# Optical properties of CuO single crystals

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Structural features have been observed in the absorption spectra of single crystals of the antiferromagnetic semiconductor CuO in the interval 0.08–1.50 eV. The nature of these features is discussed in connection with the known spectra of high-temperature superconductors based on CuO and the spectra of $3d$-antiferromagnetic insulators.

An important role is played by Cu-O–Cu bonds in the properties of high-temperature superconductors based on CuO. The reflection and absorption spectra of CuO single crystals in the interval 0.08–1.50 eV have been studied on a computer-controlled IKS-21 spectrometer in an effort to learn about the nature of these bonds. A band of absorption and optical-frequency conductivity (0.3–0.5 eV) is observed[1,2] in high-temperature superconductors in this interval. This band may be due to electronic excitations which are responsible for superconductivity.[2–4] There has been only one previous study[5] of the optical properties of CuO. There the reflection spectrum of a polycrystalline CuO sample was measured at energies below 0.08 eV (the phonon spectrum).

The CuO single crystals, with dimensions of $8\times3\times2$ mm, were grown from a molten solution. Some typical values of the monoclinic crystal lattice of CuO are $a = 4.77$ Å, $b = 3.88$ Å, and $c = 5.00$ Å. The angle between the $a$ and $c$ axes is 99.5°. Neutron-scattering data[6] show that CuO is an antiferromagnet ($T_N = 230$ K) with a complex magnetic structure. The antiferromagnetic bond in the Cu–O–Cu chains forms an angle of 146°; the bond between nearest-neighbor Cu ions is ferromagnetic. The crystals were polished along the (110) plane, which contains the $c$ axis.

The electrical resistivity of the CuO single crystals along the $c$ axis at room temperature is $10^2$ Ω·cm, and by 100 K it has increased to $10^{12}$ Ω·cm. The anisotropy of the resistance at 293 K is $\rho_{\perp c}/\rho_{\parallel c} = 1.7$. The activation energy $\epsilon_a$ near 293 K varies over the interval 0.12–0.16 eV for the various samples. Near 190 K, there is an obvious slope change on the $\log\rho(1/T)$ curve. During cooling, $\epsilon_a$ increases to 0.28–0.30 eV and remains constant down to 100 K. All of the CuO samples exhibit a $p$-type conductivity and a low charge-carrier mobility [$<0.1$ cm$^2$/(V·s)].

The reflection spectrum (the inset in Fig. 1) is characteristic of a semiconductor in the region between the interband and lattice absorption regions. In the absorption spectra (Fig. 1) of the CuO single crystal we see an absorption band at $0.220 \pm 0.004$ eV. Superimposed on this band are phonon repetitions with an energy $\sim$0.02 eV ($\sim 160$ cm$^{-1}$), which corresponds to a low-energy phonon band which has been observed in the spectra of CuO, $La_2CuO_4$ (Ref. 5), and $YBa_2Cu_3O_{7-\delta}$ (Ref. 7) and which in the latter compound undergoes a softening at the transition to the supercon-

  

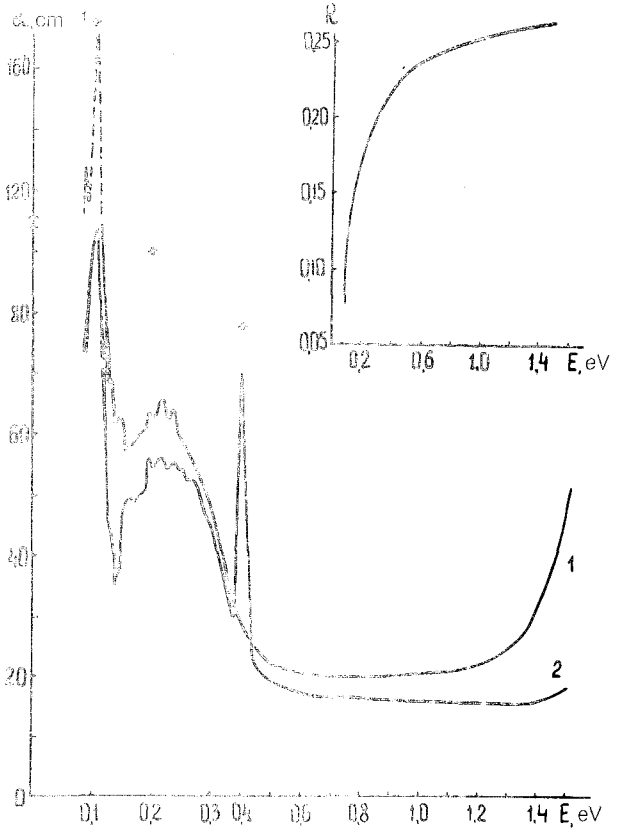


FIG. 1. Absorption spectra of a CuO single crystal at (1) 293 K and (2) 80 K. The dashed line shows the spectrum in polarized light with $\mathbf{E}\|c$. The inset shows the reflection spectrum.

ducting state. The absorption band at $0.086 \pm 0.003$ eV, whose phonon repetitions are observed, is split by its own first repetition only in polarized light ($\mathbf{E}\perp c$ or $\mathbf{E}\|c$) and is possibly associated with an intracenter transition in the Cu ion (without a charge transfer).

