Localization effects in atomically disordered high-temperature superconductors

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We have investigated the structure (using neutron and x-ray methods), the superconducting transition temperature T_c, the upper critical field H_{c2}, the electrical resistance $\rho(T)$, the magnetic susceptibility $\chi(T)$ and the NMR response of the oxide ceramics $RBa_2Cu_3O_{7-\delta}$ (R = Y, Er, Ho), $La_{1.83}Sr_{0.17}CuO_{4-y}$, Bi–Sr–Ca–Cu–O and single-crystal $YBa_2Cu_3O_{7-\delta}$ all of which were irradiated by fast neutrons at liquid-nitrogen temperatures. The results we obtained [exponential growth of $\rho(T)$ under radiation-induced disordering, etc.] show that even for small degrees of disorder there exist localized states in these systems. The localization causes T_c to decrease, until the superconductivity is entirely suppressed in the region of strong localization. A theoretical interpretation of the experimentally observed effects is given. For comparison, we present the results of our investigations of the oxygen-deficient compounds $YBa_2Cu_3O_x$ ($x = 6.0$ to 6.95) using the same methods.

1. INTRODUCTION

Widespread experimental study of the new high-temperature superconductors (HTS), which began after their discovery in 1986 (Ref. 1), has brought to light important experimental facts which characterize the superconductivity of these oxide compounds. One of the well-worked-out methods of probing ordered compounds to obtain unambiguous information on their properties is irradiation by fast neutrons. This method makes it possible to introduce defects in precise amounts and in a highly reproducible way, without changing the compound's stoichiometry; the defects are distributed in a macroscopically uniform way throughout the sample volume, allowing the behavior of T_c and of other properties to be studied in the presence of disorder.

It is well known[1] that decreasing the mean free path l of electrons by increasing the defect concentration does not change the value of T_c so long as (1) there is no important modification of the "band" parameters of the electron and phonon subsystems (i.e., the electronic density of states at the Fermi level $N(E_F)$ and the average phonon frequency $\langle\omega\rangle$, and (2) an Anderson-type metal–insulator transition, which could lead to localization of the electrons, does not occur.

Case (1) is encountered in narrow-band intermetallics, among which the best-studied are the compounds with the A-15 structure. Irradiation of these materials by fast neutrons and other high-energy particles[3] can lead either to a decrease (Nb_3Sn, V_3Si, etc.) or an increase (Mo_3Si, Mo_3Ge) of the superconducting transition temperature T_c. This variation of T_c can be explained by changes in parameters such as $N(E_F)\langle\omega\rangle$ due to significant restructuring of the crystal at large defect concentrations. The behavior of the electrical resistance $\rho(T)$ in this case is characteristic of metals: for small fluences of fast neutrons Φ there is an increase in the residual resistivity $\rho(0)$ which is proportional to the defect concentration, i.e., $c_{\text{def}} \sim \Phi$, while for high fluences $\rho(0)$ saturates at values on the order of 150–300 $\mu\Omega\cdot$cm. The derivative $d\rho/dT$ increases as $\rho(0)$ increases (and as the temperature increases for compounds with strong electron-phonon coupling, such as Nb_3Sn and V_3Si), so that for high defect concentrations, when l is close to the inter-atomic spacing, ρ is practically independent of temperature.

Case (2) is encountered in the HTS. The disorder induced by neutron irradiation increases T_c and leads to a qualitatively different variation of the electrical resistivity: the linear dependence of ρ on T is converted to an exponential dependence $\rho(T) \propto \exp(Q/T^{1/4})$, which is characteristic of hopping conductivity between localized states.[4] We note that the electrical resistivity of the unirradiated (ordered) HTS has an unusual temperature dependence. Over a wide interval of temperatures [from 40 to 1000 K for $(La–Sr)_2CuO_4$, see Ref. 5] we find $\rho(T) \propto T$ for all the oxide compounds in this class. The large values of $\rho(T) \approx 0.3$ to 3 m$\Omega\cdot$cm, which correspond to minimum Mott conductivities $\sigma \approx 3\cdot 10^2$ $(\Omega\cdot\text{cm})^{-1}$, imply that for these materials the mean free path is close to the interatomic spacing. In this case, the fact that $\rho(T)$ does not saturate at high T invalidates any explanation of the linear dependence in terms of electron scattering by some appropriate quasiparticles (e.g., phonons) whose number increases linearly with T. This means that the conductivity mechanism in HTS is still obscure, and requires more detailed study.

The first investigations of HTS irradiated by fast neutrons showed[4,6] that disorder causes changes in their properties which are correlated in ways never observed previously in experiment. However, we have found that at least some of these changes are subject to satisfactory interpretation within the framework of the theory of electron localization in strongly-disordered systems. For this reason, detailed investigations are of interest both from the experimental and theoretical points of view.

In this article, we present results of our investigations of T_c, crystal structure, electrical resistivity $\rho(T)$, the derivative of the upper critical field $(dH_{c2}/dT)_{T=T_c} \equiv H'_{c2}$, the magnetic susceptibility $\chi(T)$, and NMR response of the compounds $RBa_2Cu_3O_7$ (R = Y, Er, Ho), $La_{1.83}Sr_{0.17}CuO_4$, and Bi–Sr–Ca–Cu–O after irrdiation by fast neutrons, along with a theoretical interpretation of the effects observed. In order to eliminate possible "thermochemical" effects connected with diffusion of oxygen (for $RBa_2Cu_3O_7$ these effects are usually observable at tempera-

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tures only slightly greater than room temperature), the irradiation was carried out at liquid-nitrogen temperatures.

2. EXPERIMENTAL METHODS

The samples of $RBa_2Cu_3O_7$ were obtained via ceramic technology from the oxides R_2O_3, CuO and barium carbonate.[7] The samples were single-phase according to x-ray analysis; our studies of the AC susceptibility χ_{AC} showed sharp superconducting transitions with complete screening of the volume by the supercurrents. The width of the superconducting transition as determined from χ_{AC} and the jump in the specific heat, amounted to $\Delta T_c \lesssim 4$ K. The Bi–Sr–Ca–Cu–O samples which were prepared using the technology described in Ref. 8 contain insignificant (no more than 5%) quantities of CuO, and had $T_c(\rho = 0) = 72$ K, $\Delta T_c \approx 10$ K, $\rho_{120\text{ K}} = 0.95 \cdot 10^{-3}\ \Omega \cdot$cm, and $\rho_{300\text{ K}}/\rho_{100\text{ K}} = 1.8$.

It is well known that the properties of the compounds $RBa_2Cu_3O_{7-\delta}$ are sensitive to oxygen content. Therefore, in investigating the effects of radiation-induced disorder, we must first of all clarify what changes are induced in the oxygen sublattice by irradiation. To this end, we investigated the structures of both irradiated and oxygen-deficient $RBa_2Cu_3O_{7-\delta}$. Samples of the latter were prepared using a special equilibrium method, which differed from quenching in that while the temperature was slowly lowered the oxygen pressure was lowered along with it in such a way that the thermodynamic equilibrium conditions appropriate for each composition with the given oxygen content were preserved at all times. Detailed results of studies of the oxygen stoichiometry in $YBa_2Cu_3O_{7-\delta}$ were published in Ref. 9.

Structural investigations were carried out at room temperature using x-ray diffraction ($\lambda = 1.79$ Å) and neutron diffraction ($\lambda = 1.52$ Å with a spread $\Delta d/d \approx 0.3\%$). In order to determine the crystal structure more precisely, the diffraction data were processed with a semiquantitative analysis technique based on the Rietveld method[10] in which the intensities of 153–194 reflections were used. In these calculations the lattice parameter values were refined, as were the atomic coordinates, the Debye–Waller factor in the isotropic approximation, and the occupancy of the crystallographic positions. The lattice parameters obtained by neutron and x-ray diffraction studies coincided to within 0.002 Å. Measurements of the electrical resistivity were carried out using the standard four-probe method at constant current. The temperature was recorded using a germanium resistance thermometer whose error was less than 0.05 K in the interval $1.5 < T < 20$ K. Above 20 K the temperature was recorded with a platinum thermometer to an accuracy of 0.05 K. The magnetic susceptibility was measured by the Faraday method in the interval of temperatures from 4.2 K to 300 K in a field of 0.6 Tesla. The NMR methods were described in Refs. 11 and 12.

Irradiation by fast neutrons ($E \gtrsim 1$ MeV) was carried out at liquid nitrogen temperatures with fluences from $2 \cdot 10^{18}$ to $5 \cdot 10^{19}$ cm^{-2}.

