Absorption spectra of CuO single crystals near the absorption edge and the nature of the optical gap in copper oxides

Yu. P. Sukhorukov, N. N. Loshkareva, and A. A. Samokhvalov

Institute of Metal Physics, Urals branch of Russian Academy of Sciences, 620219 Ekaterinburg, Russia

A. S. Moskvin

A. M. Gorkii Ural State University, 620083, Ekaterinburg, Russia

This paper presents the first direct measurements of optical absorption in CuO single crystals near the fundamental absorption edge. The absorption band is of excitonic nature, and the unusual structure of the band edge at high temperature corresponds to a prediction based on the cluster model that transitions with charge transfer responsible for the exciton-like edge of the absorption band in copper oxides including CuO_4 clusters take place between b_{1g} and e_u states. © *1995 American Institute of Physics.*

1. INTRODUCTION

The elementary copper oxide CuO presents a convenient model for studying the semiconducting phase of cuprate high-T_c superconductors and the entire class of oxides of transitional $3d$-metals. The problem of fundamental importance for all these compounds is the nature of the optical gap and, more broadly, of the fundamental absorption band. The first measurements of CuO optical spectra were published relatively recently. IR absorption spectra were studied in detail,[1,2] and the band above the fundamental absorption edge was investigated by the ellipsometric technique.[3]

Most information about their optical characteristics in the 1–3 eV band was derived from ellipsometric and photometric measurements, which do not yield accurate spectra of their optical parameters. Therefore, it is difficult to discover the nature of electronic transitions responsible for the optical parameters in the fundamental absorption band, specifically, the nature of the optical gap.

At the same time, optical spectra of copper-oxide compounds based on CuO_4 clusters are very similar in the 1–3-eV band,[2] although their chemical compositions and crystal structures are very different. This indicates that electron transitions in CuO_4 clusters largely determine the nature of the absorption band, and a simple cluster model may be used.

In square CuO_4 clusters, which are basic units of CuO and copper-oxide HTS and determine their electron spectra, three electric dipole transitions with charge transfer from the $Cu3d$–$O2p$ hybrid b_{1g} ground state to purely oxygen states $e_u(\pi)$, $e_u(\sigma)$ ($E\perp C_4$ polarization) and a_{2u} ($E\|C_4$ polarization) are allowed.[2]

According to cluster model calculations,[2] the transition $b_{1g}-e_u(\pi)$ has the lowest energy, $\hbar\omega\sim1.5$ eV. The energy of the $b_{1g}-a_{2u}$ transition is about 0.5 eV higher, and that of the $b_{1g}-e_u(\pi)$ transition is much higher (~5 eV) and determines the width of the $p-d$ hybrid band in the cluster approximation. The structure of wide bands due to transitions with charge transfer is determined by the three factors: a) states in electron bands; b) electron-phonon interaction; c)

correlation effects. The latter factor is assumed to be responsible for the excitonic nature of charge-transfer absorption spectra, which is commonly observed in copper oxide systems. These combined spectra usually include a low-energy narrow (exciton-like) line due to a transition to a strongly correlated (i.e., localized) state and a high-energy wide band due to a transition to uncorrelated or weakly correlated dissociated state. This phenomenological model presumes the existence of two types of final states and can be formalized in terms of Hirsch's concept[4] of two types of $2p$ oxygen states in oxides-weakly and strongly localized (correlated) states. In Hirsch's semi-empirical model the two final states are incorporated by introducing a pseudospin of 1/2 and an effective Hamiltonian

$$\hat{H} = \omega_1(n)\hat{\sigma}_z + \omega_2(n)\hat{\sigma}_x,$$

where the energy parameters $\omega_{1,2}(n)$ are functions of the hole concentration, n, in the $2p$ shell.

