Superconductivity of Cu/CuO_x interface formed by shock-wave pressure

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Abstract. A mixture of powdered Cu and CuO has been subjected to shock-wave pressure of 350 kbar with following quenching of the vacuum-encapsulated product to 77 K. The ac magnetic susceptibility measurements of the samples have revealed metastable superconductivity with $T_c \approx 19$ K, characterized by glassy dynamics of the shielding currents below T_c. Comparison of the ac susceptibility and the DC magnetization measurements infers that the superconductivity arises within the granular interfacial layer formed between metallic Cu and its oxides due to the shock-wave treatment.

1. Introduction

Since the discovery of superconductivity above 30 K in lanthanum barium copper oxide, many similar high-critical-temperature superconductors have been found [1]. Superconductivity in all of these multilayered oxides is believed to originate in the planes of copper and oxygen atoms, common to these compounds. Therefore, fabrication of synthetic multilayers on the basis of the copper oxide layers is promising for realization of new HTSs. For example, a HTS-like phenomenon was observed by means of electric conductivity measurements in the samples consisting of Cu film deposited onto natural faces of CuO single crystal under special conditions [2]. The phenomenon manifests itself as a giant step-like rise of the electric conductivity of the samples by a factor $\approx 10^5$ as the temperature decreases below the critical value T_c, which varied in the range 200–500 K depending on the thermal treatment conditions of the samples. At $T < T_c$, the electric conductivity of the Cu/CuO samples was found to be suppressed by applying the external magnetic field, as well as by increasing of electric current in the sample. These experimental facts suggest the superconductivity in the Cu/CuO interface with T_c significantly higher than room temperature [2]. A strong indication to superconductivity at 20–90 K has been revealed by dynamic magnetic susceptibility measurements in Cu/CuO_x samples prepared by surface oxidation of powdered copper followed by thermal treatment in vacuum. By comparative dynamic and static magnetic susceptibility measurements, the superconductivity was attributed to weakly coupled superconducting islands formed spontaneously in the Cu/CuO_x interfacial areas during the heat treatment process. Superconducting interfaces of such prepared Cu/CuO_x samples are instable at room temperature, as inferred from a decay of the superconducting transition after a ≈ 20-hour exposure of the vacuum-encapsulated samples to room temperature.

However, quenching of the vacuum-encapsulated Cu/CuO$_x$ samples to low temperature (77 K) has helped to stabilize the superconducting Cu/CuO$_x$ interfaces and prevent the decay of superconductivity. A success in stabilization of the superconducting Cu/CuO$_x$ interfaces by the low temperature quenching has motivated our attempts to apply a shock-wave pressure to the Cu/CuO mixture for their preparation. During the shock-wave impact, the stroke energy applied to the sample evokes relative displacements of local parts of the sample matter, resulting in a series of high-pressure shock-waves propagating throughout the sample within 10^{-6}–10^{-9} s. The energy of the shock-waves leads to local, non-equilibrium overheat of the sample regions at the shockwave front, followed by their rapid cooling (quenching) as the shock-wave is passed, thus fixing the sample in the metastable state. Furthermore, highly non-equilibrium conditions caused by propagation of the high-pressure shock-waves in the sample can stimulate phase transitions or mechanochemical reactions inaccessible by any equilibrium processes, i.e. static pressure–temperature mode, resulting in new materials [3].

In this paper we report on metastable superconductivity at $T_c \approx 19$ K revealed by the ac magnetic susceptibility measurements of the powdered mixture of Cu and CuO subjected to shock-wave pressure ≈ 350 kbar.

2. Sample preparation and measurement techniques

The samples were prepared by means of flat-type shock-wave pressure setup described in detail earlier in article [4]. The starting samples were tablets, 9.6 mm in diameter and 0.9 mm thick, prepared by pressing of 99.99%-pure copper powder, 5–50 μm grain size, covered by 0.2 mm layer of powdered 10–40 μm grain size, 99.99%-pure copper oxide CuO. For preparing the superconducting Cu/CuO$_x$ samples, the optimum value of the shock-wave pressure, within 1 Mbar range, was found ≈ 350 kbar. After the shock-wave pressure treatment, the conservation cell was cut open and the samples were extracted. Within 3–5 min, the extracted samples were vacuum-encapsulated to a residual pressure 1–5 Pa into 5 cm-long quartz ampoules having 0.9 mm-thick walls and 6 mm outer diameter, and stored in liquid nitrogen to prevent their degradation under normal conditions. We have to note that quenching of the bare (vacuum-unsealed) shock-wave pressure treated samples into liquid nitrogen did not result in superconductivity, apparently due to destruction of the superconducting phase by adsorbed gaseous layer on the sample surface during the sample cooling. In addition, for comparative studies, the samples of compacted powdered pure Cu as well as pure CuO and Cu_2O have been prepared separately under the same conditions as described above.

