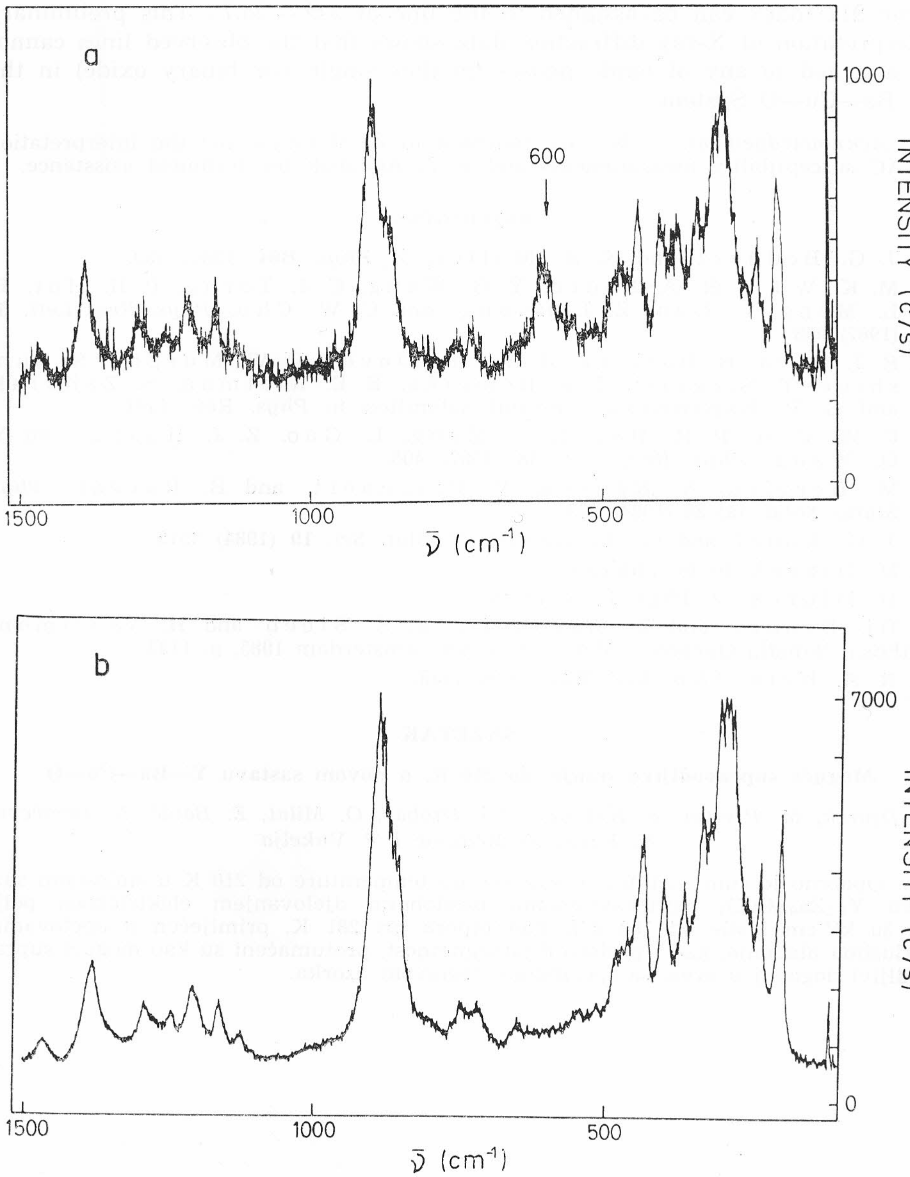

Figure 3. Raman spectra of treated (a) and non-treated (b) samples.

specimens at RT by Guinier-de Wolf camera using crystal monochromated $Cu_{K\alpha}$ radiation. The treated samples reveal several extra lines at $2\ \Theta$ angles: 25.0°, 29.0°, 35.7°, 41.2°, 48.8°, 59.6°, which appeared besides the lines of single phase $YBa_2Cu_3O_{9-\delta}$ and the already known mixed phase$Y_{1.2}Ba_{0.8}CuO_{4-\delta}$. All of their d-values except for the line at $2\ \Theta = 35.7°$ belong to the lattice parameters sequence of a fcc lattice with the cell edge $a = 0.612$ nm while the cubic 211 index can be assigned to the line at $2\Theta = 35.7^{\circ}$. This preliminary interpretation of X-ray diffraction data shows that the observed lines cannot be assigned to any of oxide phases (neither single nor binary oxide) in the Y—Ba—Cu—O System.

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SAŽETAK

Moguće supravodljivo stanje, do 210 K, u novom sastavu Y—Ba—Cu—O

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Opaženo je stanje nultog otpora sve do temperature od 210 K u smjesnom sustavu $Y_{1.2}Za_{0.8}CuO_{4-\delta}$ pripravljenomu istodobnim djelovanjem električkoga polja od 30 kV/cm i sile od 180 kN. Pad otpora pri 281 K, primijećen u opetovanim ciklusima hlađenja, kao i prateća dijamagnetnost, protumačeni su kao mogući supravodljivi događaj u svezi sa specifičnim sastavom uzorka.