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Low-temperature quenching of HTSC systems ($YBa_2Cu_3O_{7-x}$)

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Effect of low-temperature quenching from 100–200 K to the superconductive transition temperature was studied for polycrystalline $YBa_2Cu_3O_{7-x}$ ($x \leq 0.1$). T_c values were determined using a contactless method based on the magnetic susceptibility changes. The quenching causes an increase in T_c that is relaxed at an isothermal exposure in the region $T_a = T_c + (4\text{ to }5)$ K. Comparison with results of resistive T_c measurements allows to discriminate qualitatively contribution of bulk and surface effects to the superconductive transition process.

Исследовано влияние низкотемпературной закалки от 100–200 K на температуру сверхпроводящего перехода T_c поликристаллов $YBa_2Cu_3O_{7-x}$ ($x \leq 0.1$). Значения T_c определялись бесконтактным методом по изменению магнитной восприимчивости. Закалка приводит к повышению T_c, которое релаксирует при изотермической выдержке в области 4–5 K. Сопоставление с результатами резистивных измерений T_c позволяет качественно разделить вклад объемных и поверхностных эффектов в процесс сверхпроводящего перехода.

First experimental studies of $YBa_2Cu_3O_{7-x}$ properties in a quenched state [1,2] were performed using the fixation of the high-temperature thermodynamical equlibrium state from the ortho-tetra transition temperature region. An increase in electrical resistance of ceramic samples under study and lowering of the superconductive transition temperature (T_c) was observed at the quenching temperature elevation or increasing vacuum exposure time and, respectively, growing oxygen vacancies concentration [3]. Yet, besides of T_c lowering with increasing oxygen index x [1,2], a possibility was demonstrated to realize these processes at an unchanged, reduced, x value, for example, when samples quenched from T_c=440–520° were annealed isothermally at 293 K what resulted in T_c increase [4–6]. Such processes are occurred at a relatively low mobility of oxygen vacancies and appear to be due to formation of various vacancial superstructures in the oxygen subsystem of the lattice; the presence of such superstructures is common for $YBa_2Cu_3O_{7-x}$ [7–10]. It is not clear from data published [1,2 4–6] how fast the temperature of samples under study was changed within 150–250 K region when dropping down to liquid nitrogen one. Numerous experimental studies of kinetic, thermodynamic and other structure-sensitive of $YBa_2Cu_3O_{7-x}$ have shown that, in the temperature region 150–250 K, anomalies are observed [11–14] evidencing the presence of a phase transition. However, structure properties investigations show the presence of the strictly orthorhombic $YBa_2Cu_3O_{7-x}$ structure at $x \leq 0.1$ [15,16].

The presence of hysteresis phenomena at heating and cooling is a specific feature of $YBa_2Cu_3O_{7-x}$ in the anomalies region [16]. But anomalies are manifested also beyond the temperature interval mentioned down to T_c [18].

In our works [19–21], the low-temperature quenching of $YBa_2Cu_3O_{7-x}$ ($x \leq 0.1$) sin-

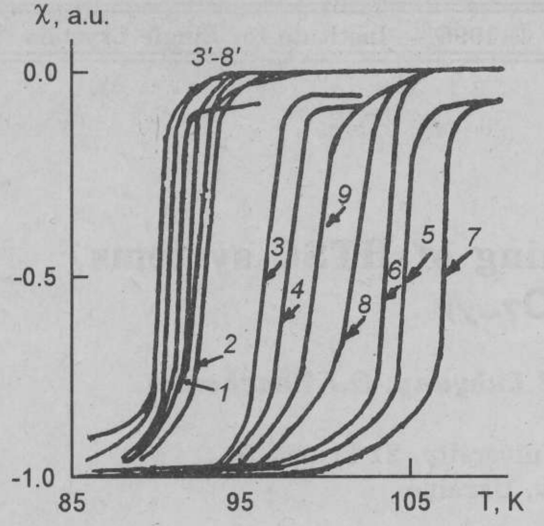

Fig.1. Temperature dependences of the magnetic susceptibility for a $YBa_2Cu_3O_{7-x}$ sample in the superconductive transition region for the initial state (1), after quenching from 95, 100, 110, 120, 130, 140, 150 and 172 K (2–9) and after annealing (3′–8′).