The samples were studied by measuring the dynamic magnetic usceptibility using a mutual inductance ac susceptometer [4]. The amplitude H_{ac} of the driving field ranged from 0.22 to 12 Oe, the driving frequency ν from 300 Hz to 10 kHz, and the superimposed DC magnetic field H_{DC} up to 300 Oe. In order to prevent degradation, warming of the samples was avoided and the measurements were done without unsealing the evacuated ampoule. The ampoule was mounted on the measuring insert at $T \approx 80$ K, which was then dipped into a precooled measurement cryostat. Static magnetization of the sealed Cu/CuO$_x$ samples was studied by SQUID magnetometer in the temperature range 5–70 K and static magnetic fields 30–300 Oe. The ac susceptibility measurements have shown that the properties of the sample sealed in the evacuated ampoule survive ≈ 15 min exposure to room temperature, which enables standard loading routine of the SQUID magnetometer. Crystal structure of the samples was investigated in the temperature range 70–300 K by X-ray diffraction measurements using Oxford Diffraction Gemini R diffractometer equipped with a cooling system that enables the measurements in the flow of cold nitrogen gas. For the diffraction measurements, the sample was extracted from the quartz ampoule in the ambience of liquid nitrogen and rapidly (within 5–10 s) mounted onto the precooled goniometer of the diffractometer.

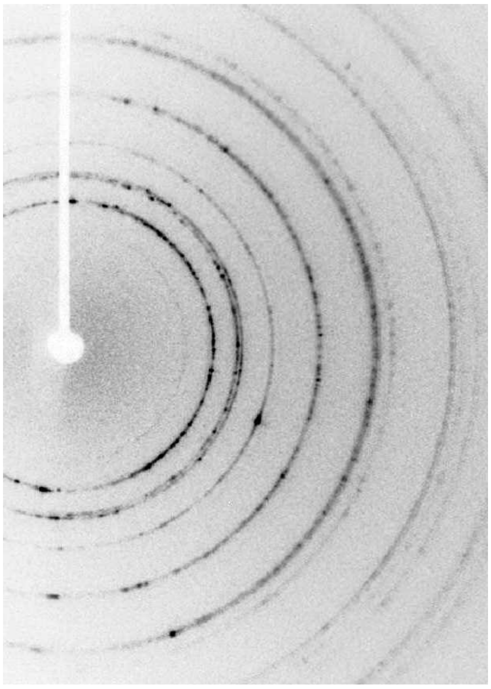

Figure 1. X-ray diffraction pattern for the shock-wave pressure treated sample Cu/CuO.

3. Experimental results

Diffraction pattern of the shock-wave pressure treated Cu/CuO$_x$ sample, recorded at $T \approx 75$ K, is shown in figure 1. All the diffraction rings in the observed pattern are a superposition of the patterns from polycrystalline CuO, Cu2O and Cu crystal structures corrected by the thermal expansion factor [14]. No change has been detected in the X-ray diffraction patterns of the Cu/CuO$_x$ samples after their exposure for ≈ 20 h at room temperature. Each cycle of $\chi(T)$ measurements started from a cooldown of the Cu/CuO$_x$ sample to 4.7 K. Next, $H_{\rm ac}$ was switched onto enable the measurements. Quite remarkably, at constant $T = 4.7$ K, χ' develops to the equilibrium value monotonously in time, t, towards the enlargement of diamagnetism. Curve 1 in figure 2a illustrates the time evolution of χ' measured at frequency $\nu = 2.1$ kHz, $H_{\rm ac} = 0.6$ Oe, $H_{\rm DC} = 0$ Oe. χ' was found to relaxexponentially to ground diamagnetic state as $a + b\exp(-t/\tau)$, shown in figure 2 by a solid line, where a, b and s are fit parameters. The extracted time constant, $\tau = 7$ min, is practically flat in frequency for the range 0.1–10 kHz, as shown in figure 2b. We have to note that the observed $\chi'(T)$ dependencies were not influenced by an effect of the sample temperature relaxation towards the equilibrium temperature, because the $\chi'(T)$ relaxation curves were found to be insensitive to the retention interval of the sample exposure at $T = 4.7$ K, until the measurements start.

