Characteristic features of the electronic structure of copper oxide (CuO): Initiation of the polar configuration phase and middle-IR optical absorption

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A model for the initiation of the polar-center phase (variable valence phase) is proposed in order to explain the characteristic features of the electronic structure and a number of physical properties of copper oxide (CuO)—the basic model object for studying high-T_c superconducting materials. The nuclei of the new phase consist of a system of electron and hole Jahn–Teller centers—CuO_4^{7-} and CuO_4^{5-} clusters, respectively. The optical signatures of the nuclei are absorption bands in the middle-IR range as well as new lines in the Raman light-scattering spectrum. The spectral, polarization, and temperature dependence of the absorption of CuO single crystals in the range 0.1–1.0 eV was studied experimentally. The two absorption bands observed at 0.1 and 0.2 eV are associated with transitions in singlet hole centers. The proposed model gives a unified description of the characteristic features of CuO spectra in the middle-IR range, the Raman scattering spectra, and the characteristic features of the temperature dependence of the electric conductivity and magnetic susceptibility.

1. INTRODUCTION

Copper oxide (CuO), the last compound in the series of the simplest oxides of transition metals with an unfilled 3*d*-shell, has a number of interesting physical properties, and in the last few years it has been intensively studied by experimenters and theoreticians.

Copper oxide has a monoclinic crystalline lattice with the space group[1] C_{2h}^6. Antiferromagnetic ordering has been discovered in CuO below $T_{N_1} \approx 231$ K: noncollinear in the range 213–231 K and collinear below $T_{N_2} \approx 213$ K with spins parallel to the *b* axis of the crystal.[1] A characteristic feature of the magnetic structure of CuO is the existence of antiferromagnetic chains—CuO^{2+}–O–Cu^{2+}–O along the $[\bar{1}01]$ directions with bond angle $\theta \approx 146°$, favorable for strong antiferromagnetic exchange [$J \approx 0.08$ eV (Ref. 2)]. The antiferromagnetic chains $[\bar{1}01]$ are coupled with one another by relatively weak ferromagnetic exchange via the bonds CuO^{2+}–O–Cu^{2+} ($\theta_1 \approx 104°, \theta_2 \approx 109°$). Above $T = T_{N_1}$ CuO exhibits magnetic behavior that is typical for low-dimension magnetics.[2–4]

The semiconductor properties of CuO are characterized[5,6] by low carrier mobility, conduction activation energy in the range $\Delta E_a \approx 0.12$–0.16 eV at temperatures $T > T_{N_1}$ and up to 0.28–0.30 eV at temperatures $T < T_{N_2}$, hole thermo-emf and unusual temperature dependence, and very weak Hall effect and very low magnetoresistance.

The optical properties of CuO are in many ways typical of the oxides of 3*d* elements. According to the photoelectrochemical data the energy of the fundamental absorption edge is 1.35 eV.[7] Ellipsometric investigations of CuO single crystals indicate high absorption coefficients ($\geqslant 10^4$ cm^{-1}) at energies above 1.4 eV and strongly anisotropic real and imaginary parts of the permittivity with the plane of light incidence oriented perpendicular and parallel to the *c* axis in the (110) plane.[8]

Three wide bands with maxima at 2.0, 2.5, and 3.4 eV are seen quite clearly in the spectrum of the imaginary part of the permittivity in the range 1.4–1.5 eV.[8] Judging from their intensity, these bands are associated with charge transfer of the form $O_{2p} \rightarrow Cu_{3d}$.

The great interest in CuO stems from the fact that this compound is, in many respects, considered to be a model system for studying the dielectric (semiconductor) phase of a large class of high-T_c copper oxides and, primarily, the general physical properties owing to the identical Cu–O bonds. In this respect, CuO has the advantage that the ions Cu^{2+} and O^{2-} are of only one type.

The analogy between CuO and the high-T_c copper-oxide materials extends to the physical properties characterizing both the ordered impurity-free phase (low-dimension antiferromagnetism, optical absorption, band-structure characteristics[9]) and the impurity or pseudoimpurity (associated with the electronic and lattice instability) subsystem. In CuO, just as in the classical high-T_c system YBaCuO, lattice instability[10] and anomalous low-temperature paramagnetic behavior of the susceptibility and magnetostriction[3,10] are observed. Mössbauer and μ-meson resonance data indicate the existence of electronic nonuniformity in CuO.[12] Low-mobility carriers of the small-polaron type with combined band-polaron and hopping conductivities are characteristic for copper oxide, just as for the high-T_c copper-oxide compounds in the semiconductor phase.[6]

The different physical properties of copper-oxide high-T_c materials and copper oxide CuO are similar principally because they have a structural element in common—a slightly distorted square cluster CuO_4. The present paper is devoted to the study of the properties of this cluster.

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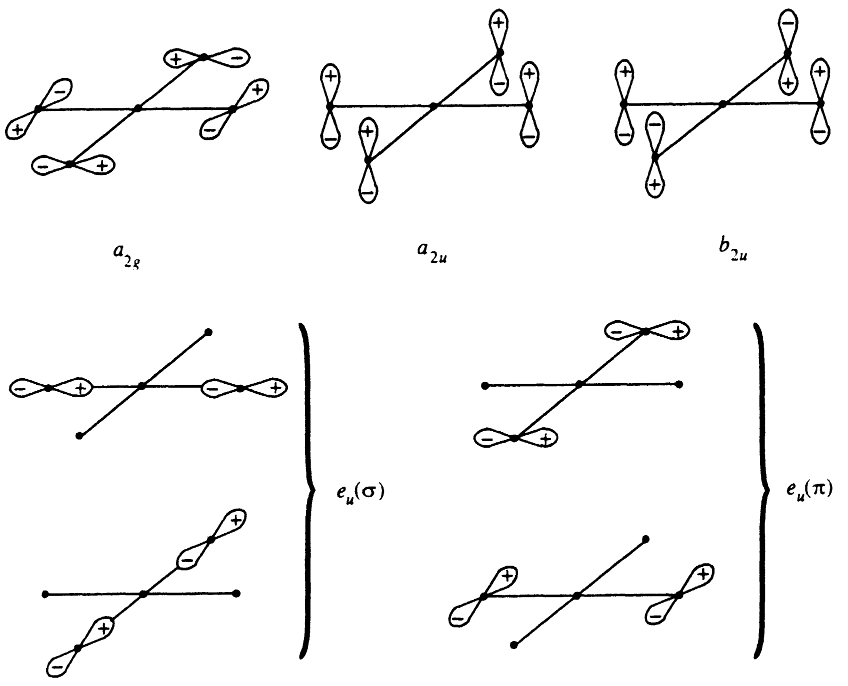

FIG. 1. Orientation of the $2p$ orbits for purely oxygen molecular orbitals in square clusters CuO_4.

In Sec. 2 a semi-empirical cluster model is developed for the electronic structure and the energy spectrum of clusters of the form CuO_4. In Sec. 3 the characteristic features of the pseudo-Jahn–Teller effect in polar configurations of the cluster CuO_4^{6-}, the vibronic correlations caused by this effect, and the formation of nuclei of a new phase are examined. Finally, in Sec. 4 the results of an experimental investigation of optical absorption in the middle-IR range and its relation to the characteristic features of the electronic structure and nuclei of the phase of polar Jahn–Teller configurations in CuO are presented.

2. CHARACTERISTIC FEATURES OF THE ELECTRONIC STRUCTURE AND ENERGY SPECTRUM OF CuO_4 COPPER CLUSTERS IN QUASI-TWO-DIMENSIONAL OXIDES

One of the most important problems in the theory of high-T_c superconducting materials is the problem of determining the character of the electronic ground state of hole-doped copper-oxide planes CuO_2. Difficulties in solving this problem within the band approach have led to the development of diverse semiempirical cluster models, based on well-known atomic and quantum-chemical ideas as well as quantitative calculations of a number of parameters from the band theory.