Unlike the common single-particle approach, in this case the probability of the charge-transfer transition depends on the overlap of the initial and final pseudospin ($\pm$) states:

$$P_{12}^{\pm} = P_{12}\begin{cases}\sin^2\dfrac{\beta}{2} \\ \cos^2\dfrac{\beta}{2}\end{cases}, \quad \tan\beta = \frac{\omega_2}{\omega_1}.$$

Electron transitions between a cluster and delocalized states in the lattice lead to broadening of spectral lines to an effective width $\Gamma^{\pm}$, which in a simple model can be expressed in terms of the widths $\Gamma^{\uparrow}$ ($\Gamma^{\downarrow}$) of bands due to transitions to states with definite pseudospin projections if the bandwidth is proportional to the matrix element of the transition from the respective ($\pm$) state:

$$\Gamma^{\pm} = [(\Gamma^{\uparrow})^2 + (\Gamma^{\downarrow})^2]^{1/2}\begin{cases}\left|\sin\left(\dfrac{\beta}{2} + \alpha\right)\right| \\ \left|\cos\left(\dfrac{\beta}{2} + \alpha\right)\right|\end{cases},$$

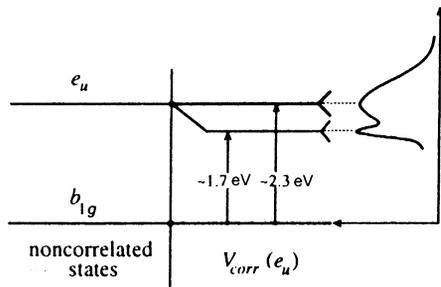where $\tan\alpha = \Gamma^{\uparrow}/\Gamma^{\downarrow}$.

FIG. 1. Diagram of $b_{1g}-e_u$ transitions with charge transfer responsible for the fundamental absorption band.

If the state $(+)$ is strongly correlated and $(-)$ is uncorrelated, $\Gamma^\uparrow \ll \Gamma^\downarrow$. Figure 1 illustrates the model of the exciton-like absorption edge.

The doublets $e_u(\pi)$, $e_u(\sigma)$ due to transitions to states of equal symmetry are classic Jahn–Teller A-E transitions,[5] and their bands should have a complex structure (usually of two bands) corresponding to transitions to two branches of the adiabatic potential of the e_u doublet. The widths and shapes of the lines are determined by both electron–vibron interaction and energy bands. In distorted CuO_4 clusters the degeneracy of e_u states can be lifted by crystal fields of a lower symmetry.

The doublet structure of the 1.5–3-eV absorption band near the fundamental absorption edge was detected in the semiconducting phase of several copper oxide compounds including CuO_4 clusters. In the spectrum of the imaginary part of the dielectric function in $YBa_2Cu_3O_{6.1}$, there is a narrow exciton-like peak centered at 1.7 eV and a broad intense band with a maximum in the 2.1–2.5 eV range.[6] Spectra with a similar shape are observed in semiconducting compounds R_2CuO_4, where R denotes La, Nd, Sm, Eu, or Gd.[7] For example, in Eu_2CuO_4 the exciton peak at 1.6 eV is about 0.3 eV wide, and the wide band due to dissociated states has a peak at 2.1 eV and a width of ~ 1.4 eV at a ratio of oscillator strengths of 1:6.5.

The spectral positions, similar polarization features of these two subbands, and the ratios of their oscillator strengths and widths are strong arguments in favor of the excitonic structure of the absorption edge, and this suggests the importance of correlation effects even in the semiconducting phase of copper oxide compounds.

The lack of observable splitting in these subbands, which should take place in $b_{1g}-e_u(\pi)$ transitions according to cluster models,[2] indicates that the characteristic Jahn–Teller energy is low $(E_{JT} \sim 0.1$ eV), or the splitting due to the crystal field is small and comparable to the widths of the $e_u(\pi)$ subbands. The latter fact derives from the quasi-two-dimensional nature of the compounds and tetragonal symmetry of the CuO_2 plane.

Given the quasi-one-dimensional structure of CuO due to chains in the $[\bar{1}01]$ direction, the nearly rectilinear shape of the Cu–O–Cu bonds $(\theta \approx 146°)$, and nearly rectangular shape of the Cu–O–Cu bonds between chains $(\theta_1 \approx 104°$, $\theta_2 \approx 109°)$,[8] there is a unique possibility of detecting the doublet structure of $b_{1g}-e_u(\pi)$ subbands. This possibility is supported by two more factors:

a) A considerable difference between widths of the two doublet components because the motion of an $e_u(\pi)$ hole from chain to chain is forbidden. One doublet component corresponds to a strongly localized state and is a narrow exciton-like line in the $b_{1g}-e_u(\pi)$ spectrum.

b) The strong effect of interchain exchange on the exchange splitting of the doublet components, hence a considerable effect of three-dimensional antiferromagnetic ordering on the shape of $b_{1g}-e_u(\pi)$ subbands.

