Photostimulated changes in Raman scattering of $YBa_2Cu_3O_{7-\delta}$

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Photostimulated changes in the spectra of two-magnon scattering of light by $YBa_2Cu_3O_{7-\delta}$ films have been studied. The intensity of the two-magnon scattering band is reduced by an Ar^+ laser beam. The changes observed in the Raman spectra are long-lived: It takes 2 days for the samples to relax to their original state, before the illumination, at room temperature.

Studies of the semiconducting phases of the high-T_c superconducting compounds by Raman spectroscopy have revealed a broad band of B_{1g} symmetry in the high-frequency part of the spectra.[1-3] This band has been attributed to a scattering of light by two-magnon excitations. As was reported in Refs. 2 and 3, however, two-magnon scattering of light, with an intensity depending on the oxygen concentration, is also observed in superconducting samples. One might accordingly suggest the possibility of a coexistence of a magnetic order and a superconductivity, and one might suggest that high-energy spin fluctuations are involved in the mechanism for the pairing of charge carriers. More recent studies[4] have shown that a two-magnon scattering of light in superconducting $YBa_2Cu_3O_{7-\delta}$ samples can be observed because of the nonuniformity of the oxygen content, i.e., because of the existence of macroscopic regions in which the oxygen concentration corresponds to a semiconducting phase. Analysis of their reflection spectra and the Raman scattering spectra of different parts of a $YBa_2Cu_3O_{7-\delta}$ single crystal ($T_c \approx 60$ K) suggests that the two-magnon scattering band weakens and disappears with increasing density of free carriers (with decreasing δ).

It was shown in Ref. 5 that photoexcitation of carriers may be thought of as a

method for varying the density of free carriers and for increasing the amount of superconducting phase in a semiconducting $YBa_2Cu_3O_{7-\delta}$ sample. It was also shown that this mechanism is unrelated to a change in the chemical composition of the material. Our purpose in the present study was to determine how the light-induced carriers affect the intensity of two-magnon scattering of light.

We studied $YBa_2Cu_3O_{7-\delta}$ films with thicknesses greater than 1000 Å which were grown by laser deposition on $SrTiO_3$ substrates. Silver contacts deposited on the surfaces of the films made it possible to measure the electrical resistance in various regions. The Raman scattering was excited by an Ar^+ laser ($\nu_{exc} = 20\,492\ cm^{-1}$). Lines of the plasma discharge were removed from the laser beam by means of a diffraction grating. The dimensions of the excitation region on the surface of the sample were 0.1×2.5 mm. The beam power did not exceed 0.08 W/mm^2. The Raman spectra were recorded by a Jobin–Yvon U1000 spectrometer with single-channel photon counting.

Figure 1 shows a spectrum of the Raman scattering of light by a superconducting $YBa_2Cu_3O_{7-\delta}$ film ($T_c = 88$ K) at room temperature. There is a broad structural feature in the high-frequency region: a band of two-magnon scattering with a peak frequency $\omega_{max} \approx 2500\ cm^{-1}$ (these spectra have not been corrected for the spectral sensitivity of the photomultiplier and the spectrometer). This band is evidence of an impurity semiconducting phase in the sample.

For the first time, our measurements have revealed that the two-magnon band is weakened by laser light. Figure 2 shows the time evolution of the intensity of the