Although there are inadequacies in its description of the real physical situation, the cluster model is attractive because of its physical content, convenience, and simplicity of implementation with extensive possibilities for computer modeling and because there exist well-developed and tested quantum-chemical computational methods. The difficulties and doubts associated with the large (as a rule) number of model parameters are eliminated, though perhaps not completely, because their physical meaning is clear and they can be chosen on the basis of experimental data and independent theoretical (including *ab initio*) calculations. Semi-empirical cluster models have the undoubted advantage that they can be expanded and narrowed (refined and coarsened) and, finally, they enable the most diverse situations to be modeled on the basis of a reasonable number of parameters.

The cluster model enables a detailed study of the role of the interelectronic interaction, resulting in splitting of the energies of different configurations into terms and the interaction of multielectron configurations, i.e., effects which are difficult, if not impossible, to describe correctly within the traditional band approaches.

Finally, cluster calculations can provide the justification for choosing a model theoretical description of the electronic states of the crystal.

A number of ideas which are fundamental to the theory of high-T_c materials have been formulated on the basis of the cluster approach: in particular, the model of the ${}^1A_{1g}$ ground state of the complex CuO_4^{6-} with an additional hole (Zhang–Rice singlet[13]) and the Rice–Wang model[14] for explaining the appearance of absorption bands in the middle-IR range and vibronic effects accompanying doping of CuO_2 copper-oxide planes with holes.

Good agreement with the XPS spectra of CuO—a successful model object for the dielectric phase of high-T_c materials—has been obtained in the cluster model developed recently by Eskes, Sawatzky *et al.*,[15,16] for complexes of the form CuO_4. The cluster model has also been used for detailed investigation of the properties of the Zhang–Rice singlet in CuO_4^{5-} complexes.

Deliberately simplifying the model the authors confined their attention to Cu_{3d} and O_{2p} atomic bases and they neglected the nonorthogonality of the atomic orbitals of different centers, effects of the crystal lattice for Cu_{3d} and O_{2p} states, and purely "oxygen" states of the form a_{2g}, a_{2u}, b_{2u}, $e_u(\sigma)$, $e_u(\pi)$ (see Fig. 1), which do not hybridize with Cu_{3d} states of the form $a_{1g}(d_{z^2})$, $b_{1g}(d_{x^2-y^2})$, $b_{2g}(d_{xy})$, $e_g(d_{yz},d_{xz})$.

The actual nonorthogonality of Cu_{3d}–O_{2p} and O_{2p}–O_{2p} may indeed not have any fundamental effect on the results of the semi-empirical model; it could merely result in renormalization of the parameters. The crystal-field effects are quite large even for Cu_{3d} states. According to data obtained by different authors[17,18] they can give rise to a total splitting $\Delta\varepsilon_{3d}\sim 0.5$–1 eV, but they are especially important both in magnitude [$\Delta\varepsilon_{2p}\sim 3$–4 eV (Ref. 19)] and with respect to the character of the splitting for the O_{2p} states. The energy [~ 3–4 eV (Ref. 19)] of the $2p_\pi$ holes in the CuO_2 copper-oxygen planes (see Fig. 1) is significantly lower than that of the $2p_\sigma$ holes because of the stronger repulsion of the latter holes from the nearest Cu^{2+} cations.

This is why the purely oxygen a_{2g} and $e_u(\pi)$ orbitals, "engendered" by the $2p_\pi$ states, play an important role in determining the structure of the lower energy levels of both the CuO_4^{6-} cluster and the "two-hole" CuO_4^{5-} cluster.

The fact that the purely oxygen molecular orbitals (MOs) of the type a_{2g}, a_{2u}, b_{2u}, $e_u(\sigma)$, and $e_u(\pi)$ were excluded from the analysis not only kept the authors of Refs. 15 and 16 from explaining a number of physical properties of the clusters CuO_4^{6-} and CuO_4^{5-} (for example, the optical absorption of copper oxides associated with them) but it also cast doubt on some fundamental results of their work.

The study of the optical absorption spectra of quasi-two-dimensional copper oxides, especially the absorption bands associated with the CuO_2 planes, gives very important experimental information about the energy levels of a number of purely odd oxygen molecular orbitals.[20]

Assuming that $b_{1g}(d_{x^2-y^2})$ character of the ground (hole) state of the cluster CuO_4^{6-} has been established reliably, we conclude that such a cluster has three types of allowed electric dipole transitions with charge transfer $b_{1g}\rightarrow e_u(\pi)$, $e_u(\sigma)$ ($\mathbf{E}\perp C_4$ polarization) and $b_{1g}\rightarrow a_{2u}$ ($\mathbf{E}\parallel C_4$ polarization).

Analysis of the optical absorption spectra and their polarization properties in an extensive series of quasi-two-dimensional copper oxides, including the simplest oxide CuO,[20] shows that the fundamental absorption band with an edge at $\hbar\omega\sim 1.0$–1.5 eV (in different oxides) is associated with an allowed $b_{1g}\rightarrow e_u$ transition (e_u is the hybrid $e_u(\pi)$–$e_u(\sigma)$ state) with charge transfer in the cluster CuO_4^{6-} and it yields important information about the position of one of the purely oxygen states that must be taken into account in any model description of the cluster.

Elaborating the Eskes–Sawatzky model[15,16] on the basis of the Cu_{3d} and O_{2p} atomic basis, we implemented the standard MO–LCAO approach to the description of the "single-hole" cluster CuO_4^{6-} and the "two-hole" cluster CuO_4^{5-}, using the well-known semi-empirical Mulliken–Wolfsburg–Helmholtz model[21] including crystal-field effects for Cu_{3d} and O_{2p} states and the nonorthogonality of the atomic orbitals of the nearest atoms (Cu_{3d}–O_{2p} and O_{2p}–O_{2p}).

The single-center matrix elements of the single-particle Hamiltonian in the hole representation were expressed as

$$\langle i\nu|H|i\nu\rangle=\varepsilon_i+\Delta\varepsilon_{i\nu}, \tag{1}$$

where ε_i is the effective energy of the ith atomic state ($i=Cu_{3d}$ or O_{2p}) and $\Delta\varepsilon_{i\nu}$ is the correction to the energy ε_i due to crystal field effects (neglecting the contributions of covalence and overlapping).

TABLE I.

Parameters	Model estimate; published value	This work
ε_{3d}	10.4 eV—Cu ionization potential	10.3 eV
$\Delta\varepsilon_{z^2}$	+0.5 point-charge model	+0.2
$\Delta\varepsilon_{xz,yz}$	+0.4	0
$\Delta\varepsilon_{xy}$	−0.6	0
$\Delta\varepsilon_{x^2-y^2}$	−0.7	−0.2
ε_{2p}	13.6 eV—O ionization potential	12.0 eV
$\Delta\varepsilon_{2p_\sigma}$	+1.6 point-charge model	+1.0
$\Delta\varepsilon_{2p_z}$	0	−1.8
$\Delta\varepsilon_{2p_\pi}$	−1.6	−0.2
$S_\sigma(2p-2p)$	0.2–0.3 [17]	0.25
$S_\pi(2p-2p)$	$\sim\frac{1}{2}S_\sigma(2p-2p)$	0.15
$S_\sigma(3d-2p)$	0.1 [17]	0.15
$S_\pi(3p-2p)$	$\sim\frac{1}{2}S_\sigma(3d-2p)$ [17]	0.07
$K_\sigma(2p-2p)$	~1–2 [21]	1.38
$K_\pi(2p-2p)$		0.75
$K_\sigma(3d-2p)$		1.15
$K_\pi(3d-2p)$		0.8
A	6.5 eV [16], ≈14 eV-free ion Cu^{2+} [23]	7.5 eV
B	0.15-free ion Cu^{2+} [23]	0.15
C	0.58-free ion Cu^{2+} [23]	0.58
$F^0(2p)$	5 eV [16], ≈20.5 eV-free atom O [25]	6.5 eV
$F^2(2p)$	6.9-free atom O [23]	0.15
U_{dp}	0–1 eV [16, 18]	0.3 eV
$U_{pp'}$	0–0.5 [16, 18]	0.2

The following were chosen as the "seed" or approximate values of these quantities: for ε_i—the ionization potentials of the neutral Cu and O atoms, respectively, from the $3d$ and $2p$ states[22,23] and for $\Delta\varepsilon_{i\nu}$—the values corresponding to the contribution of the nearest neighbors in the point-charge model for the CuO_2 planes (see Table I).

