

Photoinduced-reflection spectroscopy of insulating La_2CuO_4 single crystals

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Photoinduced optical transitions in La_2CuO_4 single crystals can be detected by a method based on a differential reflection of light. Light-induced electronic transitions have been observed in the spectral interval 0.1–0.6 eV. At a high excitation level, the intensity ratio of the low-energy transitions and the 0.55-eV transition is a stronger than linear function of the intensity of the exciting light. Photoinduced transitions are discussed on the basis of a model of spin-polaron complexes.

Studies of the photoinduced absorption spectra in the semiconducting phases of high- T_c superconductors have shown that a hole introduced in the valence band by doping or optical excitation forms a self-localized state in the band gap of the crystal.^{1–3} As a result, an absorption band appears in the mid-IR part of the spectrum, as do local phonon modes. The experimental results have been explained on the basis of a polaron model of the self-localized state.^{2–4} In the case of La_2CuO_4 (the 2-1-4 compound), however, a theoretical prediction of the optical conductivity spectrum⁴ which has been offered to describe the line at 0.5 eV is substantially at odds with the experimental results in the energy interval 0.1–0.3 eV. Mihailovic *et al.*⁴ attributed this discrepancy to the low quality of the 2-1-4 samples which had been studied previously, but recent measurements have revealed an even greater discrepancy between theory and experiment.¹ The reason for this discrepancy may be methodological: The studies of photoinduced absorption actually involved measurements of the transmission spectrum of a 2-1-4 powder in a matrix of KBr or CsI. The photoinduced change in the coefficient for the reflection and scattering of light by the 2-1-4 grains, $\approx 1 \mu\text{m}$ in size, was disregarded. The wavelength of the light in the region in which the polaron theory is at odds with experiment is at this scale, specifically, $4 \mu\text{m}$ in KBr for $\hbar\omega = 0.2$ eV. A change in the scattering of light as the result of the appearance of a photoinduced polaron transition corresponding to 0.5 eV may thus reduce the transmission of light by the powder in the spectral interval 0.1–0.3 eV. Accordingly, homogeneous single crystals must be studied in order to determine whether the discrepancy between the polaron model and experiment is a manifestation of additional photoinduced electronic transitions or is instead determined by a change in the scattering of light.

In practice, it is difficult to use the optical transmission method in the case of bulk crystals. We accordingly studied the photoinduced reflection spectra of 2-1-4 single crystals. The $\text{La}_2\text{CuO}_{4+x}$ crystals, grown by the method of Ref. 5, had dimensions of $4 \times 4 \times 4$ mm and a Néel temperature $T_N = 250$ K. A composition close to stoichiometric was achieved by annealing the original crystals at $T = 600^\circ\text{C}$ for 4–6 h in a

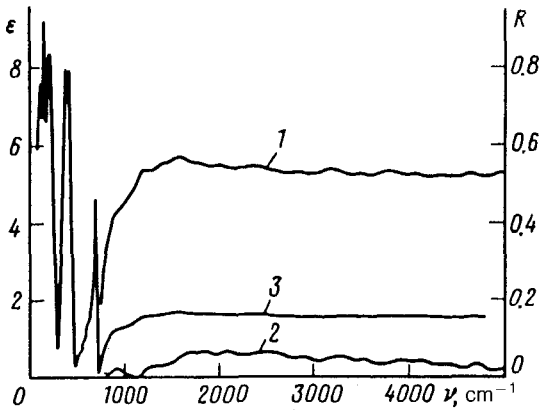


FIG. 1.

vacuum of 1 Pa. The resulting samples had $T_N=318$ K. According to the dependence of T_N on the dopant concentration,⁶ the oxygen content in these samples was $x \approx 0$. Spectra of the photoinduced reflection were measured by a Fourier spectrometer in the range 35–600 meV at $T=5$ K. The ratio of reflection spectra $R_1(\nu)/R(\nu)$ was measured. Here $R_1(\nu)$ is the spectrum found when the crystal is illuminated with an auxiliary beam from a He–Cd laser ($\hbar\omega=2.8$ eV), and $R(\nu)$ is the spectrum found without this laser excitation. We thus find the spectrum of the photoinduced reflection: $\Delta R/R = [R_1(\nu) - R(\nu)]/R(\nu)$.