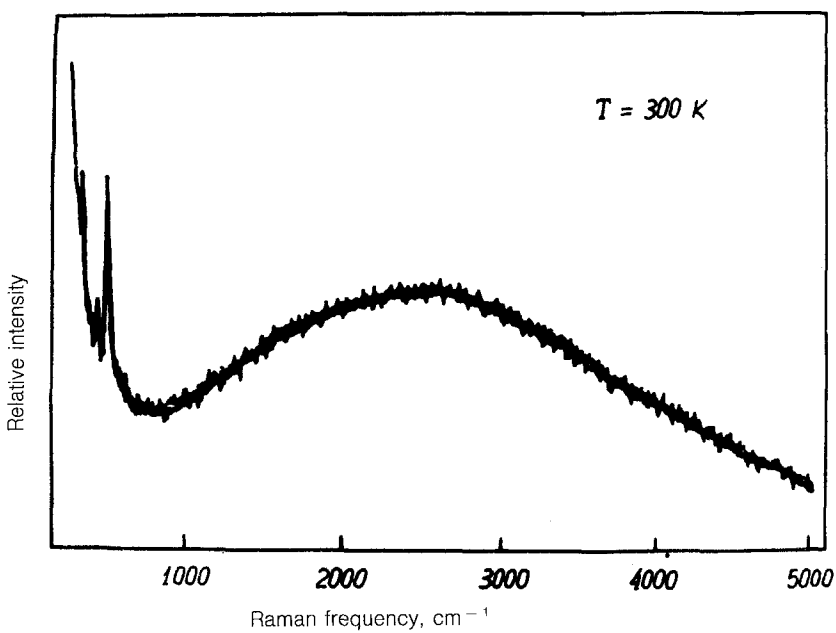

FIG. 1. Raman scattering spectrum of ceramic $YBa_2Cu_3O_{7-\delta}$ ($T_c = 88$ K) at room temperature.

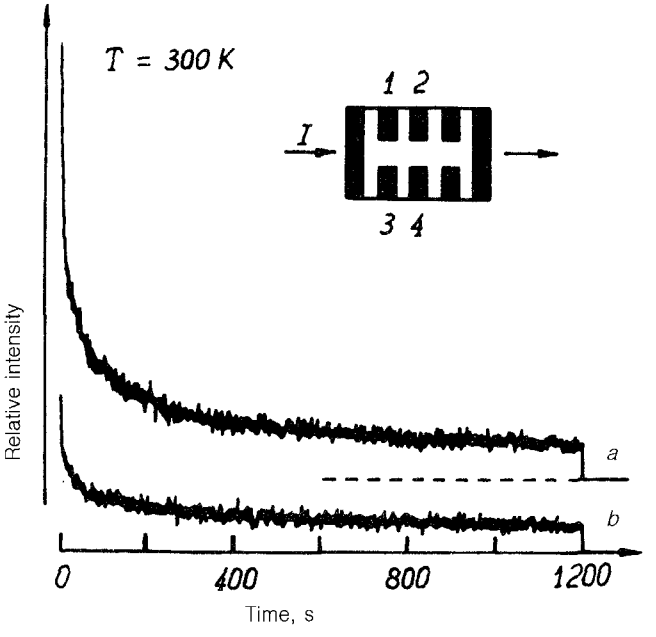

FIG. 2. Time evolution of the intensity of the two-magnon band for an inhomogeneous $YBa_2Cu_3O_{7-\delta}$ film. a—For the region between contacts *1* and *2* ($T_c = 84.6$ K); b—for the region between contacts *3* and *4* ($T_c = 88.1$ K).

Raman signal at the frequency corresponding to the peak of the two-magnon band as found from two regions on an inhomogeneous $YBa_2Cu_3O_{7-\delta}$ film. The illumination of the sample begins at the origin of the time scale. The laser beam is fixed in place between contacts *1* and *2*, with $T_c = 84.6$ K in this region, and also between contacts *3* and *4*, with $T_c = 88.1$ K. We see from this figure that the weakening of the intensity of the two-magnon band becomes less apparent as T_c increases.

The changes observed in the Raman spectra persist for a long time. At room temperature, it takes a sample 2 days to return to its original state, before illumination. The dynamics of this relaxation is shown by Fig. 3; curve *b* was obtained 1 h after the previous illumination, and curves *c* and *d* were obtained 16 h and 24 h, respectively, after the previous illumination. A lowering of the temperature leads to an increase in the relaxation time: Curve *f* was recorded at $T = 28$ K, 24 h after the initial illumination. As the temperature is raised above room temperature, the time required to return to the unilluminated state decreases substantially. When the sample is briefly heated to 400 K and then cooled in air, its original properties are completely restored.