A similar effect is essentially ruled out in quasi-two-dimensional copper oxides, where three-dimensional antiferromagnetic ordering is due to exchange between CuO_2 planes.

In this paper we report a direct optical measurement of the fundamental absorption band in CuO in the energy range up to ~ 3.5 eV using unpolarized light, and with polarizations parallel and perpendicular to the c-axis, over the temperature range 80–300 K, including typical temperatures of three-dimensional antiferromagnetic ordering, $T_{N_1} \simeq 213$ K and $T_{N_2} \simeq 231$ K.[8]

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

Samples were cut from CuO single crystals grown from solution in melt. Typical parameters of the CuO monoclinic crystal lattice are given in Refs. 1 and 2. The samples were ground and polished using diamond pastes. Two samples have been investigated. The sample 1 with the larger plane (110) including the d-axis is (41 ± 1) μm thick with an area of 2×2.5 mm^2. The sample 2 is not oriented, 47 μm thick with an area of 2×2.5 mm^2.

Transmission spectra of CuO were recorded by the standard one-beam technique using a KSVU-12 spectroscopic facility produced by LOMO (St. Petersburg). Measurements were preformed in the 1–3.5 eV band. The light source was a 30-W incandescent lamp, and the polarizer was a Glan prism. The sample was mounted in an optical cryostat. The holder was designed to avoid vignetting of light beams. The holder temperature was controlled using a copper-constantan thermocouple. The temperature calibration was checked before and after measurements. In measurements of the incident beam intensity, I_0, NS-10 and NS-13 neutral-density filters produced by LOMO were set under the beam; their attenuation is

$$a = \frac{1}{d} \ln(1-R)^2 \frac{I_0}{I}.$$

The reflectivity in this spectral band was considered constant at $R = 0.22$.

The relative uncertainty of absorption measurements near the absorption edge was 1.2% and for the absorption edge position measured as a function of temperature, it was 0.5%. The spectrometer slit width at 3 and 1.6 eV was 0.02 and 0.005 eV respectively. The relative temperature uncertainty was 2%.

3. EXPERIMENTAL RESULTS

Figure 2 shows absorption spectra of samples 1 and 2 recorded at 293 K. A sharp rise in the CuO absorption from
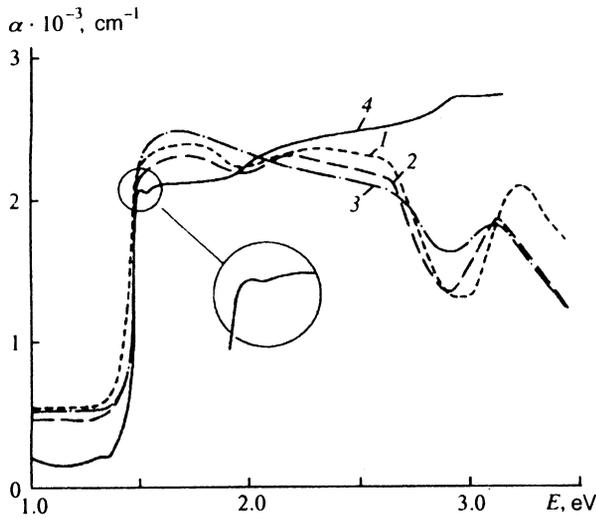
FIG. 2. Absorption spectra of CuO crystals: curves (*1, 2, 3*), cut in the (110) plane; curve (*4*), not oriented: *1*) E⊥c; *2,4*) unpolarized light; *3*) E∥c.

FIG. 3. Absorption spectra (E∥c) of the CuO single crystal at (*1*) 293 K and (2) 80 K. *1, 2*) T=293 K; *3,4*) T=80 K: *3,4*) unpolarized light; *1,2*) E⊥c.