The two-center matrix elements of the single-particle Hamiltonian were expressed in the Mulliken–Wolfsburg–Helmholtz approximation as

$$\langle i\nu|H|i\nu'\rangle=\frac{K_{i\nu;j\nu'}}{2}(\varepsilon_{i\nu}+\varepsilon_{j\nu'})S_{i\nu;j\nu'}, \tag{2}$$

where K are empirical coefficients of the approximation employed and were assumed to be different for O–O, Cu–O, σ, and π bonds; $S_{i\nu;j\nu'}$ are the overlap integrals of the atomic states (Cu_{3d}–O_{2p}, O_{2p}–O_{2p}).

Figure 2 displays a model spectrum of the energies of the single-particle molecular orbitals of the cluster CuO_4^{6-}.

The ground state of a cluster is described by the b_{1g} molecular orbitals

$$\Psi_{b_{1g}}=c_d\Phi(d_{x^2-y^2})+c_p\Phi(O_{2p}b_{1g}) \tag{3}$$

with $c_d\approx -0.83$ and $c_p\approx 0.56$. This agrees well, in particular, with the existing experimental value of the local magnetic moment $\mu_{Cu}\approx 0.65\mu_B$.[1] The closest excited hole (va-

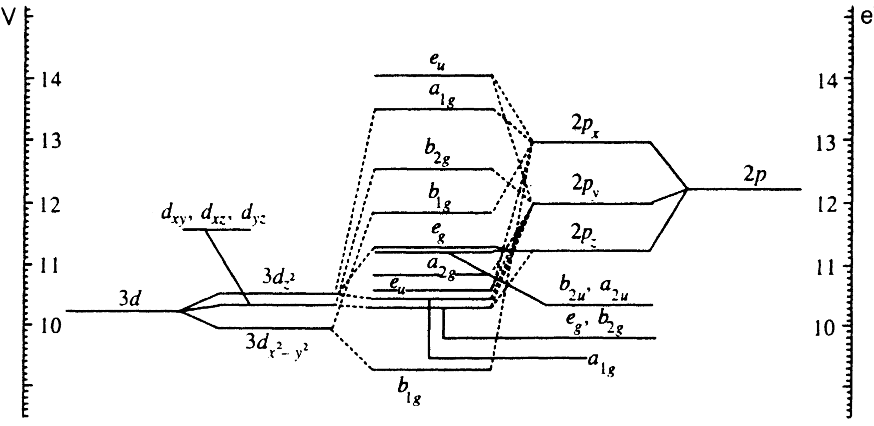

FIG. 2. Model spectrum of the energies of single-particle states of the square cluster $[\mathrm{CuO}_4^{6-}]_{JT}$. The parameters of the model are given in Table I.

lence electronic) states are separated by a gap ~1.0–1.5 eV and are formed by e_g, b_{2g}, a_{1g}, e_u, and a_{2g} molecular orbitals, among which the e_u orbital, representing a superposition of $e_u(\sigma)$ and $e_u(\pi)$ orbitals

$$\Psi_{e_u}=c_\pi\Phi(e_u(\pi))+c_\sigma\Phi(e_u(\sigma)) \tag{4}$$

with $c_\pi \approx 0.80$ and $c_\sigma \approx 0.61$, plays a special role. The point is that it is the electric-dipole transitions with charge transfer $b_{1g}\to e_u$ in the clusters CuO_4^{6-}, allowed in $\mathbf{E}\perp C_4$ polarization and having a high oscillator strength

$$f(b_{1g}\to e_u)=\frac{m\omega_0}{3\hbar}|c_\pi c_\sigma|^2(R_{dp})^2 \approx 10^{-2} \tag{5}$$

that determine the fundamental absorption band in the dielectric phase of quasi-two-dimensional copper oxides.

The even levels a_{1g}, b_{2g}, e_g,... lie somewhat lower than the e_u level, but forbidden transitions of the type $b_{1g}\to b_{2g}$, a_{1g},... correspond to weak absorption bands, masked by the strong "tail" of the fundamental absorption band $b_{1g}\to e_u$.

The two-particle (two-hole) configurations of the complex CuO_4^{5-} was calculated by directly diagonalizing the electrostatic interaction matrix $\langle\gamma_1\gamma_2 S\Gamma|U|\gamma_1'\gamma_2' S\Gamma\rangle$. This enabled taking into account completely the configurational interaction of terms having the same symmetry. The single-center integrals in the matrix U were found in terms of the corresponding combinations of the Slater parameters F_0 and F_2 for the O_{2p} states or the Racah parameters A, B, and C for the Cu_{3d} states.[15,16]

The charge-charge contributions to the two-center Coulomb integrals were expressed in terms of the parameters U_{dp} and U_{pp} for the Cu–O and O–O bonds, respectively.[18] The electrostatic interaction parameters were chosen in accordance with the idea that only the screening of the charge-charge (monopole) interactions of electrons (holes) in the crystal is strong.[24] The two-center exchange integrals were calculated in the Mulliken approximation; the three- and four-center integrals were neglected.

In analyzing the two-hole configurations of the cluster CuO_4^{5-} we neglected the possible change of the single-particle energies and states of the cluster CuO_4^{6-} when it is singly ionized. Such a change can be especially noticeable for the purely "oxygen" or predominantly "oxygen" molecular orbitals. This is because the energy and character of the O_{2p} orbitals depend strongly on the number of holes in the $2p$ shell with $n_{\mathrm{hole}}\sim 0$–1 (correlation effect of the "soft" anionic core[25]).

The qualitative consequences of this effect in our case are screening of the parameter F_0, decrease of CuO_{3d}–O_{2p} and O_{2p}–O_{2p} overlapping and covalence with increasing average number of O_{2p} holes, and the contribution to the relative decrease of the energy (stabilization) of predominantly oxygen hole states.[1)] The quantitative estimates made in Ref. 25 indicate that the correlation contributions owing to the dependence of the anionic core on the effective number of holes are significant.

Generally speaking, the effects considered can be taken into account within the cluster model, though this requires introducing an entire series of additional parameters, for example, parameters determining the dependence of the CuO_{3d}–O_{2p} and O_{2p}–O_{2p} overlap integrals on the number n_{hole} of O_{2p} holes.

We either employed the values of the model parameters presented in the first column of Table I directly with no changes or regarded them as approximate values. In the latter case we strove to preserve only the fundamental aspect of the corresponding estimates. Thus, in choosing the parameters of the crystal-field splitting of Cu_{3d} and O_{2p} levels we took into consideration only the estimate of the total splitting and the type of the lower $3d$ level.