3. EXPERIMENTAL RESULTS

(a) Superconducting Properties

When the HTS [$La_{1.83}Sr_{0.17}CuO_4$, $RBa_2Cu_3O_{6.95}$ (R = Y, Er, Ho), and Bi–Sr–Ca–Cu–O] are irradiated, their superconducting transition temperatures T_c fall more rapidly than those of previously studied compounds (e.g., The A-15 and Chevrel compounds).[3,13] For example, irradiation at a fluence of $1.2 \cdot 10^{19}$ cm^{-2} causes a drop in the T_c of Nb_3Sn of $\approx 25\%$, in $SnMo_6S_8$ of 70%, while in $RBa_2Cu_3O_{6.95}$ and Bi–Sr–Ca–Cu–O the superconductivity disappears.

The dependence of T_c on $\rho_{\Phi}^{100\text{ K}}/\rho_{\text{unirr}}^{100\text{ K}}$, which is a quantity which characterizes the relative disorder of the system, is close to linear according to the data in Table I; this result coincides with the results obtained in Ref. 14. In all the compounds listed, introduction of defects leads to strong broadening of the superconducting transition temperatures (Figs. 1,2). According to the AC susceptibility data, for $\Phi \lesssim 7 \cdot 10^{12}$ cm^{-2} samples of $RBa_2Cu_3O_{6.95}$ annealed at 300 K show complete screening of the volume by supercurrents. In a sample irradiated with a fluence of 10^{19} cm^{-2}, the screening amounts to only $\sim 20\%$ of the volume, although according to electrical resistivity measurements we are still seeing the full superconducting transition. The magnitude of T_c in irradiated samples partially recovers after annealing at temperatures 200 K and 300 K in the course of 20 min. A week's annealing at room temperature leads to further recovery of T_c and to narrowing of the width of the superconducting transition (Figs. 1,2).

After irradiation with a fluence of $7 \cdot 10^{18}$ cm^{-2} superconductivity is no longer observed down to 1.7 K in the compounds $HoBa_2Cu_3O_{6.95}$, $ErBa_2Cu_3O_{6.95}$, and Bi–Sr–Ca–Cu–O while the temperature dependence of $\rho(T)$ points to localization of the conduction electrons. After annealing at 300 K, a superconducting transition again appears in these compounds (Fig. 2 for Bi–Sr–Ca–Cu–O); however, the nonmetallic character of $\rho(T)$ is preserved (i.e., $d\rho/dT < 0$).

In the compounds $La_{1.83}Sr_{0.17}CuO_4$ and $YBa_2Cu_3O_{6.95}$, the magnitude of the derivative of the upper critical field H'_{c2}, measured at the midpoint of the superconducting transition is correlated to the limit of experimental indeterminacy with the large broadening of the superconducting transition, which does not change as $\rho_{100\text{ K}}$ grows by an order of magnitude. We note that in metallic disordered compounds the increase in electrical resistivity must lead to growth in H'_{c2}, which was observed previously in irradiated A-15 compounds (Ref. 3) and Chevrel phases (Ref. 13).

(b) Structure of Disordered Samples

Basic information about radiation-induced structural changes in the compound $YBa_2Cu_3O_{6.95}$ (this was the composition of unirradiated samples) is obtained from neutron-diffraction studies. In order to calculate the structural parameters, we used the unit-cell model proposed in Ref. 15 (i.e., the space group P^{mmm}). Difference patterns taken between the experimental and calculated profiles of the neutron diffraction pictures of all the samples studied showed good agreement (the goodness-of-fit factor satisfied $R \lesssim 5\%$) and additional peaks did not appear. This indicates that the samples were of single phase both before and after irradiation. The refined structural parameters for samples with various degrees of disorder are shown in Table I. For comparison, we present in Table II the analogous structural information for oxygen-deficient samples of $YBa_2Cu_3O_{7-\delta}$ (Ref. 9). We note that in the latter the width of the reflections does not change with δ, which indicates the absence of impurities of the isostructural phases with close values of the

TABLE I. Parameters of $YBa_2Cu_3O_{7-\delta}$ samples before and after irradiation.

Φ, 10^{18} cm^{-2}	t	a, Å	b, Å	c, Å	$N(O(4))$	$N(O(5))$	B_{D-W}	$7-\delta$	$b-a$, Å	R	T_c^ρ, K
		according to neutron-diffraction data									
0	–	3.823	3.884	11.670	0.90±0.05	0	0.59	6.90±0.05	0.060	3.41	93
2	2 hours	–	–	–	–	–	–	–	–	–	83
2	2 weeks	3.826	3.886	11.695	0.69	0.08	0.77	6.77	0.060	2.82	84
5	2 hours	–	–	–	–	–	–	–	–	–	66
5	2 weeks	3.828	3.887	11.696	0.73	0.08	0.99	6.81	0.059	4.05	71
7	2 hours	–	–	–	–	–	–	–	–	–	51
7	2 weeks	3.837	3.894	11.705	–	–	–	–	0.057	–	60
10	2 hours	–	–	–	–	–	–	–	–	–	20
10	2 weeks	3.843	3.898	11.717	–	–	–	–	0.054	–	35
20	2 hours	–	–	–	–	–	–	–	–	–	–
20	2 weeks	3.844	3.893	11.724	0.62	0.16	1.1	6.78	0.049	4.00	–

Note: B_{D-W} is the generalized Debye-Waller factor, including static shifts of the atoms, R is a goodness-of-fit factor, $N(O(I)$ sitions, t is the anneal time at 300 K.

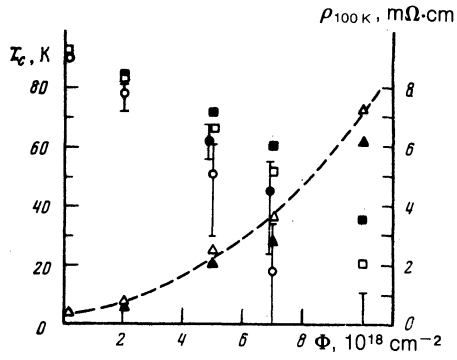

FIG. 1. Dependence of the superconducting transition temperature on fast neutron fluence for the compound $YBa_2Cu_3O_{6.95}$, as determined from measurement of the electrical resistance (T_c^ρ) and AC susceptibility (T_c^χ) (left hand scale), and from measurement of the electrical resistivity $\rho_{100\,K}$ at $T = 100$ K (right-hand scale); ○, ● show T_c^χ after irradiation at 80 K and after annealing at 300 K for two weeks, respectively; the vertical error bars show the transition widths; □, ■ show T_c^ρ after annealing at 300 K for two hours and two weeks, respectively; △, ▲ show $\rho_{100\,K}$ after annealing at 300 K for two hours and two weeks, respectively.

crystallographic parameters (i.e., with different values of δ). This implies that in samples with decreased oxygen content prepared using equilibrium technology, the oxygen is quite uniformly distributed throughout the volume. From Table I it is clear that the oxygen content in irradiated samples is practically unchanged. Although the total occupation of the oxygen positions O(4) and O(5) is easily decreased (from $x = 6.95 \pm 0.05$ in unirradiated samples to $x = 6.78 \pm 0.05$ at $\Phi = 2 \cdot 10^{19}$ cm^{-2}), weighing the samples before and after irradiation shows that the mass of the sample decreases by at most 0.15% (most likely because of mechanical damage). This corresponds to a decrease of δ of less than 0.01. Measurement of the heat capacity of the irradiated samples[4] and comparison with the data on the heat capacity of oxygen-deficient samples[9] confirms that irradiation does not lead to any important decrease in $x = 7 - \delta$. Therefore, the degradation of T_c caused by radiation is not a result of decreasing the concentration of oxygen in the sample.

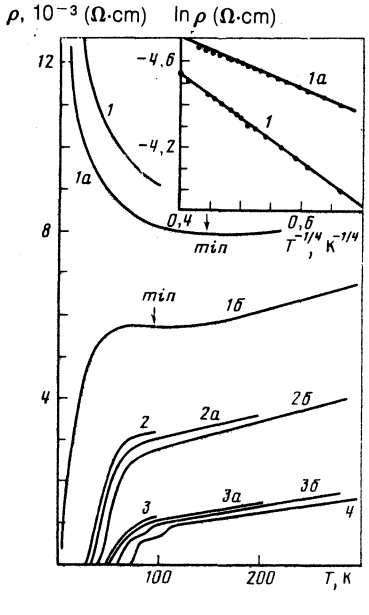

FIG. 2. Temperature dependence of the electrical resistivity ρ for the compound Bi–Sr–Ca–Cu–O irradiated by fast neutrons with fluences $\Phi = 7 \cdot 10^{18}$ cm^{-2} (1), $\Phi = 3 \cdot 10^{18}$ cm^{-2} (2), $\Phi = 2 \cdot 10^{18}$ cm^{-2} (3), $\Phi = 0$ (4). The subscripts *a*, *b* correspond to annealing at $T = 200$ K and $T = 300$ K for 20 min.