Figure 1 shows the reflection spectrum $R(\nu)$ in the polarization $E \parallel C$, along with spectra of the real and imaginary parts of the dielectric constant, $\epsilon_1(\nu)$ and $\epsilon_2(\nu)$, respectively. The latter two properties were found by Kramers–Kronig transformations from the reflection spectrum measured between 0.005 and 3 eV. No free-carrier component was found in these spectra in the region 0.005–0.6 eV. In the mid-IR region (0.09–0.5 eV), $\epsilon_2(\nu)$ is small and satisfies $|\epsilon_1| \gg \epsilon_2$. In general, the photoinduced reflection is determined by changes in both ϵ_1 and ϵ_2 , but under the condition $|\epsilon_1| \gg \epsilon_2$ we have $dR/R \approx 2d\epsilon_1/[(\epsilon_1 - 1)\epsilon_1^{1/2}]$. We use the standard approximation of $\epsilon_1(\nu)$ in the mid-IR range of a dielectric crystal as a set of Lorentzian oscillators: $\epsilon_1(\nu) = \epsilon_\infty + \sum \alpha_i N_i (E_i^2 - \nu^2) / [(E_i^2 - \nu^2)^2 + \Gamma_i^2 \nu^2]$, where $\alpha_i = 4\pi e^2 / m_i^*$, N_i is the concentration, E_i is the resonant frequency, and Γ_i is the damping of the i th electronic transition. We find that the photoinduced reflection is proportional to the photoinduced changes in the oscillator density, dN_i : $dR/R \approx \sum A_i(\nu) dN_i$.

Figure 2a shows a spectrum of the photoinduced reflection of a stoichiometric 2-1-4 single crystal in the polarization $E \perp C$ ($T=5$ K) at a laser power density $I_0=0.2$ W/cm². In addition to the known transition at 0.55 eV, we find some photoinduced electronic transitions in the interval 0.1–0.3 eV, which are predominant in the spectrum. The discrepancy between experiment and the polaron theory⁴ thus implies that the model of a self-localized state in the semiconducting phase of the high- T_c superconductor must be refined.

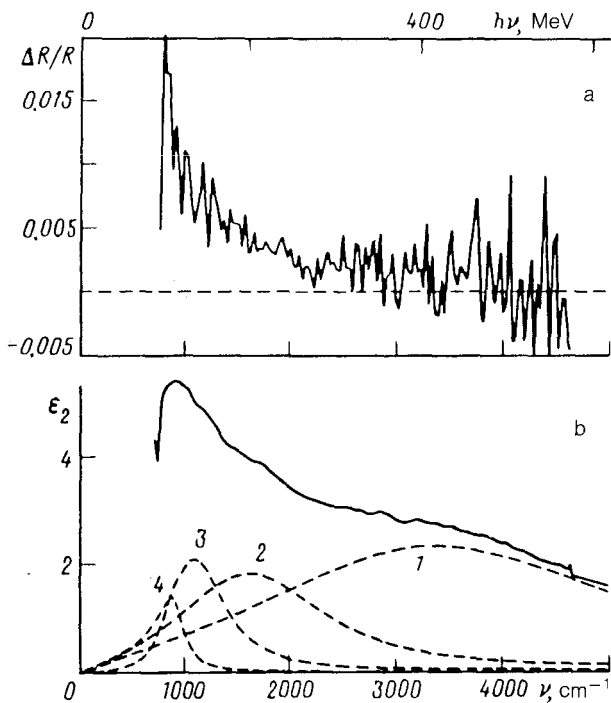


FIG. 2.

Further study of oxygen-doped homogeneous 2-1-4 single crystals ($T_N=250$ K) showed that the mid-IR absorption which arises upon doping can be described by a contribution of several Lorentzian oscillators which are active in the polarization E1 C. In Fig. 2b, this absorption is approximated by four oscillators with different partial weights. A point of particular importance for our purposes is that the number of these oscillators is greater than one. The qualitative agreement between the photoinduced reflection spectrum of the undoped, stoichiometric single crystal and the IR spectrum of an oxygen-doped crystal (Fig. 2) indicates that the same factor is responsible for the changes in the spectra in the two cases.