One of the few internal constraints on the values of the model parameters was dictated by fixing the position of the lowest e_u level ($\varepsilon(e_u)\approx 1.5$ eV). In so doing we assumed that any even levels, whose small contribution to optical absorption will be masked by the strong "tail" of the band of the allowed transition $b_{1g}\to e_u$, can lie in the "transmission window" slightly below the e_u level. In addition, definite constraints, associated with the requirement that the computed density of states agree semi-quantitatively with the experimental photoemission spectra, were imposed on the choice of model parameters.[15]

At the present time it is difficult to determine the optimal set of parameters, so that we limited ourselves to performing a number of test calculations, focusing attention on the manifestation of the interelectronic interactions in the structure of the energy spectra and the two-particle states of the complex CuO_4^{5-}. We were interesting primarily in the lower terms, whose structure determines the

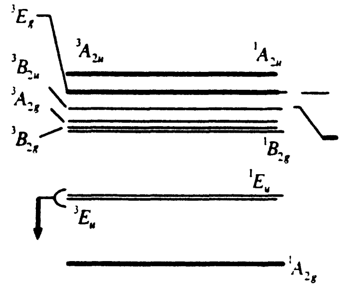

FIG. 3. Fragment of the energy structure of terms of the two-hole cluster $[\mathrm{CuO}_4^{5-}]_{JT}$. The arrow marks the direction of displacement of the terms ${}^{1,3}E_u$ when the correlation effect of the "soft" anionic core is taken into account.

most diverse aspects of the effect of the additional holes in the CuO_2 planes on the physical properties of quasi-two-dimensional copper oxides. The values of the parameters for one variant of the test calculation are given in the second column of Table I.

The cluster CuO_4^{5-} has a rich structure of two-particle configuration terms (see Fig. 3).

The calculated density of states (both full and partial; see Fig. 4) on the whole correctly convey a sense of the basic features observed in photoemission spectra of the oxide CuO.1[15]

We now turn to some important results of CuO_4^{5-} cluster calculations. The dominant term, as in the model described in Refs. 15 and 16, is the ${}^1A_{1g}$ Zhang–Rice singlet, which is more than 90% bonded to the $(b^a_{1g})^2$, $b^a_{1g}b^b_{1g}$, and $(b^b_{1g})^2$ configurations; the latter compromise the antibonding (a) and bonding (b) b_{1g} orbitals. With parameter values taken from the last column of Table I, the Zhang–Rice singlet wave function is clearly of a correlated nature:

$$|{}^1A_{1g}\rangle \approx 0.82|(b^a_{1g})^2\rangle + 0.55|b^a_{1g}b^b_{1g}\rangle - 0.16|(b^b_{1g})^2\rangle.$$

Representing the energy of the term of the predominant configuration $\gamma_1\gamma_2$ in the form

$$E(\gamma_1\gamma_2 S\Gamma) = \varepsilon_{\gamma_1} + \varepsilon_{\gamma_2} + U_1(\gamma_1\gamma_2 S\Gamma) + U_2(\gamma_1\gamma_2 S\Gamma) \tag{6}$$

(U_2 is the correlation correction owing to configuration interaction), we have in the case of the Zhang–Rice singlet

$$E(b^2_{1g}\,{}^1A_{1g}) = 2\varepsilon_{b_{1g}} + 4.69 - 3.49 = 2\varepsilon_{b_{1g}} + 1.2(\mathrm{eV}). \tag{7}$$

We call attention to the anomalously high correlation correction $U_2(b_{1g}b_{1g}\,{}^1A_{1g})$, stabilizing the Zhang–Rice singlet, as well as the significant role of covalence effects, which substantially decrease U_1, determining the contribution of the diagonal matrix elements of the electrostatic interaction matrix to the energy of the term. The real value of U for the ${}^1A_{1g}$ singlet is found to be significantly less than the value $U_0 = A + 4B + 3C \approx 10$ eV for the atomic configuration $(d_{x^2-y^2})^2$. We call attention to the anomalous stability of the Zhang–Rice singlet with respect to a change in the parameter A of the interatomic electrostatic interaction. Thus, the singlet energy increases by only 0.04 eV when A increases by 2 eV; this is due primarily to the compensating effect of the configuration interaction.

In contrast to the results of Refs. 15 and 16, however, the Zhang–Rice singlet in the cluster CuO_4^{5-} is not a well-isolated level (see Fig. 3) because of the direct proximity to it of both the odd terms ${}^1E_u$ and ${}^3E_u$ of the configuration $b^a_{1g}e_u$ $(E({}^{1,3}E_u) - E({}^1A_{1g}) \approx 0.4$ eV), and the even terms ${}^{1,3}B_{2g}$ of the configuration $b^a_{1g}a_{2g}$ $(E({}^{1,3}B_{2g}) - E({}^1A_{1g}) \approx 0.8$ eV). This result remains valid in a quite wide range of values of the model parameters near their seed values.

The correlation effect of the "soft" anionic core should additionally decrease the energy of E_u terms, which differ by the high hole density in the O_{2p} states. This lead to the formation of an isolated group of close terms ${}^1A_{1g}$, ${}^1E_u$, and ${}^3E_u$, in the ground state of the cluster CuO_4^{5-}.

Thus we have to deal with the appearance of pseudodegeneracy in the ground state of singly ionized CuO_4^{6-} clusters and the possibility of a transition under the conditions of a strong pseudo-Jahn–Teller effect.

3. STRONG PSEUDO-JAHN–TELLER EFFECT IN POLAR CONFIGURATIONS OF THE CLUSTER CuO_4^{6-} AND NUCLEI OF A NEW PHASE[2)]

The electron-vibrational interactions under conditions of a strong or pseudo-Jahn–Teller effect (vibronic interactions) can result in strong electronic correlations and a radical rearrangement of the electronic structure of atomic clusters in solids. In many cases such restructuring requires a significant alteration of the generally accepted ideas about the basic organizational principles of the electronic structure. The solution of the complicated problem of the role played by the electron-vibrational interaction in systems with a variable number of particles N and, most importantly, in the problem of the transition $M \to M^{\pm}$ to polar configurations is of special theoretical and practical interest. Strictly speaking, a many-particle adiabatic potential of the system must be found in each specific case with a definite value of N. It is obvious that the use of simplified model approaches, based on a fixed single-particle potential, can give a satisfactory description only if the two-particle interaction is completely neglected or if the dependence of the lower branch of the single-particle potential on the number of particles N is obviously weak. The appearance of electronic degeneracy or quasidegeneracy (close levels) in the ground state of a system with a definite value of N transfers the system into a state when the Jahn–Teller effect or a strong pseudo Jahn–Teller effect with a radical change in the adiabatic potential comes into play and new correlation effects must be taken into account (strong polarization interaction and vibronic reduction of electronic interactions). In this case the traditional approach to the analysis of the electron-vibrational interaction in systems with a variable number of particles N is applicable only if the change in N does not destroy the weakness of the pseudo Jahn–Teller effect.

That the Jahn–Teller effect can play a decisive role in the explanation of high-T_c superconductivity in copper-oxygen systems has been pointed out in many works (see, for example, Refs. 14 and 27–30).