Furthermore, it follows from the data presented in Tables I and II that the falloff of T_c in these cases is accompanied by various changes of the crystal structure. As x decreases the lattice parameter c grows linearly while the degree of orthorhombicity (i.e., the value of the parameter difference $b - a$) decreases, and for $x \approx 6.2$ the structure becomes tetragonal. By studying the dependence of T_c both on x (this was already observed in Refs. 16, 17) and on $b - a$ (both dependences have a similar form) we can identify intervals of x-values ($6.4 < x < 6.8$) and ($b - a$)-values ($0.04 < b - a < 0.055$ Å), within which T_c varies more slowly than it does outside of them. The superconductivity disappears for $x \approx 6.3$, i.e., near the transition to the tetragonal structure. Under irradiation the superconductivity is entirely suppressed in samples with significant orthorhombicity $b - a \approx 0.05$ Å. The falloff of T_c, therefore, is not connected with the orthogonal-tetragonal conversion *per se*. In both cases we investigated the oxygen vacancy concentration in the Cu(1)–O plane is also different. In radiation-disordered samples the oxygen atoms are partially redistributed between the positions O(4) and O(5) (this probably also leads to the decrease in $b - a$). In oxygen-deficient samples the occupation of the O(4) positions decreases, but the O(5) positions are very weakly filled; furthermore, this filling only occurs just before the transformation to the tetragonal structure when the superconductivity is already gone. Naturally, in the tetragonal phase the equivalent positions O(4) and O(5) are filled with equal probability.

Radiation-induced disorder leads to a significant increase in the generalized Debye–Waller factor, which takes into account the static and dynamic atomic shifts (Table I). As the oxygen content decreases, the Debye–Waller factor increases by a small amount (Table II).

Thus, the structural investigations show that in $YBa_2Cu_3O_{6.95}$ there occurs a partial rearrangement of the oxygen atoms between positions O(4) and O(5) as radiation-induced defects are introduced; in addition, the Debye–Waller factor grows and the lattice parameters *a*, *b*, and *c* increases (Table I). It is very likely that because of the significant atomic shifts (static plus dynamic) from their "regular" positions a random potential arises in the lattice which also determines the other changes in the physical properties of HTS induced by disorder which will be discussed below.

(c) Electrical Resistivity

In Figs. 2 and 3 we show the temperature dependences of the electrical resistivity $\rho(T)$ of the compounds Bi–Sr–Ca–Cu–O, $YBa_2Cu_3O_{6.95}$, and $La_{1.83}Sr_{0.17}CuO_4$, which were irradiated by fast neutrons at 80 K and annealed at various temperatures. In all these materials the $\rho(T)$ curves for ordered compounds vary in the same way. For small fluences $\Phi < 5 \cdot 10^{18}$ cm^{-2}, the linear dependence of $\rho(T)$ is preserved for $T > T_c$, while the value of $d\rho/dT$ increases by approximately 30%. In the range of fluences $(5–10) \cdot 10^{18}$ cm^{-2}, portions with $d\rho/dT > 0$ (high temperatures) and with $d\rho/dT < 0$ (low temperatures) are simultaneously present on the $\rho(T)$ curves. For $\Phi > 1 \cdot 10^{19}$ cm^{-2}, $\rho(T)$ fol-

TABLE II. Parameters of $YBa_2Cu_3O_{7-\delta}$ samples with various oxygen contents.

$7-\delta$	a, Å	b, Å	c, Å	$N(O(4))$	$N(O(5))$	B_{D-W}	R	T_c^{ρ}, K	T_c^{χ}, K	$\rho_{100\,K}$, mΩ·cm
6.90±0.05	3.823	3.884	11.670	0.90±0.05	0	0.59	3.41	93	91	0.40
6.69	3.825	3.884	11.707	0.67	0.02	0.66	3.94	71	64.5	0.73
6.56	3.828	3.881	11.709	0.53	0.03	0.71	5.1	60	59	0.95
6.44	3.837	3.878	11.741	–	–	–	–	52	48.5	1.58
6.36	3.840	3.876	11.747	0.34	0.02	0.72	5.00	37.5	34.5	3.03
6.23	3.850	3.872	11.787	0.17	0.06	0.68	4.47	–	–	19.3
6.15	3.859	3.859	11.809	0.075	0.075	0.70	4.3	–	–	70
6.1±0.05	3.859	3.859	11.816	0.05	0.05	0.70	4.55	–	–	–
6.0±0.05	3.863	3.863	11.831	0	0	0.55	7.01	–	–	–

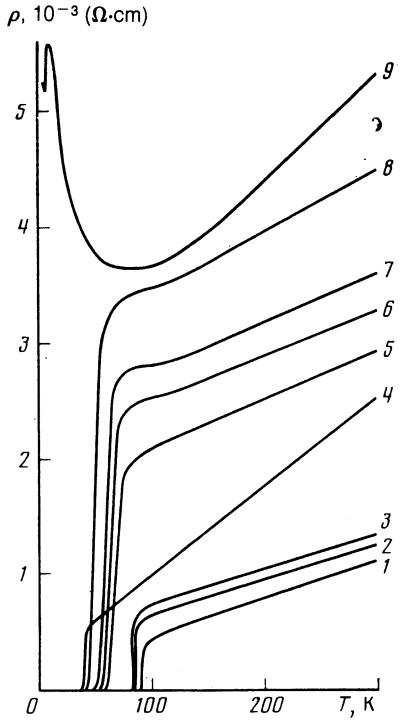

FIG. 3. Temperature dependence of ρ for samples of YBaCuO (curves 1–3 and 5–8) and LaSrCuO (curves 4, 9) irradiated by fast neutrons: 1—$\Phi = 0$; 3, 6, 8—irradiated at 80 K with fluences of $\Phi = 2.5$ and $7 \cdot 10^{18}$ cm^{-2} plus annealing for 2 hours at 300 K; 2, 5, 7—irradiated with $\Phi = 2.5$ and $7 \cdot 10^{18}$ cm^{-2} plus annealing for 2 weeks at 300 K; 4—$\Phi = 0$; 9—irradiated with $\Phi = 5 \cdot 10^{18}$ cm^{-2} plus annealing for 2 hours at 300 K.

lows a dependence which is characteristic of the conductivity via localized states:

$$\rho(T) = a \exp(Q/T^{1/4}),$$
$$Q = 2.1[N(E_F) R_{loc}^3]^{-1/4}. \quad (1)$$

In the fluence range $\Phi > 1 \cdot 10^{19}$ cm^{-2} (where superconductivity is absent), $\rho(T)$ is well described by the dependence (1) over a wide interval of temperatures 2–300 K (Figs. 2,4).

The radiation-induced defects which appear in HTS after irradiation by fast neutrons at $T = 80$ K are relatively unstable: isochronic annealing over the course of 20 min at $T = 200$ K and 300 K leads to a partial recovery of T_c (Figs. 2–4). For longer annealing at room temperature (two weeks) there is a further recovery of T_c and other properties.

In Table I we present the parameters of $YBa_2Cu_3O_{7-\delta}$ for various defect levels. We note that the increase in $\rho(T)$ with fluence at fixed temperature [for example, $\rho(100)$] is superlinear, even in the range of small fluences $\Phi < 7 \cdot 10^{18}$ cm^{-2} (in superconducting samples). A more obviously nonlinear increase (exponential, to be exact) of $\rho_{80\ K}$ with increasing fluence Φ is visible in Fig. 5, in which we show the dependence of ρ on Φ obtained from measurements made in the actual process of irradiation on the compounds La_2CuO_4, $La_{1.83}Sr_{0.17}CuO_4$, $YBa_2Cu_3O_{6.95}$, and Bi–Sr–Ca–Cu–O, along with similar measurements on single-crystal samples of $YBa_2Cu_3O_{7-\delta}$ ($T_c \approx 80$ K; the measurements of $\rho(T)$ were done in a direction perpendicular to the c axis). We also show here the analogous dependence for the compound $SnMo_6S_8$, whose electrical resistivity ρ is proportional to fluence for small Φ and saturates for large Φ. The exponential growth of ρ with increasing Φ (or defect concentration) in all the HTS can be related to localization effects, which already appear for very small degrees of disorder in samples having relatively high T_c. In the cases where T_c is reduced or completely driven to zero (Figs. 2,3), the localization can still be observed directly through the characteristic temperature dependence of the electrical resistivity (1).

