Effect of superconducting transition in the cathodoluminescence of $YBa_2Cu_3O_7$

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The electron-photon emission spectra of $Y_1Ba_2Cu_3O_{7-\delta}$ ceramics with various degrees of oxygen deficiency have been studied. It is shown that the wide-band emission and the line emission which are observed are intrinsic. Pronounced changes have been observed in the emission intensity at the superconducting transition. A suppression of superconductivity erases the structural features in the emission at the transition.

1. A promising method for studying high-temperature superconductors is luminescence spectroscopy as a sample is excited by electrons at various energies. The electron-photon emission can be used effectively for diagnostics of band excitations in both insulating[1] and metallic[2] systems. The luminescence spectra of ceramic Y-Ba-Cu high-temperature superconductors were found in Ref. 3 at temperatures below the superconducting transition. Whether the spectrum observed in Ref. 3 corresponds to an intrinsic emission of the ceramic or the emission of some impurity remains unresolved, however. No proof that the superconducting transition has a direct effect on the nature of the spectrum has been found. In this letter we are reporting a study of the electron-photon emission of a Y-Ba-Cu high-temperature superconductor over the wide temperature interval 130–10 K. We focused on the behavior of the spectrum in the immediate vicinity of the superconducting transition. Comparative measurements were carried out for samples in which the superconductivity was suppressed by radiation damage and by high-temperature annealing. As a result, we were able to observe a direct effect of the superconducting transition on the structure of the Y-Ba-Cu emission spectrum and to establish a direct relationship between the extent of the oxygen deficiency and structural features in the spectrum. Together, the data obtained in this study make it possible to identify the two narrow lines α and β, which we describe below, and also the intense continuum as consisting of intrinsic emission of the Y-Ba-Cu samples.

2. The superconducting sample of $Y_1Ba_2Cu_3O_{7-\delta}$ was synthesized at the Physicotechnical Institute of Low Temperatures, Khar'kov, by sintering powdered $Y_2O_3BaO_2$ and CuO in flowing oxygen at 950°C. An x-ray structural analysis showed that the orthorhombic phase makes up at least 97% of the initial sample, and the size of an individual crystallite is ≈ 10 μm. In the course of the optical experiments we carried out control measurements of the resistivity $\rho(T)$. In a first cycle of measurements (sample I) the temperature of the superconducting transition was 98 K, and its width 1.5 K. "Cathodoexcitation" of sample I at a total dose ~ 2000 J/cm^2 (over 2 months) did not alter its resistive characteristics. A subsequent increase in the dose to 3000 J/cm^2 resulting in a lowering of the superconducting transition temperature to

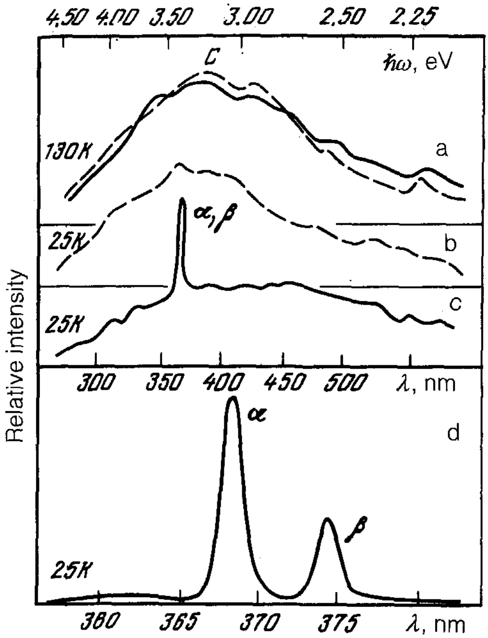

FIG. 1. Solid lines—Emission spectra of the $Y_1Ba_2Cu_3O_{7-\delta}$ sample in the orthorhombic phase (sample I); dashed lines—in the tetragonal phase (sample III). Spectrum *b* was recorded with a large scanning step (50 Å), so lines α and β have merged. The spectra have been collected for the spectral sensitivity of the photocathode of the FÉU-100 photomultiplier.

94 K and a broadening of the transition to 3.5 K (sample II). The temperature dependence of the resistance of sample II remained the same in the region of metallic behavior ($T > 102$ K). This behavior of $\rho(T)$ after prolonged bombardment with electrons agrees with the interpretation that the concentration of lattice oxygen decreases during radiative damage of Y-Ba-Cu samples.[4] After the completion of a systematic cycle of optical measurements with sample II over 3 months, we subjected the sample to a rapid quenching at 850 °C in liquid nitrogen and put it in a tetragonal phase. In the tetragonal phase ($Y_1Ba_2Cu_3O_{7-\delta}$ with a large oxygen deficiency, $\delta > 0.4$), the superconducting properties of the sample were suppressed almost completely (sample III).