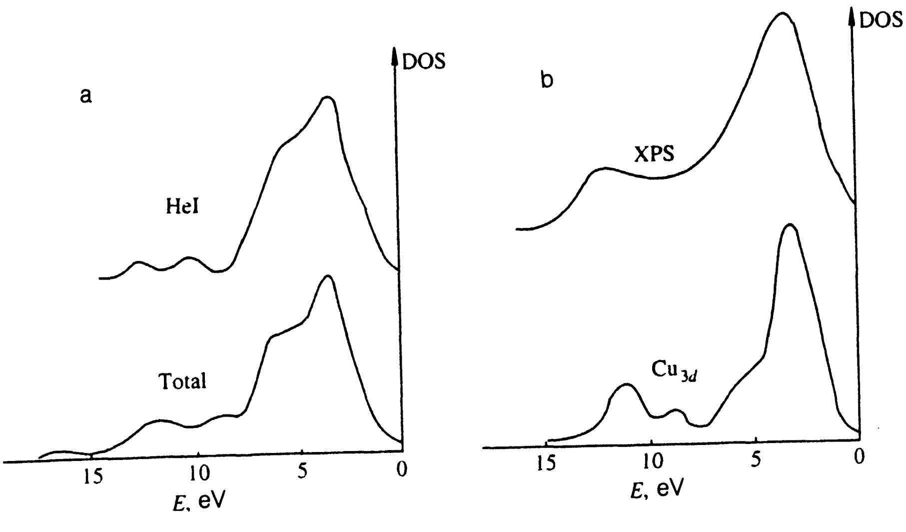

FIG. 4. Model density of states of the cluster $[CuO_4^{5-}]_{JT}$: a) total density; b) Cu_{3d} density. The parameters of the cluster model are presented in Table I. The experimental photoemission spectra with two values of the excitation energy are indicated for comparison.[15,16]

Focusing on applications to copper-oxygen high-T_c superconducting materials, we consider as an example the simplest single-particle (single-hole) center—an atomic cluster M_{sp}^h with only two single-particle valence shells of the s and p type (s is the ground orbital of the singlet state and p is a singly, doubly, or triply degenerate state) under the conditions of a weak pseudo-Jahn–Teller effect[31]

$$\Delta_1 = E_p - E_s > 4E_{JT} = \frac{2V^2}{K}, \tag{8}$$

where V is the electron-vibrational interaction constant, and K is the stiffness of the vibrational mode Q_{sp} which is active in the Jahn–Teller effect. The addition of another particle (a hole) can cause a transition of the center to conditions of a strong Jahn–Teller effect with radical restructuring of the adiabatic potential, even without any change in the electron-vibrational interaction constant. For this, the appearance of quasidegeneracy in the ground state of the two-particle system, in particular, closeness of the energies of the singlet terms of the s^2 and sp configurations and satisfaction of the conditions[31]

$$\Delta_2 = E(sp;{}^1P) - E(s^2;{}^1S) = \Delta_1 + U(sp) - U(s^2) < 4E_{JT}, \quad (Q_{sp}=0), \tag{9}$$

is sufficient. This condition is entirely realistic if the repulsion of s and p particles is weaker than the repulsion of $2s$ particles. We note that the possibility of a transition between a weak and strong pseudo-Jahn–Teller effect in the system accompanying a change $N=1 \rightarrow N=2$ obviously presupposes the existence of an appreciable electrostatic repulsion between particles in the valence shells. We designate symbolically the reaction in which a hole is attached to an M_{sp}^h center with the formation of a hole center exhibiting a strong dynamic pseudo-Jahn–Teller effect as

$$M_{sp}^h + h = [M_{sp}^h]_{JT}^+. \tag{10}$$

The adiabatic potential of such a center has a complicated form (see Fig. 5) with diverse unique properties:[31]

—existence of Jahn–Teller stabilization energy E_{JT}, in our case playing the role of a unique pairing energy of two fermions in a quasiboson formation—a vibronic shell;

—strong s^2–sp hybridization of vibronic origin with participation of an active vibrational mode (modes) Q_{sp}, formation of stationary states described by correlation functions—vibronic biorbitals;

—appearance of a new scale of superlow energies, associated with the energy of "free" or "hindered" rotation

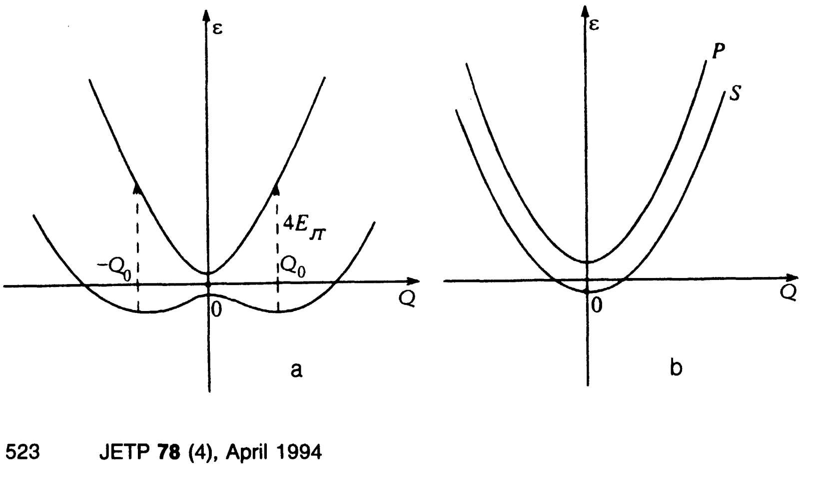

FIG. 5. Schematic form of the adiabatic potential of a dynamic Jahn–Teller center. The form of the adiabatic potential in the case of a weak pseudo-Jahn–Teller effect is presented for comparison.

of the field of displacements (energy of rotational quantum or tunneling splitting, respectively)[31]

$$\delta \sim \left(\frac{\hbar\omega_0}{4E_{JT}}\right)\hbar\omega_0 \tag{11}$$

($\hbar\omega_0$ is the characteristic energy of a quantum of the vibrational mode Q_{sp});

—anomalously high (generally speaking, temperature-dependent) electric polarizability;

—redistribution of the intensity of an allowed s^2–sp electric-dipole transition ($\hbar\omega = \Delta_2$ at the point $Q_{sp}=0$) in a wide range of the spectrum from the band at $\hbar\omega \simeq 4E_{JT}$ (transition between the lower and upper branches of the adiabatic potential) up to bands corresponding to transitions between tunneling states ($\hbar\omega \sim \delta$) within the lower branch of the adiabatic potential;

—softening of the vibrational modes which are active in the pseudo-Jahn–Teller effect and increase in the intensity of the corresponding IR bands;

—anomalous manifestation of orbital magnetism of a Jahn–Teller center, including both the electronic contribution (with unfrozen orbital angular momentum of a doubly or triply degenerate p state) and, generally speaking, an ionic contribution associated with the possible "rotation" of ions of the cluster along distinctive orbits;[31]

—possibility of introducing orbital quasispin in order to describe the lower tunneling states of the center with an anisotropic g-factor and an effective spin-Hamiltonian of the form

$$H_S = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + \dots, \tag{12}$$

where the parameters of the "quasispin" anisotropy $D, E, \dots$ will be determined by the magnitude of the tunneling splitting.

In contrast to ordinary paramagnetic centers, in the present case the following will be observed: a) electric-dipole character of resonance transitions; b) anomalously strong quasi-spin–lattice coupling; c) ultrahigh sensitivity to small external low-symmetric electric or mechanical actions, which can transform a dynamical Jahn–Teller center into a static Jahn–Teller center with "freezing" of the quasispin and magnetic moment; d) anomalously weak coupling with the surrounding magnetic spin system due to the orbital nature of the magnetic moment and the effects of vibronic reduction of the electronic interactions. It should be noted especially that a dynamical Jahn–Teller center with an anomalously high polarizability is a source of a strong polarization pairing potential and a center of condensation of fermion pairs (quasibosons).

We considered above the reaction (10) in which a hole is captured or a cluster M_{sp}^h is ionized with the formation of a dynamical Jahn–Teller center $[M_{sp}^{hh}]_{JT}$. In the usual simplified approach the reaction in which an electron is captured by an M_{sp}^h center gives the trivial result

$$M_{sp}^h + e = M_0, \quad (Q_{sp}=0), \tag{13}$$

where M_0 denotes a core consisting of completely filled shells. However, the possibility of the formation of a new vibronic hybrid shell with $Q_{sp} \neq 0$ in a reaction of the type (10) gives one other channel for the reaction (13):

$$M_{sp}^h + e = M_{sp}^h + h + 2e = [M_{sp}^h]_{JT}^+ + (s^2;{}^1S)_0 = [M_{sp}^h]_{JT}^- \tag{14}$$

with formation of an electronic center of a new type—a bound state of a Jahn–Teller center $[M_{sp}^h]_{JT}^+$ and two electrons paired by the interaction with the vibronic shell under the necessary condition that they form a completely filled shell $(s^2{:}{}^1S)_0$ with localization at the point $Q=0$ of the adiabatic potential (S-boson). Indeed, adding a completely filled shell under these conditions does not bring about any fundamental changes in the adiabatic potential for the vibronic shell and destruction of the Jahn–Teller center.

