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RADIATION EFFECTS IN HIGH-Tc SUPERCONDUCTORS

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1. ABSTRACT

The investigation results of the influence of fast neutron irradiation at liquid nitrogen temperature on the properties of high-Tc superconductors, mainly, YBCO are discussed. It is shown that investigation of the disordering effects favours better understanding of the nature of these compounds.

2. INTRODUCTION

As known the YBCO and LSCO compounds with decreasing oxygen and strontium content show the transition from the superconducting metallic-like state to an antiferromagnetic insulator. The transition to a nonsuperconducting insulator may also occur by introducing impurities into the copper or yttrium (for example, Y is substituted by Pr) sublattice. We investigated the influence of fast neutron irradiation at liquid nitrogen temperature on the properties of HTSC's and found that the radiation-induced disorder results in the nonsuperconducting insulating state in the system$^{1-5)}$. On the basis of the experimental data we may assert that the chemical composition of HTSC's in this case does not change. Hence, the mean number of electrons per atom and, probably, the Fermi energy does not vary also. In this sense radiation disorder is one of the most

pure methods to produce the disordered state in crystals, the properties of which are related to the properties of the ordered state. Hence, investigation of the radiation effects or, in other words, the effects of disorder in HTSC's without variation of the chemical composition is the fruitful method to study these compounds.

3. PROPERTIES OF DISORDERED YBCO CERAMICS

3.1. Crystal Structure of the Irradiated YBCO Samples

According to careful neutron and X-ray powder diffraction studies of the crystal structure of YBCO$^{1,3)}$ irradiated by fast neutrons at 80K, irradiation leads to increase in the lattice parameters, decrease in orthorhombicity, partial oxygen redistribution over O4 and O5 sites (in chains) and to growth of the mean quadratic atomic displacements from the regular lattice sites. The experimental data on neutron diffraction, heat capacity$^{1,3)}$ and Hall effect (see below) allow to assert that the chemical composition of the samples including the oxygen content does not change under the fast neutron irradiation at 80K. Hence, the variation of the physical properties of HTSC's in this case is connected with the disorder itself, i.e. with the appearance of the chaotic potential in a crystal lattice.

3.2. Electrical Resistivity

In all the HTSC's under study (RBCO, R=Y,Ho,Er, LSCO, BSCCO) electrical resistivity ρ varies under disorder in the same way. The linear temperature dependence (TD) of ρ (T) characteristic of the ordered state transforms to the dependence of the type

$$\rho(T) \sim \exp\left[(T^*/T)^{1/4}\right] \quad (1)$$

for fast neutrons of fluence $\Phi > 10^{19}\text{cm}^{-2}$ (note that the concentration of radiation defects D is proportional to Φ). At fixed temperature T_0 (e.g. at irradiation temperature T=80K) electrical resistivity grows exponentially with D [1,3], but not linearly as it may be expected, i.e.

$$\rho(T_0, \Phi) \sim \exp(K\Phi) \qquad (2)$$

where K depends on temperature and the type of compound. The variation of ρ as a function of T and Φ may be described by the empirical formula[2]

$$\rho(T, \Phi) = f(T)\left[K\Phi / T^{1/4}\right] \qquad (3)$$

where f(T) changes smoothly from linear in the ordered state with high-Tc to almost temperature independent when ρ(T) follows eq.(1) and Tc is absent. Note that such a behavior of resistivity under disorder has never been observed earlier.