200 cm^{-1} to 2300 cm^{-1} at $E=1.43$ eV marks the position of the fundamental absorption edge. In the spectral band studied there are two bands peaking at 1.7 eV and 2.3 eV with notably different widths and complex shapes, and a separate high-energy band with a maximum at 3.1 eV. It is natural to relate these spectra to the excitonic structure at the edge of the $b_{1g}-e_u(\pi)$ band and to the $b_{1g}-a_{2u}$ transition. The separation between centers of the $b_{1g}-e_u(\pi)$ and $b_{1g}-a_{2u}$ lines is about 0.8 eV, which is in good agreement with cluster calculations of respective levels. Note that the positions of the exciton and continuum bands in CuO spectra are close to respective lines in $b_{1g}-e_u(\pi)$-spectra of $YBa_2Cu_3O_{6+x}$ and R_2CuO_4.[6,7] These subbands are well resolved in spectra recorded in nonpolarized light and in E⊥c polarization. The absorption edge shifts to the blue with decreasing temperature, and the intensities of all lines are lower. The positions of peaks are almost constant with temperature, except those near the absorption edge. The spectrum of the non-oriented sample 2 is significantly different from that of sample 1: its absorption gradually rises with the photon energy, and the same three weak lines are hardly seen against this background. This indicates considerable anisotropy of the absorption spectrum.

Figure 3 shows absorption spectra near the absorption edge in sample 1 at 80 and 293 K recorded in unpolarized light and with E⊥c and E∥c polarizations. The temperature coefficient of the absorption edge shift is $-5.7\cdot 10^{-4}$ eV/K which is typical of antiferromagnetic semiconductors. In unpolarized light and in E⊥c polarization at room temperature, a narrow exciton-like line shifted to the red by 0.1 eV with respect to the 1.7 eV band can be seen. When the vector E is tilted with respect to the c-axis (by 30° and 60°, for example), the exciton line is seen as a shoulder on the wide absorption line. Spectra recorded at different temperatures with unpolarized light demonstrate that this shoulder is seen only at a temperature higher than 205 K. This contradicts the familiar version that the fine structure of various broad absorption bands appears as the temperature decreases.
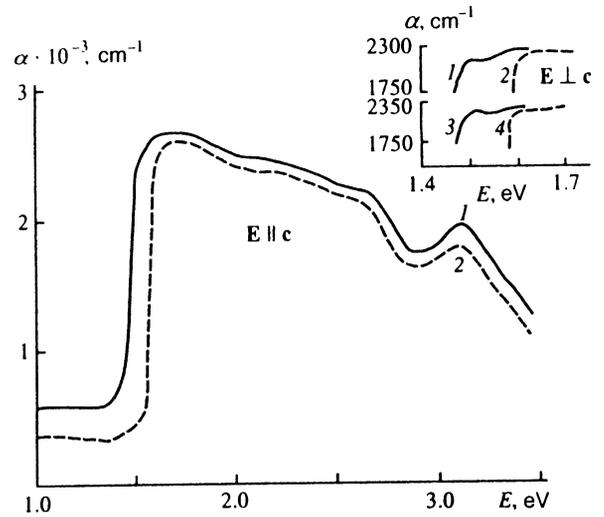
The laser of anomalies at the absorption edge of sample 1 with E∥ c enabled us to reduce the experimental data using the customary approach for semiconductors, yielding the band gap E_g, the nature of optical transitions near the absorption edge, and E_g versus temperature. The relatively low absorption near the edge ($\alpha\sim 2300$ cm^{-1}) and the fact that

$$(\alpha\hbar\omega)^{1/2}=A(\hbar\omega-E_g)$$

(Fig. 4) at α of up to 2000 cm^{-1} indicate that at 293 K the CuC absorption edge is produced by the indirect allowed transition that involves phonons with an energy of (0.05 ±0.01) eV. The exponent $n=0.35$ in the formula

$$\log(\alpha\hbar\omega)=n\ \log(\hbar\omega-E_g),$$

which is close to 0.5, also indicates that the transitions are indirect. The band gap at 290 K is $E_g=(1.446\pm0.005)$ eV and (1.565 ± 0.005) eV at 80 K.