The binding energy of an S-boson is determined by the mechanism of polarization pairing, taking into account the vibronic reduction of the electrostatic interaction of the S-boson and a vibronic shell, which are localized at different points of the configurational Q-space. In spite of the complicated nature of the binding energy E_b of an S-boson, it can be simply estimated as $E_b \simeq E_{JT}^-$, where E_{JT}^- is the energy of Jahn–Teller stabilization of an $[M_{sp}^h]_{JT}^-$ center, indicating once again the correlated character of an S-boson and a vibronic shell.

The reactions (10) and (14) also suggest a new channel for the well-known disproportionation reaction with formation of two polar Jahn–Teller centers:

$$\begin{aligned} M_{sp}^h + M_{sp}^h &= (M_{sp}^h + h) + (M_{sp}^h + e) \\ &= [M_{sp}^h]_{JT}^+ + ([M_{sp}^h]_{JT}^+ + (s^2;{}^1S)_0) \\ &= [M_{sp}^h]_{JT}^+ + [M_{sp}^h]_{JT}^-. \end{aligned} \tag{15}$$

The polar Jahn–Teller centers $[M_{sp}^h]_{JT}^\pm$ differ only in that the $[M_{sp}^h]_{JT}^-$ center has an additional completely filled s^2 shell—an S-boson. Both types of strongly polarized centers, present in a lattice of M_{sp}^h clusters, can catalyze the disproportionation reaction for M_{sp}^h clusters in their immediate neighborhood. In other words, a lattice of M_{sp}^h centers that is unstable against a weak-strong pseudo-Jahn–Teller effect when doped by an electron or hole will be unstable against a disproportionation reaction and the formation of the nucleus of a new phase—a strongly correlated Bose system, consisting of a set of hole $[M_{sp}^h]_{JT}^+$ and electron $[M_{sp}^h]_{JT}^+$ vibronic centers differing by a single S-boson. A similar situation can be observed in photoexcitation of the lattice of original centers. The new phase can be regarded as a lattice of Jahn–Teller centers $[M_{sp}^h]_{JT}^+$ half of whose sites are occupied by S-bosons with charge $-2e$ or as a lattice of Jahn–Teller centers $[M_{st}^h]_{JT}^-$ half of whose sites are filled with hole S-bosons with charge $2e$. This system can be regarded as a unique Bose liquid, which cannot exist without its reservoir—a lattice of Jahn–Teller centers. Its possible states include metallic, superfluid (superconducting), and charge-ordering states and a mixed state.[32] From the standpoint of the single-particle fermion band approach the new phase can be described as a Fermi system with a conduction band and a valence band, separated by a gap $E_g \approx E_{JT}^+ + E_{JT}^-$. We note that, generally speaking, the

Jahn–Teller stabilization energies ($E^{\pm}_{JT}$) of $[M^h_{sp}]^{\pm}$ centers are different. In the "boson" language the gap width E_g is the sum of the binding energies of two quasiboson formations—a vibronic shell and an S-boson.

The effective mass of an S-boson will be determined only by the two-particle polarization interactions:

$$\begin{aligned} m^{-1}_{\text{eff}} &\sim \langle \phi_s(r_1)\phi_s(r_2) \,|\, U_{\text{pol}} \,|\, \phi_s(r_1-R)\phi_s(r_2-R)\rangle \\ &\sim \langle \phi_s(r) \,|\, \phi_s(r-R)\rangle^2, \qquad (16) \end{aligned}$$

where U_{pol} is the effective two-particle polarization-interaction potential and $\langle \phi_s(r) | \phi_s(r-R)\rangle$ is the overlap integral of the s orbitals for the nearest centers. We emphasize that the expression (16) is valid only when the adiabatic potentials for the $[M^h_{sp}]^{\pm}_{JT}$ centers are identical; otherwise Eq. (16) will contain the overlap integral of vibrational functions, which will increase the effective mass (vibronic reduction effect[31]).

The Jahn–Teller centers forming a lattice—a reservoir for S bosons—interact with one another. This interaction could result in some type of low-temperature cooperative Jahn–Teller static or dynamic ordering of electric dipoles. The S-boson liquid will be stable, within certain limits, against changes in the character of the ordering of the lattice of Jahn–Teller centers, at least up to certain critical values of the local polarizability of the lattice. Thus for a lattice of M^h_{sp} centers, besides the known phase states—antiferromagnetic dielectric (large values of U, high disproportionation-reaction threshold) and Fermi liquid state (small U), it is also necessary to consider one other possible state—a strongly correlated Bose system with a strong pseudo-Jahn–Teller effect (moderate values of U).

The formation of nuclei of a polar configuration phase in an antiferromagnetic matrix of M^h_{sp} centers, their intergrowth and increase in number will result in suppression of the initial antiferromagnetic dielectric phase. When the percolation threshold is reached and the concentration of S bosons deviates from $n_b=0.5$, conditions arise for the system to become metallized and for a resistive superconducting transition to occur at the condensation temperature of the S-bosons. Further increase in the concentration of the doped holes (electrons) can result in strong screening of the electrostatic interaction and the system can be transferred into the "Fermi-liquid" regime. Nuclei of the polar-configuration phase are manifested in the most diverse physical properties, thereby determining the distinctive pseudo-impurity behavior of the M^h_{sp} system. It will largely depend on the concentration, sizes, and shapes of the nuclei and the distribution of centers within the nuclei and on their boundary.

In copper-oxygen high-T_c superconductors the single-hole cluster CuO_4^{6-} with D_{4h} symmetry, whose s-like ground state has a hybrid $\text{Cu}3d_{x^2-y^2} - \text{O}2p_\sigma$ character with b_{1g} symmetry, plays the role of an M^h_{sp} center. Analysis of the optical properties of a large class of copper oxides with CuO_4^{6-} clusters[20] shows that, judging from the intensity and polarization properties, the fundamental absorption band with a maximum at $\Delta_1 = 1.5$–2.0 eV is associated with an allowed transition with charge transfer b_{1g}–e_u, which in turn makes it possible to identify the first excited state of the CuO_4^{6-} cluster with a purely oxygen p-type orbital e_u-doublet. It is obvious that the predominantly "copper" character of the b_{1g} state and the purely oxygen character of the e_u state ensure that the condition $U(b_{1g}b_{1g}) > U(b_{1g}e_u)$ is satisfied; this is a necessary condition for the appearance of quasidegeneracy or closeness of the terms ${}^1A_{1g}$ and ${}^1E_u$ of the two-hole configurations b^2_{1g} and $b_{1g}e_u$, respectively. The appearance of absorption bands in the middle-IR range $\hbar\omega \sim 0.1$–0.5 eV with the introduction of holes in the CuO_2 plane of copper oxides[33,34] indicates directly the existence of quasidegeneracy in two-hole clusters CuO_4^{5-}, and hence the possibility of a weak–strong Jahn–Teller pseudoeffect transition accompanying the introduction of a hole into the initial CuO_4^{6-} cluster. There is no doubt that the real situation in CuO_4^{6-} clusters is somewhat more complicated than the simple model considered above. In particular, this concerns the two Q_{e_u} vibrational modes $[Q_{e_u}(\sigma)$ and $Q_{e_u}(\pi)]$, active in the mixing of the b_{1g} and e_u states, as well as the necessity of taking into account the $Q_{b_{1g}}$ and $Q_{b_{2g}}$ vibrational modes, active in the splitting of the e_u level. The additional vibrational modes complicate the form of the adiabatic potential and lead to "splitting" of the single transition ${}^1A_{1g} \to {}^1E_u$, characteristic for the simplest model considered above, into at least two transitions ${}^1A_{1g}$–${}^1E'_u$, ${}^1E''_u$, if the splitting of the branch of the adiabatic potential for the E_u term, including the vibrational modes $Q_{b_{1g}}$ and $Q_{b_{2g}}$, into two branches (E–b_{1g}–b_{2g} problem[31]), is taken into account. In addition, it was assumed implicitly above that the ground state of polar centers is of the ${}^1S$ type (singlet centers), though the ground state can also be a triplet term ${}^3P$ (triplet centers). The transition from a hole to an electronic center can also be accompanied by a ${}^1S$–${}^3P$ change in the ground state. Figure 6 displays several possible variants of the energy spectrum of hole $[\text{CuO}_4^{5-}]_{JT}$ or electronic $[\text{CuO}_4^{7-}]_{JT}$ centers, more accurately, the values of the adiabatic potential for different branches at the point of the configuration space corresponding to the minimum of its lower branch.