3.3. Theoretical Interpretation

At high enough disorder ρ (T) of HTSC follows eq.(1) introduced by Mott to describe the hopping conductivity with variable hopping range. It is not clear if the mechanism of Mott conductivity actually realizes in this case. It is likely, however, that in any case the exponential growth of resistivity beginning from the smallest disorder is connected with TD of the resistivity in the presence of defects. The inherent sense of the empirical formula (3) is, probably, connected with this fact. The dielectrization effects are essential even at the smallest extent of disorder so that the ordered HTSC's are close to the metal-insulator transition. Since the structure of the irradiated samples differs from the initial one in the occurrence of the chaotic potential only and in the system with strong two-dimensional anisotropy of conductivity, to which the considered HTSC's belong, the minimal metallic conductivity may reach the value of $\geqslant 10^3(\text{Ohm}\cdot\text{cm})^{-1}$, it is likely that the Anderson type transition takes place in this case. If so, the behavior of electrical resistivity is connected with a decrease in the localization radius R_{loc}. In this case the variation of R_{loc} as a function of fluence (i.e. defect concentration) may be determined by eqs.(2) and (3), and we may explain the degradation of Tc in HTSC under disorder in the framework of the localization theory. The drop of Tc results from the increase in the Coulomb repulsion effects in a single quantum localized state[6]. Hence, R_{loc} turns out to be the only parameter of the theory. The calculation results are in good agreement with the experimental ones [3,5]. In terms of this approach we may conclude that even at the smallest extent of disorder pairing takes place in the system of localized electrons. The decrease in R_{loc} leads to Tc degradation. When R_{loc} becomes comparable with the typical size of the Cooper pair in a highly disordered state, superconductivity is fully suppressed.

4. HALL EFFECT IN DISORDERED $YBa_2Cu_3O_7$ CERAMICS

In $YBa_2Cu_3O_7$ TD of the Hall effect as well as of the electrical resistivity has not yet a satisfactory theoretical explanation. For $YBa_2Cu_3O_x$ with x close to 7 the value of Hall carriers concentration $n_H=(R\ e)^{-1}$ increases linearly with temperature at $100 < T < 700$K. For $x < 7$ the drop in Tc is accompanied by a decrease in n_H, the latter being essentially temperature dependent, however[7]. Here we investigated the Hall effect on the same ceramic samples of $YBa_2Cu_3O_7$ as in Refs.1-5.

Disordering of the YBCO ceramics weakens TD of n_H that remains, however, linear (Fig.1). At low $T \sim 100$K the value of n_H practically does not change. In the oxygen de-

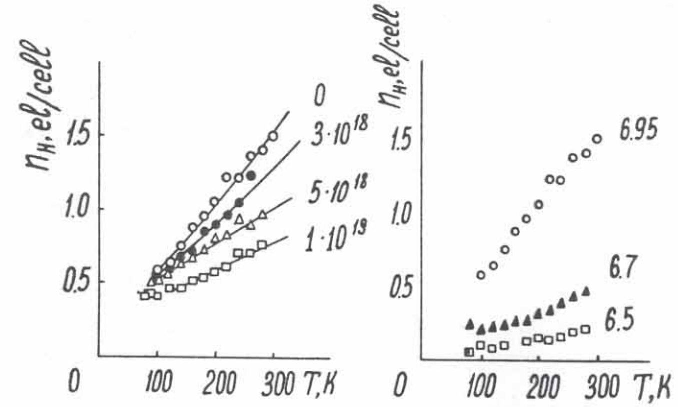

FIGURE 1. Temperature dependence of Hall concentration for the irradiated (left side) and oxygen deficient YBCO samples

ficient samples of YBCO n_H drops several times at the comparable values of Tc both for low and high temperatures (Fig.1). The data from this figure evidence that the radiation disordered samples have different qualitative behavior from that observed with decreasing oxygen content (see above). But at the same time it is seen that there is no unambiguous correlation between Tc and n_H. The results show that it is difficult to explain the variation of n_H and ρ in the disordered samples on the basis of any compensation model since unlike the experimental situation Hall effect in these models is more sensitive to alteration of compensation than ρ . In LSCO $n_H(T)$, slightly dependent on temperature in the ordered state, also does not change under disorder. The constancy of n_H for low T under disorder agrees with the above assumption concerning the localization of carriers$^{8)}$. But it is difficult to explain variation of TD of n_H under disorder. Still more surprising is the similarity of $n_H(T)$ and f (T) (Fig.2). We believe that these results are additional evidences for the fact that TD of electrical resistivity in the ordered state of HTSC's is not connected with scattering on the correspondent quasi-particles, i.e. with TD of the free path of carriers, but reflects some important features of the electronic properties of oxide superconductors.