Kim *et al.*¹ found that the intensities of the photoinduced transitions at 0.16 and 0.62 eV depend in the same way on the laser power density: I^α , where, in particular, we have $\alpha=0.25$ at $T=4.2$ K. We obtained a similar result for the photoinduced reflection spectra of the 2-1-4 compound at $I \leq 50$ mW/cm². At higher values of I , however, we found that the dependence of the intensity of the low-energy transitions, A_1 , divided by the intensity of the 0.55-eV transition (A_2 ; see Fig. 3), is stronger than linear: $A_1(I) = \text{const } A_2(I)^\beta$, where $\beta > 1$.

We believe that a hole generated by the light undergoes a self-localization, forming a self-localized state in the band gap of the crystal at a distance of 0.55 eV away from the top of the valence band. The low-energy transitions probably correspond to

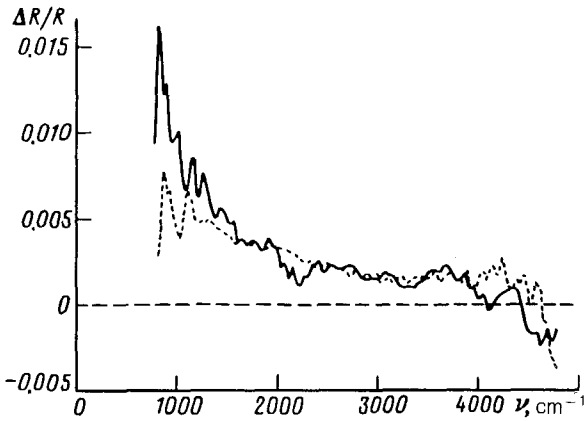


FIG. 3.

multiparticle complexes of self-localized states, in view of the stronger than linear increase in the intensity ratio of the low-energy transitions and the 0.55-eV transition as the density of photocarriers is raised. Such a process, resulting from multiparticle collisions of holes, may occur at a hole density greater than or comparable to the dark density of hole complexes.

The presence of local phonon modes in the photoinduced absorption spectra³ indicates a relaxation of the crystal lattice near the hole. This relaxation is probably governed by a Coulomb interaction of the hole with crystal ions; i.e., we are talking about polarons. However, a calculation of the polaron absorption⁴ to describe the 0.55-eV line does not explain the transitions at 0.1–0.3 eV, which appear to be multiparticle complexes of the 0.55-eV state. The formation of complexes from polarons would be hindered by their Coulomb repulsion; some long-range attraction of polarons would have to be invoked. As one explanation we suggest looking at the results of research on the magnetic properties of the semiconducting phase of high- T_c superconductors. These results demonstrate the need to consider the spin interaction of a hole with copper, which may also lead to the formation of a self-localized state in the form of a ferron⁷⁻⁹ (a spin polaron¹⁰), which is a ferromagnetic cluster 30–40 Å in diameter.^{8,9} Wood and Cooke¹⁰ have discussed the possibility in principle of a pairing of spin polarons. Such a pairing would yield a qualitative explanation of the presence of several photoinduced transitions in the energy interval 0.1–0.6 eV and the behavior of their properties as a function of the excitation level. The self-localized hole states would apparently include both a spin relaxation and a lattice relaxation.

In summary, we have studied photoinduced transitions in single crystals of cuprate oxides. This study has made it possible to rule out the plausible suggestion that light scattering affected the results of previous studies of powders. It has been shown that several photoinduced transitions occur in the energy interval 0.1–0.6 eV in nearly stoichiometric La_2CuO_4 . In addition to the identical behavior of the intensities of these transitions as a function of the power density of the optical excitation, I , which has

been established in previous studies, we have found that the intensity ratio of the low-energy transitions and the 0.55-eV transition increases faster than linearly at high values of I . We have suggested that polaron effects as well as a spin interaction, i.e., a model of ferrons and multiparticle complexes thereof, should be taken into account in order to explain the photoinduced electronic transitions.

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