Electronic excitations and luminescence of $Y_1Ba_2Cu_3O_7$ superconducting metal-insulator ceramics[1)]

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Luminescence and nonradiative transitions accompanied by the production of defects have been observed for the first time in a superconducting metal-insulator system in which a broad energy gap lies above a nearly filled valence band. The particular material was $Y_1Ba_2Cu_3O_7$. At 10 K, an emission is observed at 3.355 eV. This emission may involve a Bose condensation of biholes.

In early 1987, Wu, Chu, *et al.*[1] produced Y-Ba-Cu-O ceramics which are superconducting at liquid-nitrogen temperature and which were shown in Ref. 2 to have a distorted perovskite structure. The mechanism responsible for the superconductivity of these new materials has not yet been established.

In May of 1987 we synthesized (by analogy with Ref. 3) $Y_1Ba_2Cu_3O_7$ ceramics which lose their resistance abruptly at $T_c = 93$ K and which exhibit a well-defined Meissner effect. These ceramics were synthesized from high-purity Y_2O_3, $BaCO_3$, and CuO by a method of solid-phase reactions, by baking in an oxidizing atmosphere some tablets pressed at high pressure.

In the case of $Y_1Ba_2Cu_3O_7$, we studied nonequilibrium processes driven by electrons with an energy of 6 keV and by photons with an energy of 3–17 eV, for the first time in a superconducting oxide ceramic. Using the experimental apparatus described in Ref. 4, we carried out the first study at 10–300 K of the cathodoluminescence and

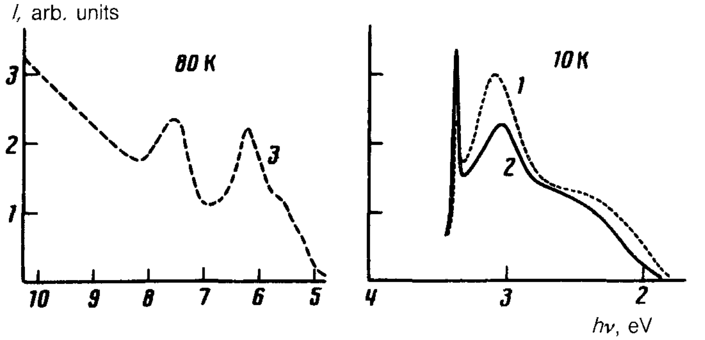

FIG. 1. Photoluminescence spectra of the ceramic $Y_1Ba_2Cu_3O_7$ measured at 10 K during excitation by photons with energies of (1) 4.88 eV and (2) 3.96 eV; 3—excitation spectrum of the broad-emission near 3 eV, measured at 80 K during the application of equal numbers of photons at various energies.

photoluminescence of ceramic samples 1 cm in diameter and 1 mm thick. The cathodoluminescence and photoluminescence spectra at 10 K (Figs. 1 and 2) have an intense, narrow line at 3.355 eV and broad-band emission at 2.2–3.2 eV, below which it is possible to distinguish a continuum, two orders of magnitude weaker, with a sharp short-wave edge at 3.9 eV. The line 3.355 eV, whose half-width is smaller than the instrumental linewidth (6 meV), shifts slightly in the long-wave direction and undergoes a pronounced thermal quenching upon heating to $T > 0.5T_c = 46$ K. At higher temperatures, we can distinguish a weak line at 3.31 eV in the spectra. This line is finally quenched by 170–180 K. The excitation spectrum of the broad-band emission with a peak at 3 eV (Fig. 1) at 80 K spans the region from 4.9 to 10.5 eV and is excited