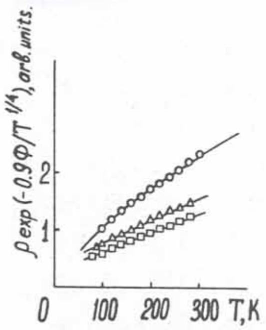

FIGURE 2. Temperature dependence of f (T) from eq.(3) for YBCO before (○) and after irradiation by fast neutrons of fluence 5 (△) and $10\text{x}10^{18}\text{cm}^{-2}$ (□).

5. ANISOTROPY OF ELECTRICAL RESISTIVITY AND UPPER CRITICAL FIELD H_{c2}

We investigated a series of the $YBa_2Cu_3O_{7-\delta}$ single crystals with the sizes by order of $1\text{x}1\text{x}0.03\text{mm}^3$ grown by crystallization from melt. The parameters of these single crystals are given in Table 1. The resistivities were measured by Montgomery method$^{9)}$.

Electrical resistivities ρ_{ab} (along the ab-plane) and ρ_c (along the c-axis) for single crystal 1 were measured at 80K directly during irradiation by fast neutrons at liquid nitrogen temperature (Fig.3). ρ_{ab} increases exponentially with Φ (i.e. defect concentration) starting from the smallest D while ρ_c grows slower and only for $\Phi > 10^{19}\text{cm}^{-2}$ they grow with the same rate. Hence anisotropy ρ_c/ρ_{ab} at 80K drops rapidly (to the value of ~30 for $\Phi = 10^{19}\text{cm}^{-2}$) and then practically does not change, so that some "residual" anisotropy exists in all the cases. In the temperature range 300K ρ_{ab} and ρ_c as functions

TABLE 1. The parameters of the $YBa_2Cu_3O_7$ single crystals before and after irradiation by fast neutrons at 80K

N	Φ $10^{18}cm^{-2}$	Tc K	ρ_{ab}(100K) mΩ·cm	ρ_c(100K) mΩ·cm	ρ_c/ρ_{ab} T=100K	ρ_c/ρ_{ab} T=300K
1	0	92	0.260	57.4	220	40
	18		1200	32200	27	
2	0	90.7	0.041	11.5	280	147
	2	77.9	0.097	20.5	212	140
3	0	91.9	0.113	15.4	137	32.6
	3	59.3	0.690	48.5	60	28
4	0	91.5	0.043	15.0	350	135
	4	43	0.324	62.5	192	
5	0	92.2	0.057	9.0	158	60
	5	9.0	0.880	71	81	48
6	0	92	0.075	15.8	212	87
	6	7.1	1.16	133.5	116	
7	0	91	0.132	35.3	268	71
	7		11.05	770	80	60

of D change with the same rate. The temperature dependence of anisotropy weakens in the disordered samples (Fig.4). Moreover, this weakening is intensified with increasing disorder. From a comparison of these results with those obtained earlier on the ceramic samples we may conclude that the exponential growth of electrical resistivity characteristic of ceramics takes place for the single crystals in the direction of the Cu-O layers and it is likely to be the inherent property of HTSC.

The upper critical fields of the YBCO single crystals were measured before and after irradiation in the fields up to 5T. TD of H_{c2} in the disordered samples is essentially nonlinear in these fields, especially for the samples with low Tc (Fig.5). According to the high-field regions on the H_{c2} vs. T curves the temperature derivative of the upper critical field $(H_{c2}^{\perp})'$ (along the c-axis) increases with disorder. To obtain the unambiguous results it is necessary to perform the measurements in high fields.

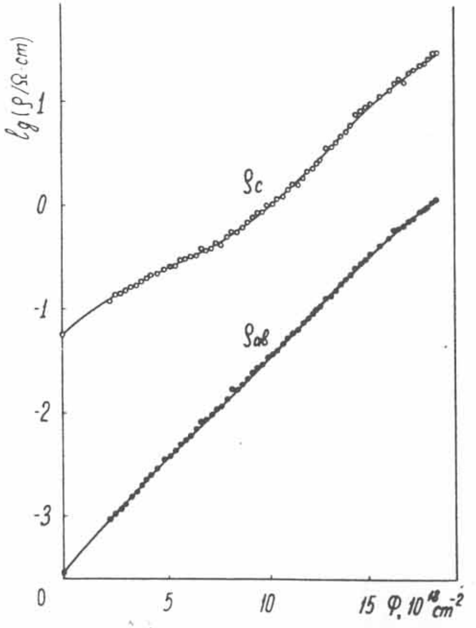

FIGURE 3. ρ_{ab} and ρ_c at 80K vs. fluence of fast neutrons for single crystal 1 obtained directly during irradiation.