Near the band at 0.22 eV we see a significant linear dichroism for light polarizations parallel to and perpendicular to the $c$ axis, which reaches $(\alpha_{\|} - \alpha_{\perp})/\alpha \approx 30\%$. This result indicates that the transition is of an electric dipole nature. From the shape of the spectrum and the $\rho(T)$ dependence we can conclude that the extrinsic absorption threshold is $\sim 0.14$ eV. This value is close to the activation energy of the electrical resistivity. The temperature dependence of the transmission at 0.14 eV follows the $\rho(T)$ curve with a slope change near $\sim 190$ K. The nature of the absorption anisotropy ($\alpha_{\|} > \alpha_{\perp}$) near the band is the same as that of the anisotropy in the electrical conductivity. A calculation of the optical-frequency conductivity $\sigma$ reveals a $\sigma$ band which coincides with the absorption band at 0.22 eV. We thus see a correlation between the optical and electrical properties, which is evidence that the band at 0.22 eV is related to the conductivity. Because of the pronounced hybridization of the $d^9$ states of $Cu^{2+}$ with the oxygen valence band, the conductivity with a low carrier mobility and the

presence of a corresponding optical transition are apparently consequences of a $d^9 - d^{10}L$ charge transfer, where $L$ is a hole at an oxygen.[8] The charge-transfer energies estimated from photoemission data[9] for $(La_{0.9}Sr_{0.1})_2CuO_{4-y}$ ($T_c = 34$ K) and $YBa_2Cu_3O_{6.69}$ ($T_c = 90$ K) are 0.4 eV and 0.5 eV, respectively. These results agree with the energies of observed optical transitions in these compounds. Consequently, there are low-mobility charge carriers in CuO, as in high-temperature superconductors.[1]

In the CuO absorption spectrum below $T_N$ a narrow peak arises abruptly at $0.40 \pm 0.01$ eV with a half-width of 0.04 eV. The position of this line does not change with the temperature, within the errors. The temperature at which the peak appears depends on the applied magnetic field (Fig. 2). The intensity of the peak depends on the cooling method and the time interval which elapses between measurements. For example, if, after measurements of the temperature dependence of the peak intensity an the sample is heated (with or without a field), the sample is recooled from a temperature just above $T_N$, the peak shrinks or is not observed at all. A time on the order of a day is required for a repeated observation of the peak after the sample is heated to room temperature. We know[10] that new lines—exciton-magnon or phonon-magnon absorption—appear in the optical spectra of $3d$-antiferromagnetic insulators in the magnetic ordering region. If we are to assume that the band at 0.40 eV is one of the two bands mentioned above, the energy of a magnon in CuO would have to be at least $\sim 1500$ cm$^{-1}$. The Raman scattering spectrum[11] of $La_2CuO_4$ reveals a two-magnon scattering band at $\sim 3000$ cm$^{-1}$ (0.37 eV) with a half-width $\sim 1000$ cm$^{-1}$ (0.12 eV), which is associated with two-dimensional spin fluctuations above $T_N$, in particular, at 300 K ($T_N = 240$ K is the Néel temperature of the three-dimensional antiferromagnetic order). In CuO there can also be a reduced-dimensionality magnetism, but it is probably not related to the apearance of the peak in CuO exclusively below $T_N = 230$

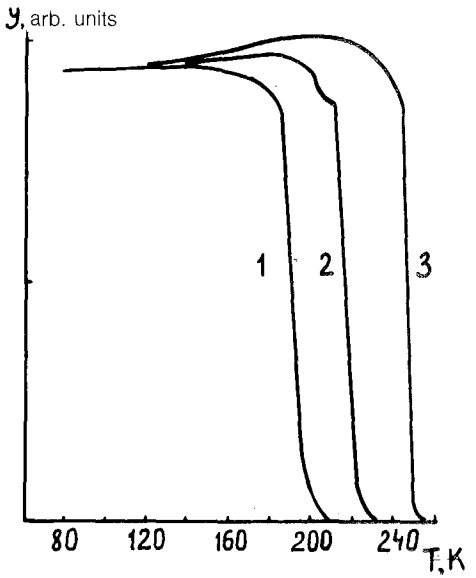


FIG. 2. Temperature dependence of the intensity of the band at 0.40 eV in a magnetic field $H = 1$ kOe. 1—$H = 0$; 2—$H \perp c$, 3—$H \parallel c$.

K. The strong temperature dependence of the peak intensity and the slow relaxation of the intensity may indicate the formation of a magnetic polaron near an oxygen vacancy, i.e., a local ferromagnetic formation in a three-dimensional antiferromagnetic matrix.[12] The interaction between the spins of an oxygen vacancy and Cu ions in the Cu–O–Cu bond leads to a parallel alignment of the spins of the copper ions. A comparatively weak magnetic field (as weak as 1 kOe) promotes this process, shifting the appearance of the peak up the temperature scale. The effect of a field is strongly anisotropic. For example, when the magnetic field is parallel to the $c$ axis, the absorption band exists up to $T = 250$ K, at which we are left with only a short-range antiferromagnetic order. The energy difference between the bands at 0.22 eV and 0.40 eV (0.18 eV) agrees with the increment in the activation energy for the electrical resistivity which accompanies magnetic ordering.

These results permit the conclusion that there is a close correspondence between the optical properties of CuO and those of oxide high-temperature superconductors based on CuO. In these superconductors, the strong Drude absorption by collectivized charge carriers sometimes makes it impossible to identify by an optical method the features which are clearly observable in CuO. Consequently, CuO is an important entity for determining the nature of high-temperature superconductivity and the role of antiferromagnetism.


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