gle crystals and polycrystalline samples from temperature region 100–300 K was experimentally studied. The $YBa_2Cu_3O_{7-x}$ state fixed by a cooling from $T_q \leq T_{an}$ temperature region (T_{an} is the anomaly temperature) differs sharply from that observable in the case $T_q > T_{an}$. For the $T_q \leq T_{an}$ region, the sample electrical resistance in the normal state grows when T_q is elevated while T_c decreases. In the $T_q > T_{an}$ range, an inverse situation takes place, i.e. drop of resistance and growth of T_q. The T_{an} value itself is dependent on the exposure time at the quenching temperature T_q, decreasing when the exposure duration grows. Such a behaviour is typical for states being formed by diffusion and is likely associated with thermal instability of vacancial superstructures (VSS), i.e., a typical process with x=const is realized. At a heating to $T_a \geq 100$ K, the ordered state with a high T_c turns out to be thermally instable. Those experiments allowed to develop a thermoactivation model of VSS instability involving a transition chain from VSS to VSS' [21].

It is to note that in [19,20], T_c was measured by the resistive method using contacts made of a silver conducting paste. In that case, substantial difficulties may arise due to a possible contribution of processes occurring on the surface and grain boundaries, e.g., changes of intergrain contacts caused by gas adsorption [22]. In principle, it is possible to discriminate the volume and surface contributions into low-temperature quenching effects by comparison of T_c values measured using magnetic and resistive methods.

This work is aimed at the study of the low-temperature quenching effect on T_c value of polycrystalline $YBa_2Cu_3O_{7-x}$ samples. T_c measurements were made using the magnetic susceptibility changes. The latter, χ, was measured in alternating magnetic fields ($f \approx 200$ kHz, $H < 0.1$ A·cm^{-1}) using method described in [23]. Plate-shaped samples to be studied were placed between coils of a parallel coupled contour. The sample transition into superconductive state caused a change in the intercoil coupling and, hence, a change in the contour tuning frequency which is proportional to the sample diamagnetic susceptibility. The χ measurement error did not exceed 10%, that of temperature, 0.01 K.

Samples to be studied were prepared according to a standard procedure from Y_2O_3, CuO and $BaCO_3$ powders which were blended and compacted at a room temperature. Then, the tablets were subjected to several stages of thermomechanical treatment including a prolonged annealing in oxygen a atmosphere at 850°C and subsequent grinding at room temperature. On the last stage, rectangular plates of 10×3×0.5 mm^3 size were cut out of tablets to perform the low-temperature quenching experiments. Initial samples state was characterized by lattice parameters at room temperature (a=3.825±0.001; b=3.890±0.002 and c=11.685±0.004 Å) and by T_c value 89–92.4 K that corresponding to $x \leq 0.1$. Experiments were performed on samples with T_c=92.4 K in the isochronic thermocycle mode [19,21] within 100–250 K range. After T_c measurement, samples were heated to the exposure temperature when being above the liquid nitrogen surface, exposed for t=10 min and quenched by immersion in the liquid nitrogen. Then, T_c was measured again repeatedly in the course of slow warming. Then again, the sample was heated to T_a=100–115 K, exposed for 10 min (annealing) and, after cooling, T_c was measured once more to control the constancy of the sample initial state. The next heating cycle was performed to a higher temperature. Exposure time at each temperature was the same (t=const).

Fig.1 shows χ(T) dependences in the superconductive transition region for a sam-

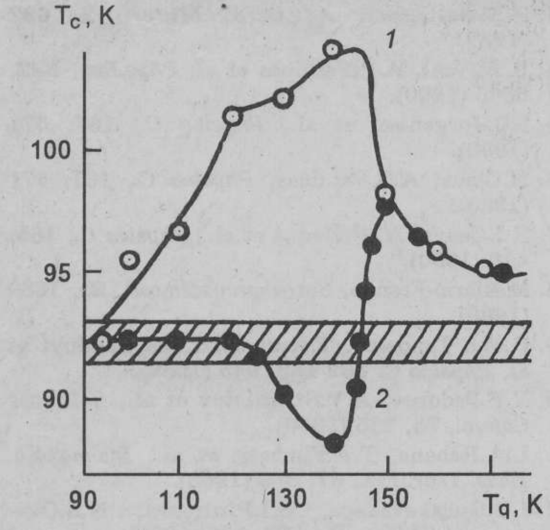

Fig.2. Dependence of the superconductive transition temperature on the quenching one: data of the magnetic susceptibility measurements (1) and resistive studies data (2) [20].