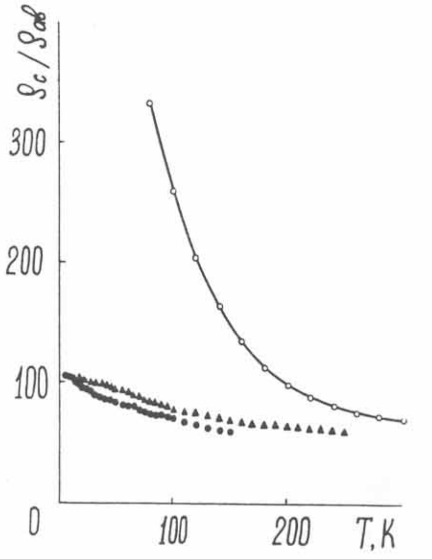

FIGURE 4. Anisotropy ρ_c/ρ_{ab} vs. T for single crystal 7 before(○) and after irradiation by $\Phi = 7x10^{18}$ cm^{-2}(●) and after heating to 300K (▲).

$(H_{c2}^{\parallel})'$ (along the ab-plane) drops in the beginning and then does not change or increases slightly. However, it is clear that the anisotropy of H_{c2} decreases for any field and in the samples with Tc ~10K the ratio $(H_{c2}^{\parallel})'/(H_{c2}^{\perp})'$ is close to unity.

Hence, we see that disorder weakens anisotropy of H_{c2} and of electrical resistivity at low temperatures, but the former disappears at the essential "residual" anisotropy of ρ .

6. NQR AND SPIN-LATTICE RELAXATION OF ^{63}Cu IN DISORDERED YBCO CERAMICS

We investigated the ^{63}Cu NQR in the disordered cera -

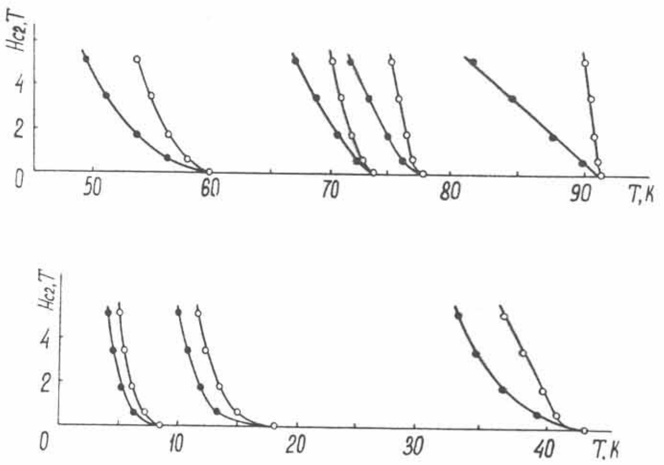

FIGURE 5. $H^{\parallel}_{c2}$(o) and $H^{\perp}_{c2}$(●) vs. temperature for the $YBa_2Cu_3O_{7-\delta}$ single crystals with different disorder.

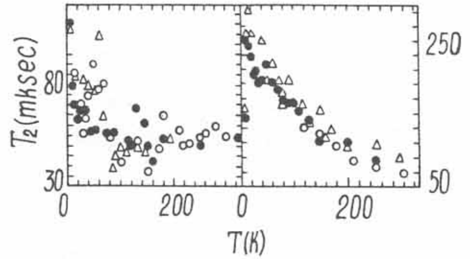

FIGURE 6. Spin-spin relaxation time T_2 for ^{63}Cu in Cu2 (31.4 MHz)(left side) and Cu1 (22.0 MHz) sites for $YBa_2Cu_3O_{6.95}$ before (o) and after irradiation by a fluence of 5(Δ) and 7x10^{18}cm^{-2}(●).