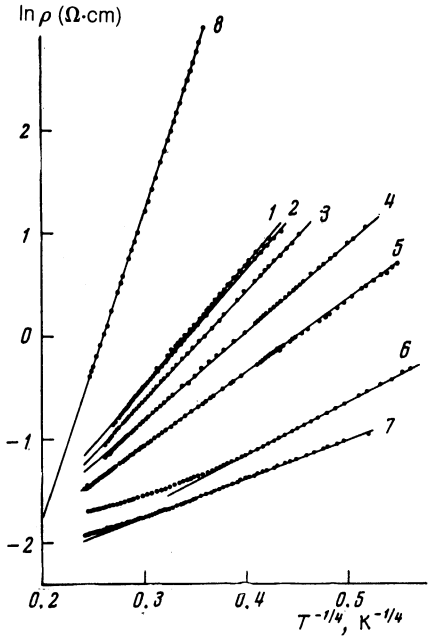

FIG. 4. Dependence of $\ln \rho$ on $T^{-1/4}$ for the compound YBaCuO irradiated with a fluence of $\Phi = 1.2 \cdot 10^{19}$ cm^{-2} at 80 K without heating (curve 1), after 20-minute annealing at temperatures $T = 150$ K, (2), 200 K (3), 250 K (4), 300 K (5), and two weeks of annealing at $t = 300$ K (7); for LaSrCuO: $\Phi = 2 \cdot 10^{19}$ cm^{-2}, annealed for 2 hours at 300 K (6); for $LaCuO_4$: $\Phi = 2 \cdot 10^{19}$ cm^{-2}, annealed for 2 hours at 300 K (8).

From this it follows that the electronic system in ordered HTS is very close to the Anderson metal-insulator transition. The observed variation of ρ as a function both of fluence and of temperature can be described using the empirical formula proposed in Ref. 4:

$$\rho(T) = f(T) \exp(b\Phi/T^{1/4}). \quad (2)$$

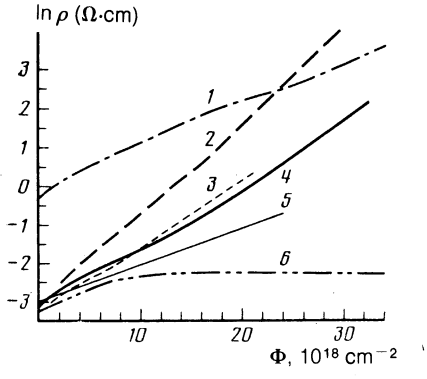

FIG. 5. Dependence of $\ln \rho$ on fluence Φ obtained in the process of irradiation at $T = 80$ K: 1—La_2CuO_4, 2—$YBa_2Cu_3O_{6.95}$, 3—single-crystal Y–Ba–Cu–O, ρ measured perpendicular to the c-axis, 4—$La_{1.83}Sr_{0.17}CuO_4$, 5—Bi–Sr–Ca–Cu–O, 6—$SnMo_6Se$.

(d) Magnetic Susceptibility, NQR, NMR

For unirradiated $La_{1.83}Sr_{0.17}CuO_{4-y}$ samples, the magnetic susceptibility decreases as the temperature falls from $0.77\cdot10^{-4}$ cm^3/mole (at 300 K) to $0.66\cdot10^{-4}$ cm^3/mole (at 40 K), which reflects the change in the spin contributions to χ as a result of the structural transition from the tetragonal to the orthorhombic phase which takes place at $T\sim300$ K.[18,19] Estimates of the spin contribution to the susceptibility for this material give $\chi_{sp}=0.35\cdot10^{-4}$ cm^3/mole for $T=40$ K. The magnetic susceptibility of the unirradiated compound $YBa_2Cu_3O_{6.95}$ does not depend on temperature.

Under irradiation the temperature dependences of the magnetic susceptibilities for the compounds $La_{1.83}Sr_{0.17}CuO_4$ and $YBa_2Cu_3O_{6.95}$ exhibit a great variety of behaviors. (a) In the temperature range from T_c to 300 K the function $\chi(T)$ is satisfactorily described by the expression $\chi(T)=\chi_0+C/(T-\Theta)$. The value of χ_0 and the Curie constant as a function of fluence Φ are given in Fig. 6. (b) In the interval of magnetic fields $B=0.1$ to 0.7 T, there is no field dependence in χ. (c) As the fluence increases a growth is observed in the temperature-independent contribution χ_0. (d) The value of θ changes from zero (for weakly irradiated samples) to $\theta=-4(2)$ K (in samples irradiated with maximum fluence). (e) The value of C is proportional to Φ. Especially noteworthy is the threefold larger slope of the function $C(\Phi)$ in samples of $YBa_2Cu_3O_{6.95}$ compared to $La_{1.83}Sr_{0.17}CuO_4$. In our view, this is evidence that the Curie-law temperature dependence is associated with changes in the immediate environment of the copper atoms which lead to localized moments on these atoms. We undertook experiments to observe EPR signals ($\nu=9\cdot10^{10}$ Hz) on samples with $\Phi=2\cdot10^{19}$ cm^{-2} in the temperature range 4 to 300 K. Its absence (apparently due to a large linewidth) allows us to find an upper bound on $T_1<10^{-10}$ sec for the relaxation times of the moments. This value is typical of the majority of transition metal alloys with strong and easily-observed paramagnetism. We note that although a Curie-Weiss law behavior appears in the magnetic susceptibility of $YBa_2Cu_3O_{7-\delta}$ as the oxygen content decreases, and also as the radiation-induced disorder increases, the temperature-independent contribution χ_0 behaves differently for these two cases: it falls as δ increases but grows with irradiation.

In an unirradiated sample of $YBa_2Cu_3O_{6.95}$, the value of χ_0 is determined by three basic contributions: a diamagnetism (χ_{dia}) due to the ionic cores, a Van Vleck paramagnetism (χ_{vv}), and a Pauli paramagnetism (χ_{sp}). When conduction band electron correlations are included, the Pauli contribution is related to the single-particle density of states at the Fermi level $N(E_F)$:

$$\chi_{sp}=2\mu_B^2N(E_F)/[1-JN(E_F)], \tag{3}$$

where J is the exchange integral. In order to clarify the tendency for χ_0 to change under irradiation, we carried out measurements of the spin-lattice relaxation time T_1 for ^{63}Cu nuclei in the Cu(1) position (in the chains the NQR line is at $\nu_Q=22$ MHz) and Cu(2) (in the planes $\nu_Q=31.5$ MHz). The evolution of the NQR spectra at ^{63}Cu nuclei in the Cu(2) position (Fig. 7), as in the oxygen-deficient samples,[12] is related to the configuration of vacancies in the O(4) positions; however, the only vacancies which are created are those due to redistribution between the O(4) and O(5) sites rather than departure of oxygen from the sample. In the normal state the value of T_1 is determined by the fluctuating portion of the magnetic hyperfine interaction between the nuclear magnetic moments and the conduction band electrons

$$(TT_1)^{-1}=H_{HF}\chi_{sp}^2K(JN(E_F)), \tag{4}$$

where H_{HF} is the magnitude of the hyperfine field created at the ^{63}Cu d-electrons through the exchange polarization of the valence and inners s-shells of the copper. The coefficient K takes into account possible deviations of the local susceptibility $\chi(q)$ from its average value. For an isotropic Fermi surface $K\approx1$; as the electron density distribution becomes more anisotropic, increased values of K become possible. This effect is most striking in the one-dimensional conductors, where $K\gg1$. In Fig. 8 we show the temperature depend-

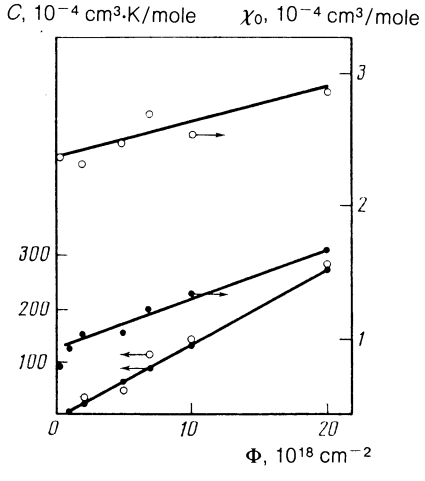

FIG. 6. Dependence of the Curie constant C and the temperature-independent contribution χ_0 to the magnetic susceptibility on neutron fluence Φ for $La_{1.83}Sr_{0.17}CuO_4$ (●) and $YBa_2Cu_3O_{6.95}$ (○). For YBaCuO the values of C are on a scale of one atom per unit cell.