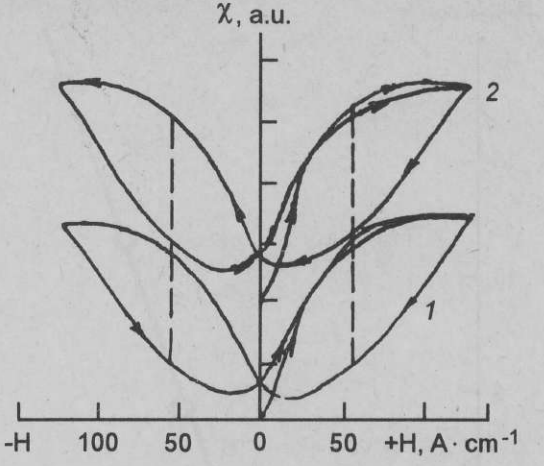

Fig.3. Experimental magnetic susceptibility dependences on the magnetic field strength in the initial state (1) and after the quenching from T_c=140 K.

ple with initial T_c value 92.4 K for several quenching temperatures. Annealing temperatures exceeded T_c values by 4–5 K, annealing duration was always the same. It is well seen that, due to the low-temperature quenching, transition curves do shift towards higher T_c region. After the annealing, curves return to the initial position (curve 1) with some scattering. The initial state T_c values are reproducible within 91.2–93.2 K limits. No appreciable variation of transition curves shape is observed when the quenching temperature grows. The amplitude of the signal drop at the transition changes somewhat (by about 5% with increasing T_c) thus evidencing perhaps a change in the superconducting phase content. Yet no calibration was performed to this end.

The superconductive transition temperature dependence on the quenching one is presented in Fig.2 (curve 1). The hatched region corresponds to the scatter of T_c values in the «initial» state. It is seen that T_c does increase with the quenching temperature and at T_q=140 K attains T_c=107±1 K what exceeds appreciably the resistive experiment results [19,20]. For comparison, the same dependence is presented for the same polycrystal but measured using the resistive method. The heat treatment shedule was identical. Distinctions between the curves are seen first of all in qualitative dependences difference for $T_q<T_q(T_c^{max})$ region. On resistive curves, a T_c drop section arises when the quenching temperature increases. It is naturally to suppose that the observed distinction of curves is due to grain-boundary effects which «block» the T_c growth effect in the case of resistive measurements (curve 2) and disappear quickly (before T_c≈140 K).

In the case of contactless measurements, the effect of T_c increase due to the low-temperature quenching is more pronounced. Accounting for a great penetration depth (λ≈0.5 μm), this fact allows to state that the T_c increasing effects observed in [19–21] are due mainly to bulk processes rather than to surface and grain-boundary ones. Note that a similar conclusion can be made for the case of single-crystalline samples where correlation between resistive and «magnetic» curves is similar to that seen in Fig.2.

Sample magnetization curves at the liquid nitrogen temperature were measured after each thermocycle. In Fig.3, typical magnetization curves are shown for the external magnetic field oscillation within the 0 to 150 A·cm^{-1} interval at a period T_c=8 s. From the magnetization hysteresis loop shape in the superconducting state, variations of the critical current density due to the quenching were determined [24]. In Fig.4, relative change of the critical current density is presented vs. the quenching temperature. The curve is very similar to the $T_c(T_q)$ dependence obtained using the resistive measurement method. First, some J_c drop is observed and then increase corresponding to that of T_c values. A substantial

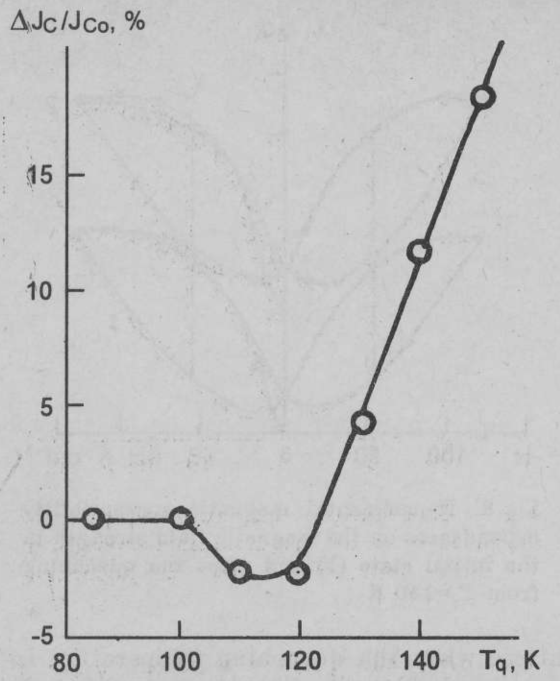

Fig.4. Dependence of relative critical current density increase on the quenching temperature.

fraction of the critical current increment should be related to the temperature «stock» increase due to T_c elevation.