In classical semiconductors, the temperature dependence of E_g is described well by the Varshni equation[9]

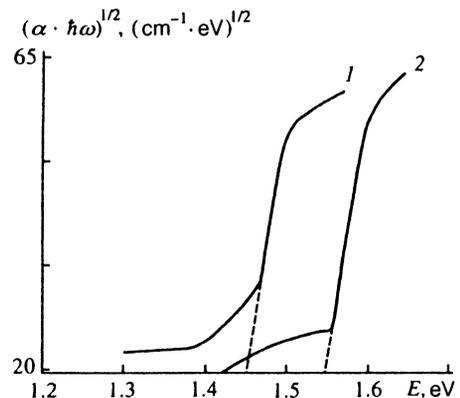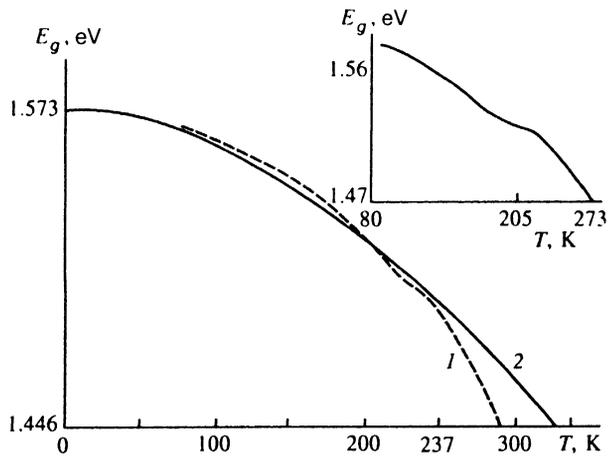FIG. 4. Identification of indirect transitions in CuO at (*1*) T=293 K and (2) T=80 K E∥c.

FIG. 5. Temperature dependence of the band gap with $\mathbf{E}\|\mathbf{c}$: *1*) experimental data; *2*) calculation by the Varshni formula. Insert: $E_g(T)$ measured with unpolarized light.

$$E_g(T) = E_g(0) - a\,\frac{T^2}{(T+\beta)},$$

where $E_g(0)$ is the band gap at zero temperature, and α and β are constants of a given material. Deviations from this function in the magnetic semiconductor MnS and semimagnetic semiconductor CdMgTe[10] suggest an influence due to magnetic ordering. For CuO, experimental data for $\mathbf{E}\|\mathbf{c}$ and the curve plotted by the Varshni formula are given in Fig. 5. The best agreement between the experimental data and calculations is achieved at $E_g(0) = (1.573 \pm 0.002)$ eV, $\alpha = 0.00146 \pm 0.00002$, and $\beta = 880 \pm 30$. The constant β is proportional to the Debye temperature. As in classical semiconductors, this constant in CuO is approximately 1.7 times the Debye temperature.[9] In the temperature range 110–300 K, the Debye temperature of CuO changes from 560 to 520 K.[8] The experimental and theoretical curves coincide at a temperature of up to 240 K. As the temperature rises, the slope of the experimental curve increases. The insert of Fig. 4 shows $E_g(T)$ measured in unpolarized light, with a knee near 212 K corresponding to the emergence of a peak near the absorption edge, suggesting anisotropy of the temperature dependence of the gap width.

4. DISCUSSION

Absorption spectra of CuO shown in Figs. 2–4 suggest a common excitonic nature of the absorption edge in CuO and in classical cuprate high-temperature superconductors, such as $YBa_2Cu_3O_{6+x}$ and R_2CuO_4, which may be due to transitions with charge transfer like $b_{1g} - e_u$ in CuO_4 clusters.

The features of CuO absorption spectra include:

-the complex (apparently doublet) shape of the narrow and wide subbands with maxima at 1.7 and 2.3 eV, respectively;

-the emergence of a narrow (less than 0.1 eV) exciton-like subband near the absorption edge at temperatures higher than $T \sim 205$ K;

-deviation of the $E_g(T)$ curve from the Varshni formula at temperatures higher than that of three-dimensional magnetic ordering;

-highly anisotropic absorption spectra.

A reasonable qualitative or even semiquantitative interpretation of these features of the CuO spectra can be derived from the cluster model developed in our previous publication[2] to account for absorption spectra in the intermediate IR band, for some anomalies in Raman spectra and in the temperature dependence of the electric conductivity.