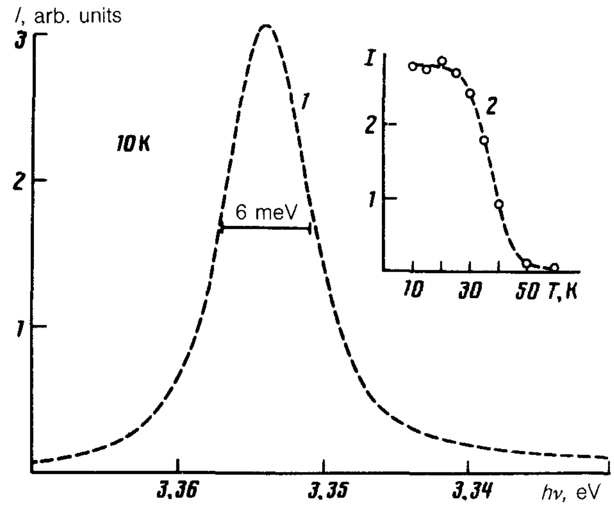

FIG. 2. 1—Luminescence spectra of the ceramic $Y_1Ba_2Cu_3O_7$ excited at 10 K by 6-keV electrons; 2—temperature dependence of the peak intensity of the cathodoluminescence at 3.355 eV.

with a significantly higher efficiency by 16.7-eV photons. At 10 K, the emission at 3.355 eV is strongly excited by the 4.88- and 3.96-eV mercury-discharge lines (Fig. 1). The emission lasts less than 3×10^{-9} s. After prolonged bombardment with an electrom beam, a surface layer of the ceramic suffers damage, and the line and broad-band emission become irreversibly weaker. The emission from the superconducting ceramic differs fundamentally from the intrinsic emission of wide-gap insulators.[5] The temperature-independent and weak continuum background with a sharp short-wave edge at 3.9 eV results from intraband radiative transitions in the nearly filled v band of the metallized ceramic. The Fermi level for the v-band electrons is apparently $E_F = 3.9$ eV. Inverse transitions in the v band give the ceramic its black coloring. The broad-band emission peaking at 3 eV probably corresponds to electron transitions from one of the unfilled (in the absence of excitation) c bands (yttrium) into unfilled high-lying levels of the v band. The narrow 3.355-eV line can be interpreted as the radiative recombination of electrons from a c band (barium) with hole that appear during bombardment or, possibly, with a Bose condensation of biholes near the Fermi level of the v band. From the sign of the thermal emf, measured at 300 K by a hot-spot method, we reach the conclusion that our $Y_1Ba_2Cu_3O_7$ samples have a p-type conductivity. A p-type thermal emf was described for $La_{1.85}Sr_{0.15}CuO_4$ in Ref. 6 at 40–80 K.

It can be concluded from these results and from an analysis of the crystal-chemistry structure of $Y_1Ba_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$ that these high-temperature superconducting ceramics should be regarded not as ordinary superconducting metallic systems but as metal-insulator crystals which combine features of a metal with incompletely filled v bands and features of wide-gap insulators with an energy gap (g). It follows from the data given in Ref. 7 for metallic lead and $Y_1Ba_2Cu_3O_7$ that the state densities near the Fermi surface are approximately the same, but the critical temperatures T_c differ by an order of magnitude. We believe that the high value of T_c is related to the large effective mass of the current carriers for systems with a nearly filled v band. The slow motion of heavy carriers may result in a strong interaction with the surroundings and in a pairing in a group of heavy carriers, accompanied by the appearance of a broad energy gap ($\sim$20 meV) and a relatively small length scale of the Cooper pairs (2–3 nm). Various mechanisms for the appearance of a group of Cooper pairs at high temperatures have been discussed by theoreticians in many places.[8]

The observation of a wide energy gap of the dielectric type in $Y_1Ba_2Cu_3O_7$ not only raises the possibility that various types of recombination emission will occur but also raises the possibility of a nonradiative annihilation of electronic excitations, accompanied by the evolution of heat (the quantum yield of the types of emission which we observed is on the order of 0.1% even at 10 K) and the production of Frenkel radiation defects. The accumulation of these defects could disrupt the structure of the superconductor. The latter effect manifests itself strongly in alkali halide crystals,[9] but is not found in radiation-resistant MgO, Al_2O_3, and Y_2O_3 crystals.[9] In this regard, the ceramic $Y_1Ba_2Cu_3O_7$ takes an intermediate position, according to our observations.

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