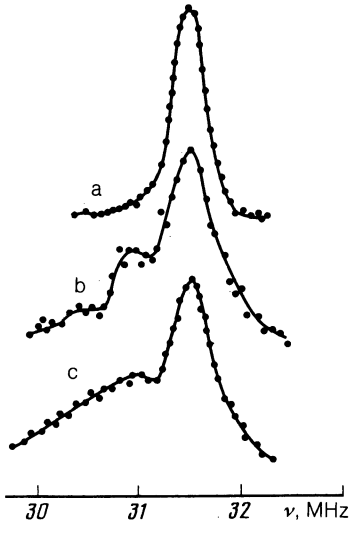

FIG. 7. NQR spectra of ^{63}Cu in the Cu(2) positions for 78 K: a—unirradiated sample of $YBa_2Cu_3O_{6.95}$, $T_c=93$ K; b—a sample of $YBa_2Cu_3O_{6.95}$ irradiated with a fluence of $5\cdot10^{18}$ cm^{-2}, $T_c=71$ K; c—a sample of $YBa_2Cu_3O_{6.8}$, $T_c=69$ K.

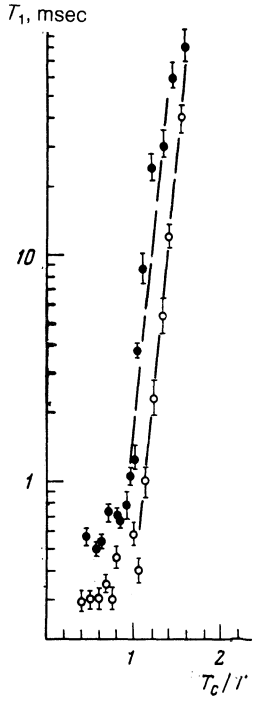

FIG. 8. Temperature dependence of the spin-lattice relaxation time of ^{63}Cu in the Cu(2) for the compound $YBa_2Cu_3O_{6.95}$: ○—unirradiated sample, $T_c = 93$ K; ●—sample irradiated by a fluence $\Phi = 5\cdot10^{18}$ cm^{-2}, $T_c = 71$ K.

ence of the relaxation time T_1 for ^{63}Cu nuclei at the Cu(1) position in unirradiated and irradiated samples of $YBa_2Cu_3O_{6.95}$ ($T_c = 70$ K and $\Phi = 5\cdot10^{18}$ cm^{-2}). In the normal state ($T > T_c$) the time T_1 increases with disorder from 0.3 to 0.57 msec. An increase in the spin-lattice relaxation time T_1 also is observed, only to a much larger degree, as the oxygen content of $YBa_2Cu_3O_{7-\delta}$ changes; an increase of δ from 0 to 0.2 ($T_c \approx 70$ K) is accompanied by an increase in T_1 by roughly a factor of 300. If, according to (4), these changes are connected only with the decrease of $N(E_F)$, then in the first case (when the samples are irradiated with a fluence of $5\cdot10^{18}$ cm^{-2}) the density of states must have fallen by a factor of 1.25, while in the second case it must have fallen by more than an order of magnitude. The growth of χ_0 under irradiation and the simultaneous increase in the spin-lattice relaxation time T_1 show that an attempt to explain their variation only as a variation of $N(E_F)$ leads to contradictions.

We observe a distribution of relaxation times associated with the Cu(1) positions of an irradiated sample in the normal state, with an overall tendency for these times to increase. The presence of such a distribution hinders analysis of the variation of T_1 at temperatures below T_c, and points to the appearance of disorder in the electronic environment of the copper atoms at the Cu(1) positions of irradiated $YBa_2Cu_3O_{6.95}$.

In studying irradiated samples in the superconducting state, i.e., for $T_c > T > T_c/2$, we observe nearly exponential growth of the spin-lattice relaxation time $T_1 \sim \exp(\Delta/kT)$ (Fig. 8) similar to what is seen in the unirradiated samples. This is connected with the appearance of a gap in the electronic spectrum. The dependence of ln T_1 on inverse temperature is practically the same in both samples; we find that $2\Delta/kT_c = 12 \pm 2$, which indicates that the regime of very strong coupling is preserved in samples irradiated at the $5\cdot10^{18}$ cm^{-2} fluence level.

We note in conclusion that the Curie–Weiss type of contribution to the magnetic susceptibility is observed in samples even in the presence of very small amounts of disorder.

4. DISCUSSION OF RESULTS

As we saw above [Sec. 3(c)], at certain levels of radiation-induced disorder the temperature dependence of the HTS electrical resistivity follows the Mott equation (1). This implies that the system is on the insulator side of the metal-insulator transition. In contrast to the 123-type oxygen-deficient systems, this transition takes place without a change in the chemical composition and consequently is due only to the appearance of a random potential (i.e., it is an Anderson transition). Neutron-diffraction studies show that we are dealing with simple defects of the random atomic displacement type, more or less chaotically distributed in space. The simple character of the defects is also confirmed by their relative instability with respect to short-time low-temperature annealing. We recall that in samples irradiated by fluences of $(5–7)\cdot10^{18}$ cm^{-2}, annealing leads to recovery of both superconductivity and linear behavior of $\rho(T)$ at temperatures above 100 K [see Sec. 3(c)]. Although a dependence of the type (1) is directly observed experimentally only at high fluences (when T_c is either small or zero), the localized states in the system apparently arise much earlier. It is natural to discuss the exponential growth of the electrical resistance with irradiation, which begins with very small fluences, the invariance of the derivative of the upper critical field H'_{c2} in spite of the rapid growth of the electrical resistivity, and probably the appearance of the Curie–Weiss contribution to the magnetic susceptibility, in terms of the existence of localized states which are present even in very weakly-disordered samples which still possess rather high values of T_c. [Since the origin of the linear temperature dependence of $\rho(T)$ in unirradiated and weakly-disordered samples is poorly understood (see Introduction), its presence cannot be considered proof of the absence of localized states.]

For small degrees of disorder, the localization radius R_{loc} is rather large. Therefore the contribution of the localized states to the resistance as given by Eq. (1) should be most evident at very low temperatures.[20] However, high values of T_c limit from below the temperature measurement interval of the electrical resistance of the normal state, so that it is not possible to observe localization effects directly in the curves $\rho(T)$. Increasing the degree of disorder leads to a decrease in R_{loc}, resulting in a widening of the temperature interval over which (1) is valid. Since this also causes T_c to decrease, at moderate fluences there appear sections in the curve $\rho(T)$ with $d\rho/dT < 0$, which extend to ever larger temperatures as the disorder increases (i.e., R_{loc} decreases). From this we can conclude that the suppression of superconductivity is related not to the appearance of localized states *per se*, but to a significant decrease in the localization radius as the disorder increases in the system.

(a) Localization and Superconductivity in Quasi-Two-Dimensional Systems (Theory)

It is well known that strong disorder can lead to a radical change in the electronic states near the Fermi level, in

particular to a metal-insulator transition caused by localization of electrons (i.e., an Anderson transition).[21] In quasi-two-dimensional systems, to which class the high-temperature superconductors studied in this paper belong, we must expect a significant enhancement of this effect, which is related to a well-known peculiarity of two-dimensional space: localization of electrons in two dimensions takes place even for arbitrarily weak disorder.[22]

In a disordered system the electrons are in certain eigenstates $\varphi_\nu(x)$ determined by exact solutioin of the one-electron Schroedinger equation in the corresponding random potential. These states can be either delocalized or localized, depending on the degree of disorder and on their energy. Cooper pairing in such a system takes place between states $\varphi_\nu(r)$ and $\varphi_\nu^*(r)$, which are related by time reversal. This problem was solved by Anderson[2] by using the postulate of self-averaging of the superconducting order parameter. Anderson showed that the superconducting transition temperature was in fact independent of the character of the states $\varphi_\nu(r)$ for a given interaction which leads to pairing near the Fermi level. A natural limitation which arises from localization of the states is related to the well-known discreteness of the electronic spectrum in the localization region (the level-repulsion effect).[21]