Figure 6 shows two versions of the diagram of e_u-hole energy levels in a CuO_4^{6-} cluster. The diagrams illustrate the complex shapes of $b_{1g} - e_u$ lines and their changes due to phase transitions corresponding to non-collinear ($T_{N_2} \simeq 231$ K) and collinear ($T_{N_1} \simeq 213$ K) three-dimensional antiferromagnetic ordering. They can be used to analyze spectral bands due to both excitonic and continuum states in $b_{1g} - e_u$ transitions, although in this section we naturally consider only the excitonic component.

Figure 6 is an analog of Fig. 6 in Ref. 2, which is the diagram of b_{1g}^2 and $b_{1g}e_u$ levels in the CuO_4^{5-} cluster (CuO_4^{6-} cluster with an additional hole due to doping). This diagram was used in Ref. 2 to interpret some experimental data.

In this context, the main conclusion of Ref. 2 was the highest efficiency of charge transfer by e_u-holes of the upper branch (e_u'') with a spin opposite to the spin of the initial b_{1g} state ($e_u''\downarrow$ in Fig. 6). In other words a relatively wide subband is related to the upper sublevel e_u'' and a narrow band to the lower sublevel e_u'. Three-dimensional collinear antiferromagnetic ordering ($T < T_{N_1}$) leads to an increase in the energy of this state by $\simeq 0.1$ eV due to a large contribution from the interchain $e_u'' - b_{1g}$ exchange. Another indication of this is the higher activation energy of conductivity.[2] The spin splitting of the lower e_u' branch should be small both above T_{n_2} and below T_{n_1}.[2] The splitting of the e_u level can be estimated from the "fine" structure of the excitonic line at ~ 1.7 eV (Figs. 2 and 3) and from the separation between the two main peaks in the CuO absorption spectrum in the intermediate IR band,[2] and these estimates yield $\simeq 0.1$ eV.

The shape of the $b_{1g} - e_u$ absorption band at $T < T_{N_1}$ and $T > T_{N_2}$ is illustrated by the diagrams of Fig. 6. The doublet structure of the absorption band at $T > T_{N_2}$ is related to the smaller exchange splitting of the upper level and the larger splitting of the lower level, which results in a larger separation between the subbands due to transitions to the states e_u'' and e_u'. At $T < T_{N_1}$, the two doublet components merge in a single exciton line.

In the diagrams of Fig. 6, the transition to the lower level of the doublet forbidden by spin conservation ($b_{1g}\uparrow - e_u'\downarrow$) is assumed to be inside the absorption line. But the opposite situation is also possible (the opposite sign of the exchange field), when this transition coincides with the line edge and complicates its shape.

