"Subthreshold" formation of defects in $Y_1Ba_2Cu_3O_{7-x}$ single-crystal films

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An increase in the resistance of $Y_1Ba_2Cu_3O_{7-x}$ single-crystal films (above the critical temperature), caused by the "subthreshold" x-ray bombardment at room temperature, has been observed experimentally. Such a subthreshold x-ray bombardment can be explained in terms of the ionization mechanism for the formation of structure defects: anion vacancies (oxygen ions).

The appearance of an above-the-threshold, elastic-collision-induced, general formation of defects in copper oxides, including the high-T_c superconducting materials, has recently been studied in several places (see, for example, Refs. 1 and 2). Study of cathodoluminescence spectra[3,4] and spectra of O^+ oxygen ion desorption[5] has shown, however, that subthreshold defect formation can occur in these materials. Here we present the results of an experimental study of the temperature dependence of the resistance of $Y_1Ba_2Cu_3O_{7-x}$ films (above the critical temperature) which were bombarded with subthreshold-energy x-rays.

As the starting materials we used $Y_1Ba_2Cu_3O_{7-x}$ single-crystal films obtained by the method of magnetron sputtering on a strontium-titanate substrate. The thickness of the films was in the range 0.3–0.6 μm. The bombardment with x-rays was carried out at room temperature. A "REIS" x-ray emitter with a copper anode was used for the bombardment of the samples. The radiation maximum in the main operating mode occurred in the region $E_R \approx 10$ keV, which is considerably lower than the threshold displacement energy, E_d, of the lightest oxygen atoms in the interval being studied; E_d may be assumed to be in the range 120–150 keV (see Refs. 1 and 6). The temperature dependence of the resistance was measured by the van der Pauw method in the temperature interval 50–300 K.

A typical temperature dependence of the resistance of one test film in the initial state (curve 1), after bombardment (curve 2; flux $\Phi = 3\times10^{15}$ cm^{-2}), and after holding the irradiated film for 1.2×10^6 and 2.4×10^6 s at room temperature (curves 3 and 4, respectively) is shown in Fig. 1. The dependence of the resistivity $\rho(T)$ is described satisfactorily in all cases up to the critical temperature by the linear law $\rho = \rho_0 + \alpha T$, where ρ_0 is the residual resistivity and the proportionality coefficient is $\alpha = (9.0 \pm 0.5)\times10^{-7}$ $\Omega\cdot$cm/K. It has been established that irradiation does not markedly affect either the critical temperature ($T_c = 89$ K) or α. Irradiation does, however, increase considerably the residual resistivity; for the data shown in Fig. 1 $\rho_0^{in} = 1.6\times10^{-5}$ $\Omega\cdot$cm and $\rho_0^{irrad} = 3.2\times10^{-5}$ $\Omega\cdot$cm. We believe that this increase is caused by the radiation-induced increase in the scattering of charge carriers by the defects in the structure. Note that after termination of x-ray bombardment the residual resistivity continued to increase for some time (when the irradiated films were held at

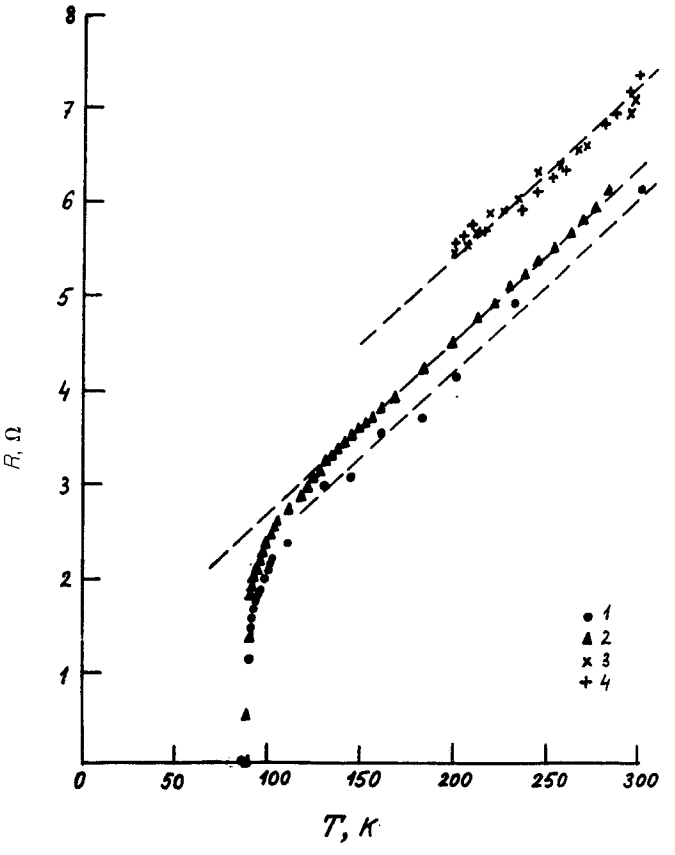

FIG. 1. Temperature dependence of the resistance of a $Y_1Ba_2Cu_3O_{7-x}$ single-crystal film in the initial state, after x-ray bombardment, and during annealing at room temperature.