By the very nature of the phenomenon of localization, it is clear that despite the fact that the averaged density of states is nonzero for all energies of the band, states which are quite close in energy are found at large spatial separations from one another. By virtue of the exponential decay of the wave functions this leads to the absence of tunneling. It is clear on the other hand that Cooper pairing can take place only between electrons whose centers of localization lie inside the surface of a sphere with a radius on the order of the localization length R_{loc} (only their wave functions overlap!). However these states are split in energy by a quantity of order $[N(E)R_{\text{loc}}^3]^{-1}$ (Ref. 21). Obviously, we must require that the magnitude of the superconducting gap Δ (at $T=0$) significantly exceed this splitting, i.e.,

$$\Delta \sim T_c \gg [N(E)R_{loc}^3]^{-1}, \tag{5}$$

i.e., that many discrete levels be located within an energy interval $\sim\Delta$ whose centers of localization are within a radius $\sim R_{\text{loc}}$. In this case the problem of Cooper pairing in the region $\sim R_{\text{loc}}$ does not differ qualitatively from pairing in the metallic state. It is obvious that (5) is equivalent to the requirement that the radius of localization be sufficiently large[23,24]:

$$R_{\text{loc}} \gg [N(E)\Delta]^{-1/3} \sim \left(\xi_0 \frac{\hbar^2}{p_F^2}\right)^{1/3} \sim (\xi_0 a^2)^{1/3}, \tag{6}$$

where $\xi_0 = \hbar v_F/T_c$ is the coherence length in BCS theory, $p_F = \hbar/a$ is the Fermi momentum (a is the interatomic spacing, v_F is the Fermi velocity). In the high-temperature superconductors with their characteristically large Δ and small ξ_0, conditions of type (5), (6) can be satisfied within a significant parameter interval when the superconductors enter the Anderson insulating state. Condition (6) has a simple physical meaning[23,24]: the localization radius in a strongly disordered system should significantly exceed the characteristic size of a Cooper pair. This also is a qualitative criterion for the existence of superconductivity in an Anderson insulator.

The preceding discussion pertains to a three-dimensional isotropic system, which was also studied in Refs. 23, 24. Of course, the qualitative conclusions can also be applied to the experimental data obtained on ceramic (polycrystalline) samples. At the same time, the quasi-two-dimensional character of the high-temperature superconductors we are investigating here leads to definite departures from the results of Refs. 23, 24, which must be kept in mind when discussing our experimental data. Therefore, in what follows we will dwell briefly on the necessary changes which must be included in the treatment of quasi-two-dimensional system. Basically, we will be interested in the coefficient of the gradient term in the Landau–Ginzburg expansion for the free energy of a superconductor, since this determines the Meissner response of the system.

As a single-electron model of the Anderson transition we will assume the self-consistent theory of localization,[25] within which framework we can carry calculations of all quantities of interest to us to the end, including also those for the quasi-two-dimensional case.[26] The character of the electron motion in a disordered system is determined in this theory by a two-particle Green's function having the diffusion form:

$$\Phi(\mathbf{q}\omega) = -\frac{N(E_F)}{\omega + iD_\parallel(\omega)q_\parallel^2 + iD_\perp(1-\varphi(q_\perp))}, \tag{7}$$

where $D_{\parallel,\perp}$ are the generalized coefficients of longitudinal and transverse (relative to the highly conducting layers) diffusion, $\varphi(q_\perp = \cos q_\perp a_\perp$, where $q_{\parallel,\perp}$ are the longitudinal and transverse components of the momentum $\mathbf{q}$, and $a_\perp$ is the distance between layers of the two-dimensional lattice. For simplicity we consider the electronic motion in the highly conducting layers to be isotropic.

The generalized diffusion coefficient is determined in this theory by the solution to a self-consistent equation of the following form[26]:

$$D_{\parallel,\perp}(\omega) = D_{\parallel,\perp}^0 - \frac{1}{\pi N(E_F)} \times \int \frac{d^3q}{(2\pi)^3} \frac{D_{\parallel,\perp}(\omega)}{-i\omega + D_\parallel(\omega)q_\parallel^2 + D_\perp(\omega)[1-\varphi(q_\perp)]}. \tag{8}$$

Here $D_\parallel^0 = v_F^2\tau/2$, $D_\perp^0 = (wa_\perp)^2\tau$ are the bare (Drude) diffusion coefficients, w is the transfer integral between planes (layers), and τ is the mean free time in a highly conducting plane of the quasi-two-dimensional system.

The position of the mobility edge on the energy scale is determined by the condition[26]

$$E_c = \frac{\hbar}{\pi\tau} \ln\left(\frac{2^{1/2}\hbar}{w\tau}\right), \tag{9}$$

so that $E_c \to \infty$ as $w \to 0$, which corresponds to full localization in the purely two-dimensional case.[22] When $E_F = E_c$ the Drude conductivity in the layer is comparable to the so-called minimum metallic conductivity[21]

$$\sigma_c'' = 2e^2 N(E_F) D_\parallel^0(E_F = E_c) = \frac{1}{\pi^2}\frac{e^2}{\hbar a_\perp} \ln\left(\frac{2^{1/2}\hbar}{w\tau}\right), \tag{10}$$

where we take into account the fact that $N(E_F) = m/2\pi a_\perp \hbar^2$, with m the effective mass of an electron. From this it is clear that in the quasi-two-dimensional case the minimal metallic conductivity is increased relative to the estimates of

Mott[21] by a logarithmic factor which grows as the decrease in the overlap of electronic states in neighboring layers. This implies that in systems with strongly anisotropic conductivity of the two-dimensional type, i.e., systems such as the high-temperature superconductors under study here, the magnitude of the minimal metallic conductivity can significantly exceed $(3–5)\cdot 10^2\ \Omega^{-1}\cdot\text{cm}^{-1}$, a value which is characteristic of an isotropic three-dimensional system. Using simple estimates, we find the following ratio of the longitudinal to the transverse conductivities:

$$\sigma_{0\parallel}/\sigma_{0\perp}=D_{\parallel}^{0}/D_{\perp}^{0}=E_F\hbar^2/w^2ma_{\perp}^2,$$

so that

$$w\tau=E_F(\sigma_{0\perp}/\sigma_{0\parallel})^{1/2}(\hbar^2/E_Fma_{\perp}^2)^{1/2}.$$

Then for the typical values $\sigma_{0\perp}/\sigma_{0\parallel}\sim 10^{-2}$, $E_F\tau/\hbar\sim 1$, $\hbar^2/E_Fma_{\perp}^2\sim 1$ we have $w\tau/\hbar\lesssim 0.1$, so that according to (10), σ_c'' can attain values $\gtrsim 10^3\ \Omega^{-1}\cdot\text{cm}^{-1}$. Based on these estimates, we can assume that the unirradiated samples of high-temperature superconductors used in these investigations are close to the Anderson transition.

Using results for $D_{\parallel,\perp}(\omega)$ obtained in Ref. 26, and carrying out calculations analogous to Ref. 23, we find for the coefficient in the gradient term of the Landau–Ginzburg expansion

$$c_{\parallel,\perp}=N(E_F)\xi_{\parallel,\perp}^2, \tag{11}$$

where for the coherence length $\xi_{\parallel,\perp}$ we obtain a number of different expressions, depending on the value of the ratio $w^2\tau/2\pi T_c\hbar$ which determines the "degree of two-dimensionality" of the problem under study. For the case

$$w^2\tau/2\pi T_c\hbar\gg 1,$$

corresponding to an anisotropic but three-dimensional system, we have

$$\xi_{\parallel,\perp}^2=\frac{\pi}{8T_c}D_{\parallel,\perp}^{0}\left(\frac{E_F-E_c}{E_c}\right)\approx\xi_{\parallel,\perp}^{0}l_{\parallel,\perp}\left(\frac{E_F-E_c}{E_c}\right), \tag{12}$$

where $\xi_{\parallel}^{0}\sim\hbar v_F/T_c$, $\xi_{\perp}^{0}\sim\hbar wa_{\perp}/T_c$, $l_{\parallel}=v_F\tau$ and $l_{\perp}=wa_{\perp}\tau$ are the longitudinal and transverse mean free paths. This expression is valid in the conductivity region $\sigma_{\parallel}>\sigma^*$, where

$$\sigma^*\sim\sigma_{\parallel}^{c}\frac{\xi_{\parallel}^{0}}{l_{\parallel}}\left(\frac{T_c^2}{E_Fw}\right)^{2/3}. \tag{13}$$

The condition $w^2\tau/2\pi T_c\hbar\gg 1$ is equivalent to the requirement

$$\xi_{\perp}\sim(\xi_{\perp}^{0}l_{\perp})^{1/2}\gg a_{\perp},$$

which clarifies its physical meaning.

In the immediate vicinity of the Anderson transition, for $\sigma_{\parallel}>\sigma^*$ we have

$$\xi_{\parallel,\perp}^2\approx\left(\frac{1}{16\pi^4}\right)^{1/3}\left(1-\frac{1}{2^{5/3}}\right)\zeta(5/3)\frac{D_{\parallel,\perp}}{(E_FT_cw)^{2/3}\tau}$$

$$\approx(\xi_{\parallel,\perp}^{0})^2\left(\frac{T_c^2}{E_Fw}\right)^{2/3}, \tag{14}$$

where $\zeta(x)$ is the Riemann ζ-function.