The effect of IR laser light (1.38 eV) and that of Ar laser light (2.41 eV) on the electrical resistance and structure of high-T_c superconducting ceramics were studied in Ref. 6. It was found by x-ray measurements that a fairly brief illumination (for $\approx$600 s) causes a transition of the initial tetragonal phases of $YBa_2Cu_3O_{7-\delta}$ and $HoBa_2Cu_3O_{7-\delta}$ to superconducting orthorhombic phases with $T_c \approx 90$ K. At a high power of the laser light, however, the samples were heated to $\approx$600 °C, so it was not

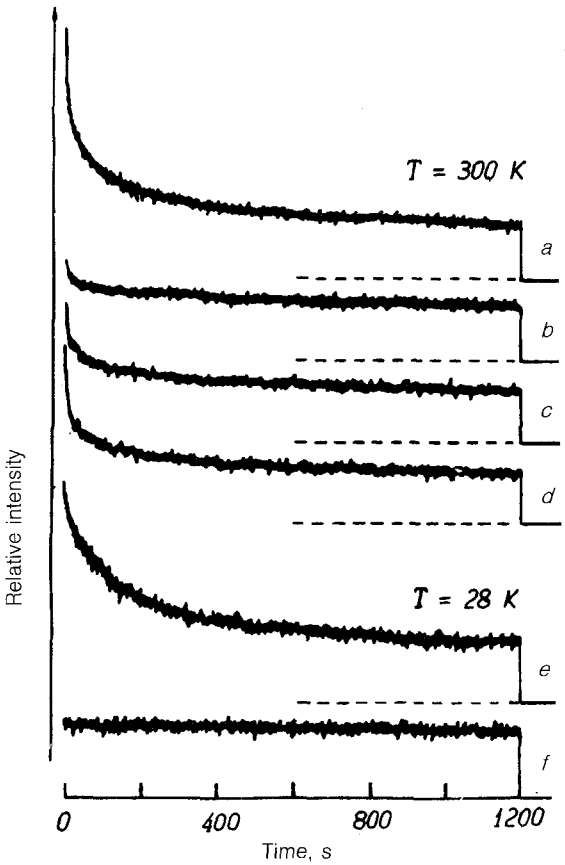

FIG. 3. Time evolution of the intensity of the two-magnon band of a $YBa_2Cu_3O_{7-\delta}$ film at temperatures of 300 and 28 K. a,e—Initial illumination; b,c—recorded 1 h and 16 h after the preceding illumination; d,f—recorded 24 h later.

possible to distinguish the effect of the illumination from the thermal effect in the atmosphere of air. Our own measurements, on samples immersed in superfluid helium, have shown that the effect which we observe is not due to a heating.

There are various ways to explain the observed effect, but the explanation which we find most attractive is based on an interaction of photoexcited carriers with the crystal lattice. Studies[7,8] of the spectra of photoinduced IR absorption in the semiconducting phases of high-T_c superconductors lead to the conclusion that the photogeneration of free carriers is equivalent to a decrease in δ in $YBa_2Cu_3O_{7-\delta}$ systems. The photoexcited carriers recombine with neutral defects, which may be associated with the presence of grain boundaries, structural defects, and deviations from stoichiometry in ceramic materials and films. The localization of carriers at defects results in the formation of charged defects[9] and in local orthorhombic structural distortions in the vicinity of these defects. Evidence that there are orthorhombic distortions (spanning several lattice constants) in the tetragonal phase of a $YBa_2Cu_3O_{7-\delta}$ crystal

($\delta = 0.75$–0.85) comes from the appearance of lines[7,8] with frequencies of 435 and 510 cm^{-1} in the spectra of photoinduced IR absorption. These lines correspond to completely symmetric Raman modes of the orthorhombic phase. Taking account of the results presented above on IR absorption, the observation[5] of a "frozen" photoconductivity in $YBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0.55$) films, and the oxygen inhomogeneity of our test samples, we can offer a suggestion about what happens in macroscopic nucleating regions in which the oxygen concentration is close to the semiconductor–metal transition. In these regions, the overlap of the photoinduced distortions and the local orthorhombic distortions associated with the excess oxygen (beyond $\delta = 1$) results in a change from a tetragonal structure to an orthorhombic structure over the entire volume of the nucleating region. As a further result, the magnetic order is destroyed.

We believe that the explanation offered here for the changes in the two-magnon scattering during the exposure to light also applies to the so-called frozen photoconductivity.[5]

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