After a half-hour ($\approx 4\tau$) delay at $T = 4.7$ K $\chi(T)$ dependence was measured upon heating at the rate of 1–1.5 K/min (slower heating rate made no visible change to the measurement result). The measured $\chi'(T)$ dependence is shown by curve 1 in figure 2c. In this plot, the drop in $\chi'(T)$ curve at 4.7 K corresponds to the $\chi'(T)$ relaxation process, curve 1 in figure 2a. As the temperature increases, a step-like rise of $\chi'(T)$ is observed at $T_c \approx 18.5$ K signifying a phase transition in the sample at this temperature. In order to exclude the influence of the $\chi'(T)$ relaxation process on the $\chi(T)$ result, all subsequent $\chi'(T)$ measurements were performed according to the measurement cycle described above. The $\chi(T)$ dependencies measured in a static magnetic field, $H_{\rm DC}$, are shown in figure 3. According to curves 1–3, an increase in $H_{\rm DC}$

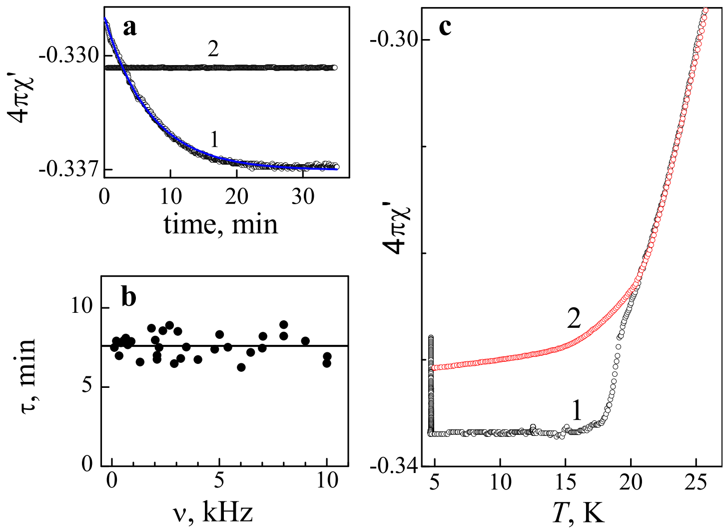

Figure 2. (a) Time evolution of $4\pi\chi$ at $T = 4.7$ K for the vacuum-encapsulated shockwave treated Cu/CuO_x sample (curve 1) and for the same sample exposed to room temperature for ≈ 20 h (curve 2). Solid curve: fit to curve 1 in the form $a + b\exp(-t/\tau)$, where a, b and τ are fit parameters. (b) The dependence of the time constant τ on drive frequency ν. (c) Temperature dependencies of $4\pi\chi'(T)$ measured before (curve 1) and after (curve 2) the sample exposure to room temperature.

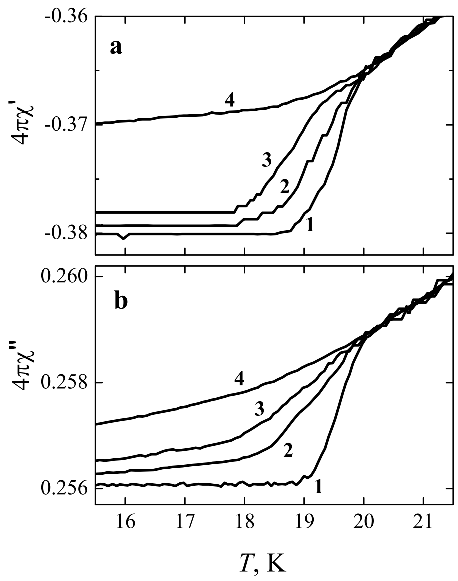

Figure 3. Temperature dependencies of the real (a) and the imaginary (b) parts of $4\pi\chi$ for the Cu/CuO_x sample measured under the DC magnetic field H_{DC}=0, 168 and 268 Oe (Curves 1–3, respectively). Curves 4 correspond to the same sample exposed for 20 h to room temperature.

suppresses the anomaly in $\chi(T)$. Increasing the driving ac magnetic field amplitude, H_{ac}, gives a similar effect, as shown in figure 4. Figure 5 shows the temperature dependencies of χ' and

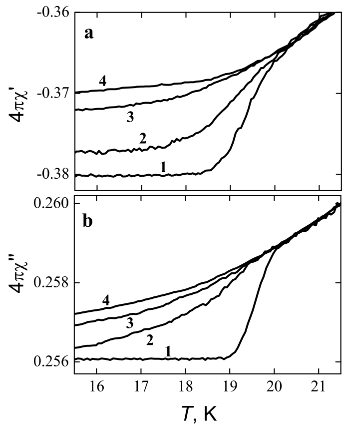

Figure 4. Temperature dependencies of the real (a) and the imaginary (b) parts of$4\pi\chi$ for the Cu/CuO_x sample measured with the amplitude of the ac driving field H_{ac}=0.22, 1.8 and 11.6 Oe (curves 1–3, respectively). Curve 4 corresponds to the same sample exposed for 20 h to room temperature.