Experiments involving electron bombardment of samples I, II, and III were carried out with the help of an optical vacuum cryostat with an adjustable temperature. The working vacuum was 10^{-7} Torr. The electron energy was varied from 0.7 to 1.3 keV at current densities of about 10–20 $\mu A/cm^2$. The emission was detected over the range 250–700 nm (4.9–1.7 eV) by a KSVU-23 computer-controlled spectral complex. The temperature dependence of the intensity in the spectrum at a fixed emission wavelength was recorded on an *x, y* chart recorded.

3. Figure 1 shows emission spectra of the orthorhombic (I) and tetragonal (III) samples. At $T = 130$ K (the normal phase of the samples), spectra I and III take the form of a broad-band continuum *C*, which begins near 5 eV and extends in the long-wavelength direction below 1.7 eV, with a noticeable red asymmetry. The maximum of *C* is at 400 nm (3.1 eV). The continua of samples I and III (Fig. 1a) are essentially similar. At low temperatures (25 K), the intensity of C decreases. For superconducting transition I, two narrow emission lines, α and β, at 3.36 eV and 3.31 eV, typically appear at $T < T_c = 98$ K (Fig. 1, c and d). The amplitude intensity of line α exceeds the intensity of the continuum (at the normal slit of the monochromator), while that of the β line is slightly weaker. The ratio of the α and β intensities generally depends on the energy of the exciting electrons (on their penetration depth). In the tetragonal sample, III, with a large oxygen deficiency, lines α and β are essentially absent (one can discern traces of these lines with an amplitude less than 1/15 of the intensity of the continuum (Fig. 1b). We might note in this connection that as the lattice oxygen is removed during the electron bombardment, the intensities of the α and β lines in sample II also fall off gradually. At the end of the measurement cycle, the intensity of the α line in sample II has fallen to a level half the initial level for the sample. The appearance of the α and β lines in the superconducting phase is therefore directly related to lattice oxygen. According to x-ray-structural data on single crystals,[5] the probability for oxygen to fill all identical positions is identical in the tetra and ortho modifications, except for sites along linear chains (the b axis). It might therefore be suggested that holes involving O1 oxygen are responsible for the appearance of the α and β lines.

4. Since it was possible to observe structural changes at the transition from the normal to the superconducting state, it became an urgent matter to carry out a detailed study of the temperature dependence of the continuum, $C(T)$, and that of the lines, $\alpha(T)$ and $\beta(T)$. Figure 2 shows $C(T)$ and $\alpha(T)$ for the orthorhombic superconducting modification (sample I), along with $C(T)$ for the tetragonal modification (sample III). The temperature dependences for sample I demonstrate pronounced changes at the superconducting transition: At the transition, $C(T)$ decreases sharply (by $\sim 40\%$), but this intensity then remains constant, independent of T, as the sample is cooled further. The temperature dependence $\alpha(T)$ involves a threshold. The α line arises abruptly at the superconducting transition at 98 K. As the temperature is then lowered, $\alpha(T)$ increases monotonically. Near 30 K, the intensity of the α line reaches saturation. For degraded sample II, the jump in the α line becomes noticeably smaller as its intensity decreases. [The curves of $\alpha(T)$, as the sample is cooled below 30 K and then heated, do not coincide; there is an asymmetric hysteresis. During heating, $\alpha(T)$

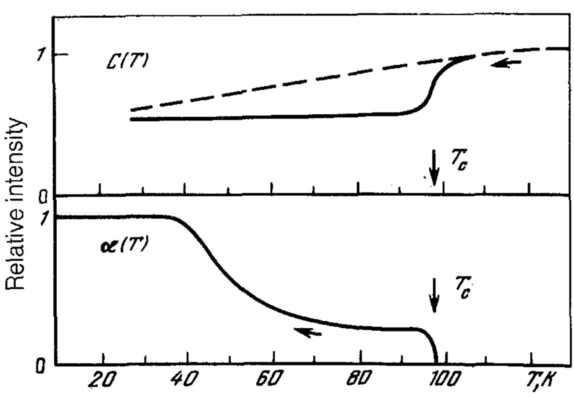

FIG. 2. Solid lines—Temperature dependence of the intensity of the continuum, C, and of line α for sample I; dashed line—that for sample III. The $C(T)$ curve was measured at the maximum in an interval ~ 100 cm^{-1} wide; $\alpha(T)$ was found by subtracting the continuum from the total signal at 3.36 eV.

remains constant up to the superconducting transition and then drops to zero abruptly at this transition.]

The α line is essentially absent from sample III, and the behavior of the continuum $C(T)$ is different from that for sample I. Beginning at high temperatures (130 K), $C(T)$ decreases monotonically, and it does not exhibit any structural features near T_c. Over the entire region, the C intensity depends on T.

In summary, although the microscopic nature of the emission has not been identified, we can assert that both the continuum and the line emission are intrinsic. Structural features on the curves of $C(T)$ and $\alpha(T)$ near T_c are associated with the superconducting transition. A suppression of the superconductivity erases the structural feature near T_c and causes a radical change in the temperature dependence of the continuum. The structural changes in the spectrum of the electron-photon emission at the superconducting transmission may reflect changes in the energy structure of $Y_1Ba_2Cu_3O_7$ upon the formation of the superconducting phase.

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