It is easy to see that for $w\sim E_F$ these expressions go over to the expressions derived in Ref. 23 for the three-dimensional case:

$$\xi^2\approx\begin{cases}\dfrac{\pi}{8T_c}D_0\left(\dfrac{E_F-E_c}{E_c}\right)\approx\xi_0 l\left(\dfrac{E_F-E_c}{E_c}\right), & \sigma>\sigma^*,\\ \left(\dfrac{D_0l}{T_c}\right)^{2/3}\sim(\xi_0l)^{2/3}, & \sigma<\sigma^*.\end{cases} \tag{15}$$

Here $D_0=\frac{1}{3}v_F^2\tau$, $l=v_F\tau$, while the characteristic conductivity equals

$$\sigma^*\approx\sigma_c(p_F\xi_0/\hbar)^{-1/2}\approx\sigma_c(T_c/E_F)^{1/2}, \tag{16}$$

where $\sigma_c=e^2p_F/\pi^3\hbar^2$ is the minimum Mott metallic conductivity.[21]

For the case $w^2\tau/2\pi T_c\lesssim 1$, which corresponds to an "almost two-dimensional" system, we have

$$\xi_{\parallel,\perp}^2\approx\left\{\begin{array}{l}\dfrac{D_{\parallel,\perp}^{0}}{\pi T_c}\dfrac{E_F-E_c}{E_c}\\ \left(\dfrac{1}{16\pi^4}\right)^{1/3}\dfrac{D_{\parallel,\perp}^{0}}{(E_FT_cw)^{2/3}\tau}\end{array}\right\}$$
$$+\left(\frac{\pi^2}{8}-1\right)\frac{D_{\parallel,\perp}^{0}}{\pi T_c}\left(1-\frac{1}{2\pi E_F\tau}\ln\frac{1}{2\pi T_c\tau}\right), \tag{17}$$

where the upper expression is valid for $\sigma_{\parallel}>\sigma^*$, and the lower for the opposite case. The essential difference between (17) and (12) and (14) consists of the appearance of a second term of "two-dimensional" type. In the purely two-dimensional problem ($w=0$) we have[27]

$$\xi_{\parallel}^2=\frac{\pi D_{\parallel}^{0}}{8T_c}\left(1-\frac{1}{2\pi E_F\tau}\ln\frac{1}{2\pi T_c\tau}\right). \tag{18}$$

For the high-temperature superconductors we are studying, it is reasonable to assume $\xi_{\parallel}^{0}\sim l_{\parallel}$, $T_c\sim w$, $T_c\sim 0.1\,E_F$, so that $\sigma^*\sim\sigma_{\parallel}^{c}$, i.e., these systems are always close to the Anderson transition, and with respect to their superconducting behavior they can be described by Landau–Ginzburg theory. For $T_c\sim w$ and $\hbar/\tau\sim E_F$, we have

$$w^2\tau/2\pi T_c\hbar<1,$$

so that for these systems we can realize almost two-dimensional behavior. The physical meaning of this condition is equivalent to

$$\xi_{\perp}\sim(\xi_{0\perp}l_{\perp})^{1/2}\sim a_{\perp},$$

i.e., the Cooper pairs effectively belong to the conducting layers and overlap rather weakly in the transverse direction. Most likely, an intermediate case is realized in the systems under study here.

Direct information on the coherence length ξ can be obtained from measurements of the critical field[28]:

$$H_{c2}(T)=\frac{\Phi_0}{2\pi\xi^2(T)},\qquad \xi^2(T)=\xi\frac{T_c}{T_c-T}, \tag{19}$$

where $\Phi_0=\pi c\hbar/e$ is the magnetic flux quantum in superconductivity theory. From this we can find the derivative of the upper critical field with temperature:

$$(dH_{c2}/dT)_{T_c}=-\frac{\Phi_0}{2\pi\xi^2T_c}. \tag{20}$$

Then for an isotropic three-dimensional system, we obtain from (15)[23]:

$$-\frac{\sigma}{N(E_F)}\left(\frac{dH_{c2}}{dT}\right)_{T_c}$$
$$=\begin{cases}\dfrac{8e^2}{\pi^2\hbar}\Phi_0, & \sigma>\sigma^* \\ \dfrac{\Phi_0}{2\pi}\dfrac{\sigma}{[N(E_F)T_c]^{1/2}}\sim\dfrac{\Phi_0}{2\pi T_c}\dfrac{\sigma}{(\xi_0 l^2)^{1/2}}, & \sigma<\sigma^*\end{cases} \quad (21)$$

We see that near the metal-insulator transition, when $\sigma<\sigma^*$ holds even the Gor'kov relation [the upper expression in (21)] is not fulfilled, and the usual growth in $(dH_{c2}/dT)_{T_c}$ with increasing resistivity is replaced by an approach to saturation. The observed experimental absence of a dependence of H'_{c2} on resistivity (Table I) is in qualitative agreement with this assertion. However, we emphasize the importance of independent experiments to determine $N(E_F)$.

In a quasi-two-dimensional system, we have in an analogous fashion[22]

$$H_{c2}^{\perp}(T)=\Phi_0/2\pi\xi_{\parallel}^2(T),\quad H_{c2}^{\parallel}(T)/H_{c2}^{\perp}(T)=\xi_{\parallel}(T)/\xi_{\perp}(T),$$
$$H_{c2}^{\parallel}(T)=\Phi_0/2\pi\xi_{\parallel}(T)\xi_{\perp}(T). \quad (22)$$

Correspondingly,

$$\left(\frac{dH_{c2}^{\perp}}{dT}\right)_{T_c}=-\frac{\Phi_0}{2\pi\xi_{\parallel}^2T_c},\quad \left.\frac{(H_{c2}^{\parallel})'}{(H_{c2}^{\perp})'}\right|_{T_c}=\frac{\xi_{\parallel}}{\xi_{\perp}},$$
$$\left(\frac{dH_{c2}^{\parallel}}{dT}\right)_{T_c}=-\frac{\Phi_0}{2\pi\xi_{\parallel}\xi_{\perp}T_c} \quad (23)$$

These equations allow us to find $\xi_{\parallel,\perp}$ from measurements of H_{c2} on single-crystal high-temperature superconductors. From the expressions (14), (17) for $\xi_{\parallel,\perp}$, in the region $\sigma_{\parallel}<\sigma^*$ [see (13)] the explicit dependence on the residual conductivity σ before irradiation (at $T=0$), which reduces to zero at the transition to the insulating state, in fact disappears, so that the qualitative behavior of $(H_{c2}^{\parallel,\perp})_{T_c}$ in a quasi-two-dimensional system turns out to be the same as in the three-dimensional case.

We note that the previous discussion is essentially based on the assumption of self-averaging of the superconducting order parameter in the vicinity of the Anderson transition. In fact, as was shown in Ref. 24, this assumption is invalid in the conductivity region $\sigma<\sigma^*$, where statistical fluctuations in the order parameter related to fluctuations in the local density of states near the Anderson transition become significant.[30] It is found that in the region $\sigma<\sigma^*$ and near T_c superconductivity appears in a spatially inhomogeneous fashion, in the form of nucleating droplets within which the superconducting order parameter is different from zero. The superconducting transition in this inhomogeneous regime must be strongly smeared out in temperature. (A broadening of the transition actually does take place in the radiation-disordered and oxygen-deficient samples.) In this case, even a uniformly disordered system can turn out to be analogous to a granular superconductor, and in fact the properties of strongly disordered single crystals and films of high-temperature superconductors can be close to the properties of ceramic materials.

(b) Decrease of T_c

Using the experimental data on electrical resistivity of disordered samples of $YBa_2Cu_3O_{7-\delta}$ (for fluences $\Phi>5\cdot10^{18}$ cm^{-2}] and the empirical expression (2) for small fluences, we can calculate the change of the localization radius R_{loc} as a function of fluence. On the other hand, (5) gives the limiting values of R_{loc} for which superconductivity can still exist in a system of localized electrons. Assuming $N(E_F)=5\cdot10^{33}$ (erg·cm^3)$^{-1}$ (in a model of free electrons this corresponds to one electron per unit cell, i.e., a carrier concentration[27] of $\sim6\cdot10^{21}$ cm^{-3}), while the left side of (5) equals $5T_c$, we obtain the result shown graphically in Fig. 9, from which it is clear that the criterion (5) ceases to be fulfilled for $\Phi\sim(5\text{–}7)\cdot10^{18}$ cm^{-2}. Taking into account the qualitative character of our estimate, we note that it is in remarkably good agreement with experiment. Figure 9 also allows us to interpret easily the data on the influence of the low-temperature anneals. Near $\Phi\sim(5\text{–}7)\cdot10^{18}$ cm^{-2} annealing increases R_{loc}, condition (5) is satisfied, and superconductivity appears. For large fluences the low-temperature anneals are insufficient for this.