Thus, effects of T_c increase at the low-temperature quenching are associated with microscale diffusion processes occurring mainly in the bulk of samples under study and accompanied by the critical current density increase.

References

1. I.D.Jorgensen et al., *Phys.Rev*, **B36**, 5731 (1987).
2. R.I.Cava, B.Batilog et al., *Phys.Rev*, **36**, 5719 (1987).
3. P.K.Gallagher, *Adv.Ceram.Mater.*, **2**, 632 (1987).
4. B.W.Veal, A.P.Paulicas et al, *Phys.Rev*, **B42**, 6305 (1990).
5. I.D.Jorgensen et al., *Physica C.*, **167**, 571 (1990).
6. H.Claus, A.P.Paulicas, *Physica C.*, **167**, 571 (1990).
7. R.I.Caava, A.W.Hewat et al., *Physica C.*, **165**, 419 (1990).
8. M.Alario-Franko, *Sverkhprovodimost'*, **3b**, 1689 (1990).
9. G.van Tendeloo, T.Krekels, I.van Landuyt et al, *Physica C*, **162-163**, 945 (1989).
10. V.F.Fedorov, A.V.Stratilatov et al., *Sol.State Comm.*, **73**, 225 (1990).
11. L.A.Rebane, T.A.Fimberg et al., *Pis'ma Zh. Eksp. Teor. Fiz.*, **47**, 360 (1988).
12. I.G.Gusakovskaya, S.I.Pirumova, N.S.Ovanesyan, *Zh.Teor.Fiz.*, **60**, 155 (1990).
13. P.P.Pal'-Val', L.I.Pal'-Val' et al., *Sverkhprovodimost'*, **4**, 1542 (1991).
14. A.N.Ozernoi et al, *Sverkhprovodimost'*, **4**, 970 (1991).
15. M.Francois, A.Yunod, K.Yoon et al., *Sol.State Coimmun.*, **66**, 1117 (1988).
16. A.Simon, I.Koehler, H.Bormann et al., *J.Solid State Chem.*, **77**, 200 (1987).
17. M.A.Obolensky, A.V.Bondarenko, V.I.Beletsky et al., *Fiz. Nizk. Temp*, **16**, 1103 (1990).
18. B.Ya.Sukharevsky et al., *Fiz. Nizk. Temp.*, **14**, 1109 (1988).
19. A.A.Mamalui, L.S.Palatnik, P.V.Bilay, *Fiz. Tverd.Tela*, **32**, 2933 (1990).
20. A.A.Mamalui, L.S.Palatnik, *Fiz. Tverd. Tela*, **34**, 2636 (1992).
21. A.A.Mamalui, L.S.Palatnik, K.V.Bednov et al., *Fiz. Nizk. Temp.*, **19**, 1180 (1993).
22. V.M.Koshkin et al., *Sverkhprovodimost'*, **3**, 2722 (1990).
23. L.Z.Lubyany, L.S.Palatnik et al., in: Abstr. of All-Union Semin. on new methods of film obtaining, Kharkov (1991), 41.
24. E.Z.Meylikhov et al., *Sverkhprovodimost'*, **2**, 5 (1989).

Низькотемпературне гартування ВТНП систем ($YBa_2Cu_3O_{7-x}$)

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Досліджено вплив низькотемпературного гартування від 100–200 K на температуру надпровідного переходу T_c полікристалів $YBa_2Cu_3O_{7-x}$ ($x\leq0.1$). Значення T_c визначались безконтактним методом магнітної сприйнятливості. Гартування призводить до підвищення T_c, яке релаксує, якщо ізотермічно витримувати загартований зразок при 4–5 K. Порівняння з результатами резистивних вимірювань T_c дозволяє якісно розділити внесок об'ємних та поверхневих ефектів у процес надпровідного переходу.