The introduction of an additional hole or electron in the CuO_2 plane results in the formation of Jahn–Teller centers[3)] $[\text{CuO}_4^{5-}]_{JT} \equiv [M^h_{sp}]^+_{JT}$ or $[\text{CuO}_4^{7-}]_{JT} \equiv [M^h_{sp}]^-_{JT}$, and nuclei (microgranules) of a new phase—a system of polar (hole or electronic) centers. The nuclei from a strongly correlated Bose system, in which S bosons, representing paired electrons in a completely filled shell $(b^2_{1g})\,{}^1A_{1g}$, corresponding to the point $Q=0$ of the configuration space, move along a lattice of Jahn–Teller centers $[\text{CuO}_4^{5-}]_{JT}$.

The appearance of nuclei of a new phase as a system of two types of Jahn–Teller centers (CuO_4^{5-} and CuO_4^{7-}) with the introduction of holes (or electrons) in the CuO_2 plane is confirmed by investigations of absorption in the middle-IR range for a large series of high-T_c superconducting materials.[33,34] According to these investigations, first, both hole and electron doping lead to the appearance of two absorption bands, which are identified with transitions from the lower to the upper branch of the adiabatic potential with $\hbar\omega \sim 4E^{\pm}_{JT}$ in $[\text{CuO}_4^{5-}]_{JT}$ and $[\text{CuO}_4^{7-}]_{JT}$ centers, respectively, and second, the total intensity of the doping-induced absorption bands indicates that the number of active centers is significantly larger than the concentration of doped holes (electrons). As expected, the Hall effect with a low degree of doping[34] records only the excess number of CuO_4^{5-} or CuO_4^{7-} centers, i.e., actually the deviation of the concentration of S-bosons in the nuclei from $n_b=0.5$. The more rapid increase in the intensity of the low-energy (LE) absorption band in the middle-IR range compared to the high-energy (HE) band with increasing hole concentration in LaSrCuO and YBaCuO systems[35] makes it possible to relate unequivocally the LE band to the hole centers $[CuO_4^{5-}]_{JT}$ and the HE band to the electronic centers $[CuO_4^{7-}]_{JT}$. Two absorption bands in the middle-IR range are also observed with photoexcitation in LaSrCuO and YBaCuO systems.[35] With photoexcitation or a low concentration of doped holes (electrons) absorption in the middle-IR range consists of a superposition of two more or less sharply differing LE and HE bands; this most likely indicates localization of S bosons in nuclei (charge ordering type state). When the concentration of S-bosons in the nuclei deviates from $n_b=0.5$ as the concentration of the doped holes (electrons) increases the charge-ordering state is replaced by a "mixed" state with delocalized S-bosons, and they can condense and form a superfluid (superconducting) state. This is reflected in the middle-IR absorption spectrum as a gradual transformation of LE and HE bands into a single wide band with a simultaneous increase in the Drude absorption in the IR range. The appearance of two types of polar Jahn–Teller centers with both hole and electron doping is confirmed independently, in particular, by the results of analysis of EELS spectra of hole and electronic high-T_c superconductors.[36] These results show that the hole states near the Fermi energy are of the same type in both cases.

In conclusion we note that the above model of a new phase is actually a two-band model, including a band of localized vibronic biorbitals as centers of a pairing potential, and a band of S-bosons that can be described with the help of a limiting variant of the Hubbard model with negative U.[32] The model has the advantage that it combines a number of physical ideas (Jahn–Teller effect, variable valence, local pairing, charge transfer, excitonic and electron-vibrational mechanisms of high-T_c superconductivity, etc.), already considered in one way or another in connection with the problem of high-T_c superconductivity. In particular, we call attention to the fruitful ideas described in Refs. 37 and 38 about the role of polar configurations and localized electron pairs in superconductivity.

The two-band character of the model makes it possible to separate quite sharply the physical properties of high-T_c superconducting materials that are associated with some band, though in many cases it also points to an extraordinary origin of the physical effect. Thus, within this model it is impossible to single out unequivocally an electron-vibrational or excitonic mechanism as the main mechanism of high-T_c superconductivity. Finally, we note that the approach employed in the present work can be easily extended to such "copper-free" high-T_c superconducting materials as $Ba_{1-x}K_xBiO_3$.

4. CHARACTERISTIC FEATURES OF THE MIDDLE-IR OPTICAL ABSORPTION IN CuO

As we have noted above, the appearance of $[CuO_5^{5-}]_{JT}$ or $[CuO_5^{7-}]_{JT}$ clusters in an antiferromagnetic dielectric matrix consisting of $[CuO_4^{6-}]_{JT}$ clusters will result in the formation of nuclei of a new phase which results from the disproportionation reaction

$$CuO_4^{6-}+CuO_4^{6-}=[CuO_4^{5-}]_{JT}+[CuO_4^{7-}]_{JT}$$
$$=2[CuO_4^{5-}]+S=\text{boson}$$

in some microregion of the lattice.

The optical signature of such a nucleus will be the appearance of two absorption bands at energies $\hbar\omega_\pm=4E_{JT}^{\pm}$ in the middle-IR region that correspond to allowed electric-dipole transitions $^1A_{1g}\rightarrow{}^1E_u$ (lower → upper branch of the adiabatic potential) in the Jahn–Teller clusters $[CuO_5^{5-}]_{JT}$ and $[CuO_5^{7-}]_{JT}$.

Such bands were observed experimentally in both "hole"

$La_{1.98}Sr_{0.02}CuO_4$: $\hbar\omega_{LE}\approx0.16$ eV, $\hbar\omega_{HE}\approx0.53$ eV (Ref. 33)

La_2CuO_{4+y}: $\hbar\omega_{LE}\approx0.13$ eV, $\hbar\omega_{HE}\approx0.6$ eV (Ref. 35)

La_2CuO_4: $\hbar\omega_{LE}\approx0.12$ eV, $\hbar\omega_{HE}\approx0.47$ eV (Ref. 35)

photoinduced absorption

La_2CuO_4: $\hbar\omega_{LE}\approx0.1$–$0.3$ eV, $\hbar\omega_{HE}\approx0.55$ eV (Ref. 39)

photoinduced reflection

$YBa_2Cu_3O_{6+\delta}$: $\hbar\omega_{LE}\approx0.16$ eV, $\hbar\omega_{HE}\approx0.62$ eV (Ref. 33)

and "electron"

$Nd_{2-x}Ce_xCuO_4$: $\hbar\omega_{LE}\approx0.16$ eV, $\hbar\omega_{HE}\approx0.76$ eV (Ref. 33)

copper-oxygen high-T_c superconductors. Thus, the existence of a spread in the experimental data, obtained either by different methods or different authors in samples with close composition, appears almost to be the rule. In Ref. 40 a wide absorption band with pronounced structure was observed in the region $\hbar\omega\approx0.1$–0.7 eV in a series of YBaCuO samples by the ellipsometric method, while direct measurements of absorption spectra in samples with close composition[48] indicate the existence of a wide structureless absorption band with a maximum at 0.3 eV.