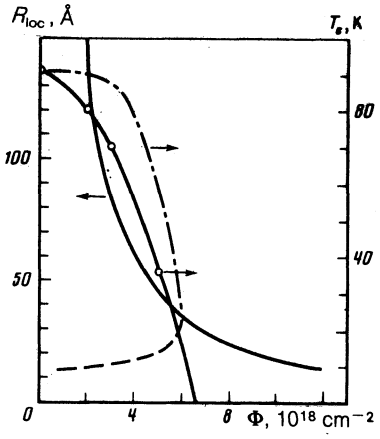

FIG. 9. Dependence of T_c on fluence Φ for the compound YBaCuO (circles). The solid curve is the localization radius R_{loc} calculated using (1), (2); the dashed-dotted curve is T_c calculated according (24a); the dashed curve is the minimum localization radius at which superconductivity can exist at a given T_c according to Eq. (5) (see text).

From the estimates we have presented, however, it is still not clear why the superconducting transition temperature must decrease at values of R_{loc} large compared to the limiting value. In the absence of a theoretical understanding of the nature of T_c in HTS it is rather difficult to express any opinion on the reason that T_c decreases with increasing disorder. At the same time, based on the conventional representation of the interaction which leads to pairing, we can offer the following observations on this problem. One of the causes of the appearance of T_c can be connected with the increase in the Coulomb pseudopotential μ^*, which describes the Coulomb repulsion of electrons which form the Cooper pairs.[23,32] This phenomenon is connected with the growth of retardation effects associated with the Coulomb repulsion in the Cooper pairs as the diffusion coefficient (conductivity) decreases in the course of the system's approach to the Anderson transition. In the localization region, we have according to Ref. 23 that

$$\ln\frac{T_{c0}}{T_c}=\Psi\left(\frac{1}{2}+\frac{\mu A_{E_F}}{4T_cN(E_F)}\right)-\Psi\left(\frac{1}{2}\right), \quad (24)$$

where Ψ is the digamma function, $\mu=v_0N(E_F)$ is the Coulomb potential, and $A_{E_F}\approx R_{loc}^{-3}$. This equation describes the

suppression of T_c because of the growth of retardation effects on Coulomb repulsion in a single quantized (localized) state. Taking into account (1) and (2), we obtain form (24)

$$\ln\frac{T_{c0}}{T_c}=\Psi\left[\frac{1}{2}+\mu T\left(\ln\frac{\rho(T)}{a}\right)^4\Big/4T_c(2,1)^4\right]-\Psi\left(\frac{1}{2}\right). \tag{24a}$$

[This expression is valid in the region of temperature where $\rho(T)$ is determined by Eq. (1) for the hopping conductivity.]

The dependence on T_c on the degree of disorder can now be calculated easily, using the data of Fig. 5 and assuming $\mu\approx 1$ (Fig. 9). It is clear that this dependence differs somewhat from the experimental dependence (we note the vanishing derivative $dT_c/d\Phi$ as $\Phi\to 0$ on the theoretical curve); however, the qualitative agreement is unarguable. The more rapid suppression of T_c for the small degrees of disorder observed in experiment can be related to an additional nonsingular contribution to the correlator from electron states neglected in the derivation of Eq. (24) in Ref. 23.

In the framework of the approach developed here we can clarify certain characteristic features of the behavior of disordered HTS. The closeness of these materials to the Anderson metal-insulator transition, and the existence of superconductivity with rather high T_c in a system of localized electrons is apparently a distinguishing feature of the HTS. Such "nonmetallic" behavior of these compounds becomes especially striking if we compare them, e.g., with the A-15 type of superconductors. The latter, with all their peculiarities—about which a little was said in the Introduction—behave like "metals" to a very much greater degree than do the HTS. Although superconductors with the Chevrel-phase structure have lower T_c than the A-15 compounds, they constitute in some sense an intermediate case between the A-15's and the HTS.

A number of the experimental facts presented in Sec. 3 have not yet been successfully explained. Because we do not know how in fact the electronic density of states $N(E_F)$ changes with disorder, and because we have only an order-of-magnitude estimate of this quantity in the unirradiated state, it is not possible to explain the variation of the temperature-independent contribution to the magnetic susceptibility χ_0; this is also the case for the spin-lattice relaxation time T_1. Let us emphasize once again that whereas in a radiation-disordered sample ($T_c\approx 70$ K) the time T_1 increases by roughly a factor of 1.5, the value of T_1 in an oxygen-deficient sample ($\delta\approx 0.2$) with a comparable value of T_c increases by a factor of 300. Such a giant variation in the parameter T_1 can hardly be a random phenomenon. However, we cannot exclude the possibility that this also could be connected with localization effects. Also still unclear is the reason for the appearance of a Curie-Weiss contribution to the magnetic susceptibility. According to Mott,[20,21] we can assume that the appearance of effective magnetic moments is related to the presence of localized states. When we estimate the value of the effective magnetic moment p_{theor} (in Bohr magnetons) in a unit cell, we have according to Ref. 25 that

$$\mu R_{\text{loc}}^{-3}\Omega_0=p_{\text{theor}}^2 \tag{25}$$

where μ is the Coulomb potential, and Ω_0 is the volume of a unit cell. For large degrees of disorder ($\Phi=2\cdot 10^{19}$ cm^{-2}) and $R_{\text{loc}}\approx 8$ Å, $\mu=1$, we obtain $p_{\text{theor}}^2=0.66$ for YBaCuO in full agreement with experiment (from the value of the Curie constant we have $p_{\text{exper}}^2=0.661$). However, for smaller fluences p_{theor} is considerably smaller than p_{exper}. Here it is necessary to note that, first of all, Eq. (25) is valid only at small values of R_{loc} (i.e., when the Fermi level is considerably below the mobility edge); secondly, the accuracy with which the Curie constant is determined in weakly-disordered samples is considerably less than in strongly-disordered samples (the Curie-Weiss contribution itself is smaller by an order of magnitude, while the temperature interval over which χ varies is limited from below by the rather high values of T_c). It is obvious that if we estimate the variation of T_c according to (24), using the experimental values of the Curie constant [we remark that the same quantities enter into Eqs. (24) and (25)], then even at $\Phi=2\cdot 10^{19}$ cm^{-2} we obtain a value of $T_c\sim 15$ K.

Thus, the question of the origin of the Curie-Weiss contribution to χ is important not only from the standpoint of its relation to the localization effects, but also from the standpoint of its effect on T_c. If in the oxygen-deficient samples magnetic moments of comparable magnitude appear on segments of the Cu(1)–O(4)–Cu(1)–vacancy chains,[9] then with regard to relatively disordered samples, by taking into account the lanthanum-strontium ceramics in which there are no chains we can conclude that magnetic moments also appear in the Cu(2)–O planes. The question then remains; why do the magnetic moments turn out to have so little influence on the superconductivity? All these questions require further study.

5. CONCLUSION

The results of this paper show that the peculiarities of the electronic system in HTS are such that they are close to the metal-insulator transition even in the ordered state, and apparently this is their distinguishing feature compared to such superconductors as, e.g., the A-15's. Even for very weak disorder the pairing takes place in a system of localized electrons. The value of T_c decreases sharply for those levels of disorder for which an exponential temperature dependence of the electrical resistivity is clearly observed in the region of low temperatures. The superconductivity is completely suppressed when the energy splitting between localized states becomes comparable to the value of the superconducting gap.

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[2)]In Ref. 4, an estimate was made of the value of the normal-state Sommerfeld constant γ from a comparison of the heat capacities of an unirradiated sample of $YBa_2Cu_3O_{6.95}$ ($T_c=93$ K) and a sample disordered by radiation ($\Phi=2\cdot 10^{19}$ cm^{-2}, leaving the sample nonsuperconducting); the authors found that $\gamma\approx 0.5$ mJ/K$^2\cdot$gm$\cdot$atm, from which they obtained a value of $N(E_F)\approx 1\cdot 10^{34}$ (erg$\cdot$cm^3)$^{-1}$ similar to the one given here. According to Ref. 31, the carrier concentration was $n\approx 10^{22}$ cm^{-3}. Since only orders of magnitude will be important in the estimates which follow in this paper, we will not take into account the possibility of a change in $N(E_F)$ in the presence of disorder.

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