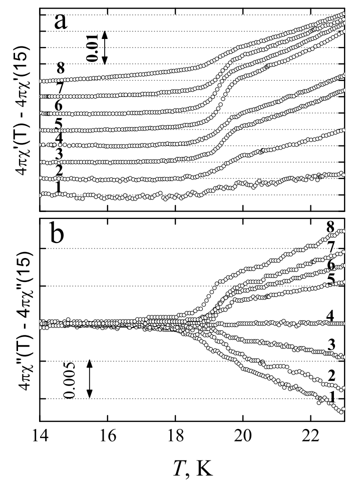

Figure 5. Temperature dependencies of the real (a) and imaginary (b) parts of $4\pi\chi$ for the Cu/CuO_x sample measured at frequencies 0.313, 0.93, 1.53, 2.1, 2.9, 3.46, 5.4 and 10.26 kHz (Curves 1–8, respectively). For visual clearness, the $4\pi\chi'(T)$ curves are separated along Y-axis by 0.005.

χ'' measured at frequencies from 0.3 to 10 kHz. One can see in figure 5 that T_c is essentially frequency independent, while the shapes of the $\chi'(T)$ and $\chi''(T)$ curves at the phase transition change dramatically with the frequency. After completion of these measurements, the insert with the Cu/CuO_x sample was finally kept for $\approx$ 20 h at room temperature.

The following measurements have shown, first of all, no time dependence of $\chi'(T)$ at 4.7 K, see curve 2 in figure 2a. Furthermore, the $\chi(T)$ dependence of the room-temperature-annealed sample does not exhibit a step-like anomaly and is independent on H_{ac} and H_{DC}, within the ranges used previously. Moreover, now $\chi'(T)$ and $\chi''(T)$ dependencies (curve 2 in figure 2c, curves 4 in figures 3 and 4) are practically identical to those of pure powdered copper sample, subjected to the shock-wave pressure treatment under the same conditions. Next, $\chi(T)$ of the shock-wave pressure treated pure copper oxide (CuO, Cu_2O) samples did not reveal any anomaly in the experimental temperature range. Thus all the measuring results denote that the phase responsible for the observed anomaly in $\chi(T)$ of the Cu/CuO_x samples is related to the interfacial area, formed between the copper and copper oxide polycrystalline phases, which is unstable at room temperature. In contrast to the ac magnetic susceptibility, the DC magnetic moment of the shock-wave pressure treated Cu/CuO_x samples, measured using a SQUID magnetometer in a standard zero-fieldcooled and field-cooling regimes, revealed no sign of the magnetic anomaly. At temperatures from 5 to 70 K, the samples demonstrated a nearly temperature-independent magnetic susceptibility in fields $H_{\rm ac}$ 30–300 Oe.

4. Discussion

Although the room-temperature exposure of the Cu/CuO_x samples leads to a dramatic decay of the superconducting fraction, no corresponding change has been detected in the X-ray diffraction patterns (figure 1). The fraction of the superconducting phase is therefore too small to be detected by the X-ray diffraction technique. In addition, none of the constituents of the sample, neither metallic Cu nor CuO_x ($x = 1, 2$), taken separately and subjected to the shock-wave pressure treatment under the same conditions, demonstrate any anomaly in $\chi(T)$. We believe therefore that the superconductivity in the shock-wave pressure treated Cu/CuO_x samples is related to the interfacial layer formed between copper oxide and metallic copper phases.

One may reasonably ascribe the superconductivity in the Cu/CuO_x samples to some unknown superconducting copper oxide structure, unstable under the normal conditions and located at the interfacial areas in the Cu/CuO_x sample. For example, we could suppose a two-dimensional CuO lattice which is formed on the surface of CuO in the Cu/CuO interfaces. This lattice, consisting of ions, may form a narrow, partially filled two-dimensional band. In this case, the onset temperature of Bose–Einstein condensation may take a value of $T_c \approx 1000$ K [5]. However, the superconductivity has been discovered for other similar objects based on metals of various groups and their oxides (Mg/MgO [4], Na/NaO_x, and Fe/FeO_x). This indicates the generality of the observed phenomenon, related to the oxygen state at the interface, rather than a unique property of Cu/CuO_x system [5]. Alternatively, consider isolated nanometer-sized metallic clusters which may spontaneously arise in the granular metal-oxide interfacial areas, formed during the shock-wave pressure [4] or the surface oxidation processes [6]. Delocalized electrons of such cluster are expected to form narrow, partially filled energy band at the Fermi level, resulting in a new hypothetical family of high-T_c (>100 K) superconductors. Besides, two-dimensional metal/oxide interfacial areas, formed in the Cu/CuO_x sample, may play a role of asymmetric confining potentials in the system of free electrons, resulting in the lack of spatial inversion symmetry at the interfaces, which may stimulate to a topological change of the Fermi surface, due to the spin–orbit splitting, and lead to the enhanced superconductivity [7].

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