mics $YBa_2Cu_3O_{6.95}$ at the frequencies ν =22.0 MHz and ν =31.4 MHz corresponding to Cu1 and Cu2 sites, respectively. The spin-spin relaxation time T_2 vs. T in Cu1 sites grows monotonously and tends to the dipole limit irrespective of disorder (Fig.6). In the normal state in Cu2 sites T_2 does not depend on temperature at any disorder up to a fluence of 10^{19}cm^{-2}(Fig.6). The spin-lattice relaxation rate T_1^{-1} in Cu2 sites at T > 100K in the disordered samples decreases as compared to the initial one and its temperature dependence is weakened (Fig.7). Below 100K in the normal state the kink in the T_1^{-1} vs. T curves is observed and $T_1^{-1} \sim T^{\alpha}$ (α =1.5 ± 0.3). The superconducting transition is accompanied by sharp decrease in T_1^{-1} which may be described now as $T_1^{-1} \sim T^{\beta}$ (β = 6 ± 1.5)(Fig.7). Similar behavior of T_1^{-1} was observed in YBCO doped with Zn10). For 4.2K T_1^{-1} is proportional to the Curie constant in our samples. This implies that the interaction of the nuclear magnetic moments with the paramagnetic centers in the defect sites is the main relaxation mechanism at low temperatures. (Note that irradiation leads to the appearance of the Curie-Weiss contribution to the magnetic susceptibility with the Curie constant proportional to defect concentration). At ϕ =2x10^{19}cm^{-2} the value of the localized magnetic moment (LMM) reaches the quantity 0.66μ_B per Cu

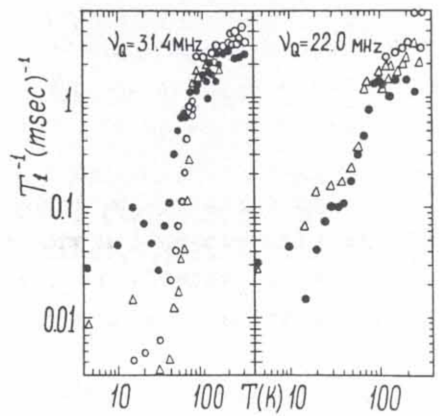

FIGURE 7. Spin-lattice relaxation rate T_1^{-1} vs. temperature for ^{63}Cu in Cu2 site (31.4 MHz)(left side) and Cu1 (22.0 MHz) sites for $YBa_2Cu_3O_{6.95}$ before (o) and after irradiation by a fluence of 5(Δ) and 7x10^{18}cm^{-2}(●).

atom that corresponds to the mean distance between LMM of order of the lattice parameters. Under these conditions one may expect a decrease of T_2. In fact, the line at 31 MHz becomes practically undetectable for $\phi = 2 \times 10^{19} cm^{-2}$ pointing to the preferential occurrence of the LMM in Cu2 sites. Irrespective of disorder the behavior of the spin-lattice T_1 and spin-spin T_2 relaxation times up to a fluence of $10^{19} cm^{-2}$ is connected, probably, with small correlation length of the Fermi-liquid exchange fluctuations. Around the defect centers these fluctuations are likely to be broken. This leads to the appearance of LMM forming a kind of another magnetic subsystem. At sufficient disorder the appearance of a spin-glass state in the system of LMM for low temperatures may be expected. At 4.2K we failed to find the correspondent NMR signal in the local field within the frequency range 80-100 MHz although TD of magnetic susceptibility in this sample ($\phi = 2 \times 10^{19} cm^{-2}$) deviates from the Curie law at $T < 10K$.

7. CONCLUSION

The experimental results suggest that:

- even the ordered HTSC's are close to the metal-insulator transition and are likely to be on the insulator side of this transition;
- disordering is likely to distort the quasi-two-dimensional character of the electron motion which is essential in the ordered state, especially at low temperatures;
- disorder leads to a variation of a magnetic state in YBCO.

Of course, further investigations are required. Nevertheless, we see that the radiation-induced disorder affects a lot of important aspects of the physics of superconducting oxides. We hope that these investigations will be useful.

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