room temperature), and then finally stabilized. This behavior suggests that the primary defects, which appear during the bombardment, are mobile at room temperature, and that they participate in the chelation. Estimates show that the activation energy E_a of the diffusion (if the coefficient of the exponential function of the diffusion coefficient is a standard coefficient) is not small (in this case $E_a \sim 1$ eV), in agreement with some of the recent results (see, e.g., Ref. 7). On the other hand, the increase in the resistivity in the case of annealing can be attributed to the fact that the secondary defects have a cross section for the scattering of charge carriers two to three times larger than that of the primary radiation defects (for films with a good initial structure the residual resistivity after the stabilization is higher than ρ_0^{irrad} by a factor of two or three).

We assume that anion vacancies (oxygen ions), whose concentration, ΔN_{vac}, is estimated to be $\Delta N_{\text{vac}} \approx \Delta\rho_0/(pe^2/m_p^*)(\sigma_{\text{vac}} v)$, are the primary radiation defects which cause the additional scattering of charge carriers in the irradiated films. Here $\Delta\rho_0 = \rho_0^{\text{irrad}} - \rho_0^{\text{in}}$, m_p^* and p are the effective mass and hole concentration, v is the

average velocity of the charge carriers, σ_{vac} is the scattering cross section of the vacancy. Substituting $v \approx 3 \times 10^7$ cm/s, $(pe^2/m_p^*) \approx 10^{30}$ s^{-2} (Ref. 8) for $Y_1Ba_2Cu_3O_{7-x}$ and using $\sigma_{vac} \approx 10^{-15}$ cm^2 for an estimate, we find $\Delta N_{vac} \approx 4 \times 10^{20}$ cm^{-3} (for $\Delta\rho_0 \approx 10^{-5}$ $\Omega \cdot$cm). We also assume that production of anion vacancies is determined by a mechanism[9] which is governed by the ionization of anions (of their deep electron K and L_1 shells), with the appearance on them of two (or three) long-lived hole states. According to Ref. 9, this mechanism, which is governed by the electrostatic instability of certain distinct local atomic configurations, can be effective at low temperatures; such an instability arises as a result of the repulsion of a positively charged ionized anion from the neighboring cations. The cross section of the process being studied, which is particularly effective in the "subthreshold" energy region in the radiation experiments, $\sigma^* \approx \sigma_{ion} w^*$, may reach the cross section of the ionization indicated above; the dimensionless probability for the formation of an anion vacancy may be large ($w^* \sim 1$), and it does not depend on the irradiation temperature. Since the ionization energy $\epsilon_{ion}^{(K)} \approx 530$ eV, $\epsilon_{ion}^{(L_1)} \approx 25$ eV and the irradiation energy $E_R \approx 10$ keV, the multiplication factor for the ionization γ is roughly estimated to be $\gamma(K) \approx 20$ and $\gamma(L_1) \approx 400$. Rough estimates show that $1 \ll \sigma_{ion}(L_1)/\sigma_{ion}(K) \ll \epsilon_{ion}^{(K)}/\epsilon_{ion}^{(L_1)}$, so that in scale value here we probably have $\Delta N_{vac} \approx N_0 \sigma^*(L_1) I_R t_R \gamma(L_1) \kappa_{vac}$, where N_0 is the total concentration of oxygen ions, $\sigma^*(L_1) \approx \sigma_{ion}(L_1) w^*(L_1)$, and κ_{vac} is the fraction of free anion vacancies. In the case under consideration we have $\Delta N_{vac} \approx 10^{21} \cdot 4 w^*(L_1) \kappa_{vac}$ (cm^{-3}) for $\sigma_{ion}(L_1) \approx 10^{-18}$ cm^2, $I_R t_R \approx 10^{15}$ cm^2, and $N_0 \approx 10^{22}$ cm^{-3}. A comparison of these estimates with the experimental estimate $\Delta N_{vac} \approx 4 \times 10^{20}$ cm^{-3} shows that $w^*(L_1)\kappa_{vac} \sim 0.1$, so that for typical values $\kappa_{vac} \approx 0.1$–0.3 the probability $w^*(L_1) \approx (1$–$0.3)$ has a sensible scale value. According to the analysis of Ref. 9, we conclude that the p-type conductivity band in $Y_1Ba_2Cu_3O_{7-x}$ is either a Hubbard band or we have, as an alternative, the previously predicted[10] slowing down of the decay of a two-hole state of the anion. A more exact quantitative analysis of the mechanism for the ionization-induced formation of defects may show that a comparison of theory with experiment does not contain an adjustable parameter ($w^*\kappa_{vac}$). This circumstance and the nature of the p-type conductivity band will be discussed in greater detail in another paper.

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