The transitions $b_{1g} - e_u''$ and $b_{1g} - e_u'$, which are orthogonally polarized in the plane of the CuO_4 cluster, provide a considerable difference in polarizations of respective
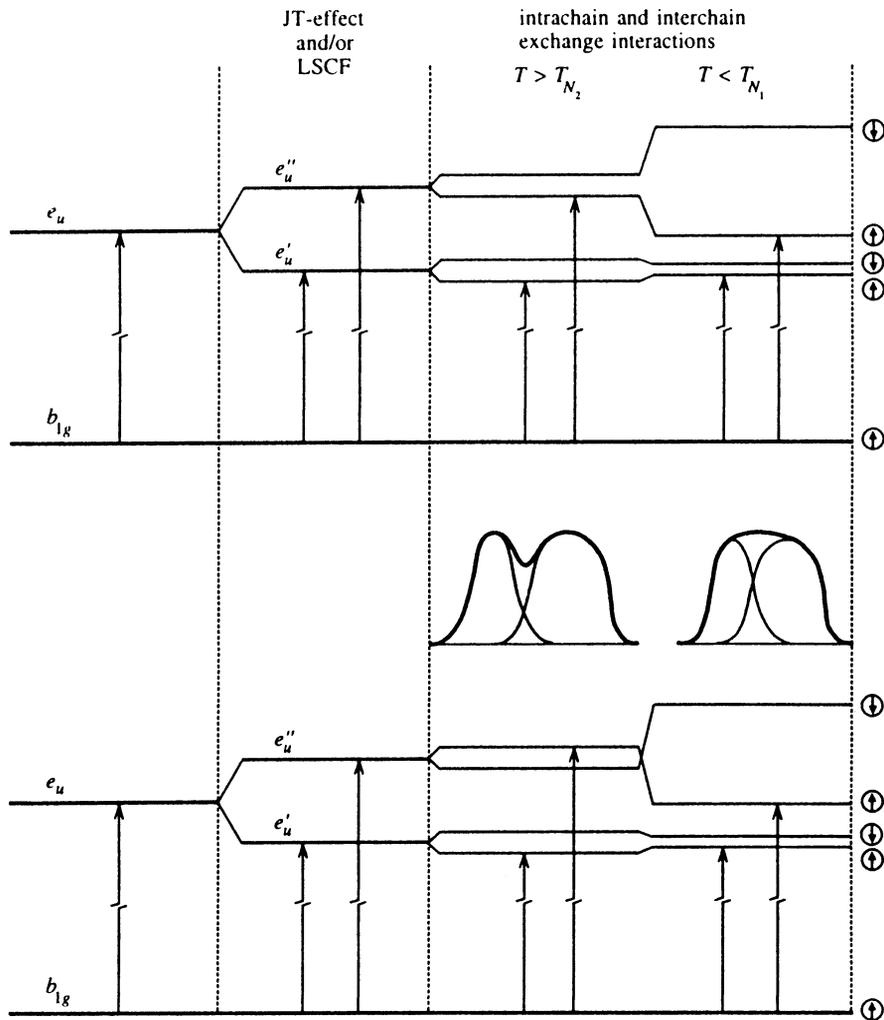
FIG. 6. Diagram of $b_{1g}-e_u$ transitions with charge transfer responsible for the fundamental absorption band in CuO.

bands of CuO absorption spectra. This effect is actually seen experimentally.

The relatively weak effect of interchain exchange on the exchange splitting of the lower doublet component e_u' results in a relatively small exchange contribution to the temperature dependence of the gap width over the temperature range 80–300 K.

The models previously developed to interpret a lot of unusual features of copper oxide compounds[2] enable us to account for the features of the fundamental absorption band in CuO. Direct measurements demonstrate the doublet structure of the exciton-like line at $E \approx 1.7$ eV observed in many cuprate superconductors, which confirms the conclusions derived from the cluster model that this band is due to $b_{1g}-e_u$ transitions.

The authors are indebted to N. M. Chebotaev and S. V. Naumov for preparing samples for the experiment, and to M. A. Sidorov and Yu. D. Panov for help in preparing the manuscript and discussions of the experiment results.

[1] A. A. Samokhvalov, N. N. Loshkareva, Yu. P. Sukhorukov et al., Pis'ma Zh. Éksp. Teor. Fiz. 49, 456 (1989) [JETP Lett. 49, 523 (1989)].

[2] A. S. Moskvin, N. N. Loshkareva, Yu. P. Sukhorukov et al., Zh. Éksp. Teor. Fiz. 105, 967 (1994) [JETP 78, 518 (1994)].

[3] L. V. Nomerovannaya, A. A. Makhnev, M. M. Kirillova et al., Sverkhpro-vodimost' (KIAE) 3, 323 (1990). [Superconductivity 3, 307 (1990)].

[4] J. E. Hirsch and S. Tang, Phys. Rev. B 40, 2179 (1989).

[5] I. B. Bersuker and V. Z. Polinger, Vibron Interactions in Crystals and Molecules, [in Russian] Nauka, Moscow (1983).

[6] A. A. Makhnev, L. V. Nomerovannaya, M. M. Kirillova et al., Sverkhpro-vodimost' (KIAE) 4, 700 (1991) [Superconductivity 4, 609 (1991)].

[7] V. V. Krichevtson, R. V. Pisarev, A. Burau et al., J. Phys.: Cond. Matter. (to be published).

[8] E. Gmelin, Indian J. of Pure and Appl. Phys. 30, 596 (1992).

[9] Y. P. Varshni, Physica 34, 149 (1967).

[10] Semimagnetic Semiconductors [Russian translation], Ed. by J. Furdyna and J. Kossut, Mir. Moscow (1992).

Translation was provided by the Russian Editorial office