The character of the middle-IR optical absorption will depend significantly on the size of the nucleus, more precisely, on the relative number of "internal" and "boundary" centers, as well as the distribution of $[CuO_5^{5-}]_{JT}$ and $[CuO_5^{7-}]_{JT}$ centers on the boundary surface. The point is that nuclei of the new phase are surrounded by an antiferromagnetic matrix consisting of $[CuO_4^{6-}]_{JT}$ clusters, so

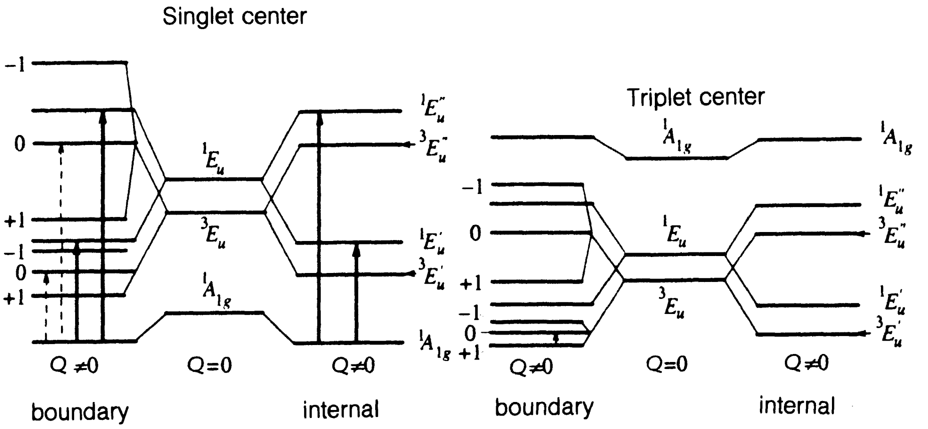

FIG. 6. Qualitative form of the energy spectrum of singlet and triplet centers of $[CuO_4^{5-}]_{JT}$ or $[CuO_4^{7-}]_{JT}$. The solid arrows indicate the observed IR-absorption transitions; the broken arrows indicate transitions observed in the Raman scattering spectra. The numbers 0 and ±1 indicate the Zeeman sublevels of the triplets $^3E_u'$ and $^3E_u''$, split by the exchange field of the matrix.

that the conditions at the boundary polar Jahn–Teller centers will be significantly different from the conditions at internal centers. First, they do not have a center of inversion and, second, a strong spin-exchange field acts on them.

Spin exchange with an antiferromagnetically ordered environment plus the spin-orbit interaction will mix the singlet and triplet terms $^1A_{1g}$, ^1E_u, and ^3E_u in polar Jahn–Teller clusters and induce new transitions of the form $^1A_{1g} \rightarrow {}^3E_u$ with a probability depending on the orientation of the spins of the antiferromagnetic environment. A qualitative picture of the energy spectrum of the singlet and triplet boundary centers, as compared with the corresponding internal centers, is displayed in Fig. 6.

If the boundary Jahn–Teller centers have no center of inversion, the corresponding lines will appear in the Raman light-scattering spectrum.

It is obvious that the contributions of boundary and internal centers of a nucleus to optical absorption will be comparable only for relatively small nuclei. The shape of the nuclei will also play an important role. Moreover, the fact that for one- and two-dimensional nuclei the separation of centers into internal and boundary centers is quite arbitrary must also be taken into account.

For singlet polar centers the LE and HE bands consist of two subbands, corresponding to the transitions $^1A_{1g} \rightarrow {}^1E_u'$, $^1E_u''$ on different branches of the adiabatic potential for the E_u term. The "fine" structure of the LE and HE bands has been observed quite clearly in, for example, the IR absorption spectrum of the system YBaCuO.[40] There is no doubt that the separation of centers into internal and boundary and, hence, the shape and size of the nuclei and character of the distribution of polar centers inside a nucleus and on its boundary play a definite role in the fine structure of LE and HE bands. These effects lead to, in particular, certain differences which are observed in the middle-IR absorption spectra even for samples whose composition is formally the same.

The $[CuO_5^{5-}]_{JT}$ and $[CuO_5^{7-}]_{JT}$ boundary centers in nuclei play the decisive role in charge-transfer processes. The corresponding energies $E_{JT}^{\pm}$ will determine the activation energy of electronic and hole conduction.

These nuclei can arise not only due to artificial electronic or hole doping or photoexcitation of the starting matrix of $[CuO_4^{6-}]_{JT}$ clusters. In principle, different defects, characterized by high electric polarizability, can serve as regions of natural nucleation. It is this situation that is apparently realized in stoichiometric copper oxide CuO, where the appearance of absorption bands has also been observed in the middle-IR range with no special doping.[42]

We investigated in detail the spectral, polarization, and temperature dependence of the absorption bands of CuO in the middle-IR region.

The samples investigated consisted of thin (160 μm thick) single-crystalline CuO wafers with *ac*(010), *bc*(100), and (110) planes, which contain the *c* axis and are oriented with an accuracy of ±2°. The measurements were performed on a modern automated IKS-21 spectrometer.

A quite wide ($2\Gamma = 0.160$ eV) band at 0.220 ± 0.004 eV and a narrow ($2\Gamma = 0.050$ eV) band at 0.106 ± 0.001 eV are observed in the absorption spectrum for unpolarized light in the region 0.1–1.5 eV [$\mathbf{k} \perp (110)$].[4),42] The general form of the spectral dependence of the absorption coefficient indicates wide bands at $\hbar\omega \sim 0.1$ and 0.2 eV with complicated structure, consisting of an entire series of subbands with different polarization characteristics and separations of the maxima, characteristic for vibrational quanta. The total intensity of the observed bands is, on the one hand, significantly higher than the intensity of purely vibrational transitions and, on the other, two to three orders of magnitude lower than the intensity of the allowed transitions with charge transfer, which form the main absorption band in the region $\hbar\omega \geqslant 1.4$ eV. The basic features of the spectrum remain in the region of antiferromagnetic ordering; only the minimum at 0.140 eV becomes substantially deeper.

In linearly polarized light under normal incidence on the (110) plane strong dichroism

$$D = \frac{\alpha_{\parallel} - \alpha_{\perp}}{\alpha_{\parallel} + \alpha_{\perp}},$$

is observed, where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the absorption coefficients for radiation whose electric vector is parallel and perpendicular, respectively, to the *c* axis. It reaches more than 40% for wavelengths ranging from 4 to 9 μm. We

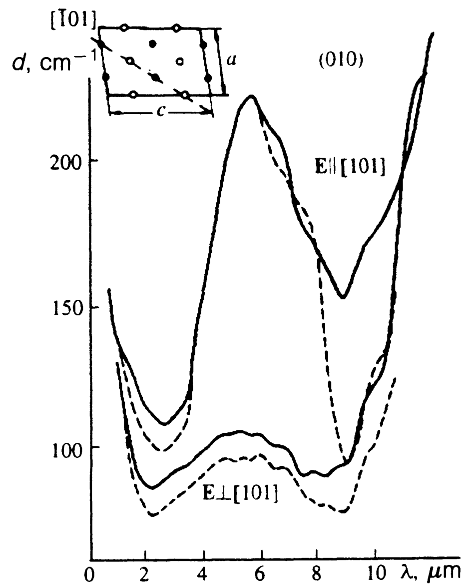

FIG. 7. Dispersion of the absorption coefficient of polarized light in a CuO single crystal [k⊥ (010)]. $T=300$ K (solid line) and 80 K (dashed line).

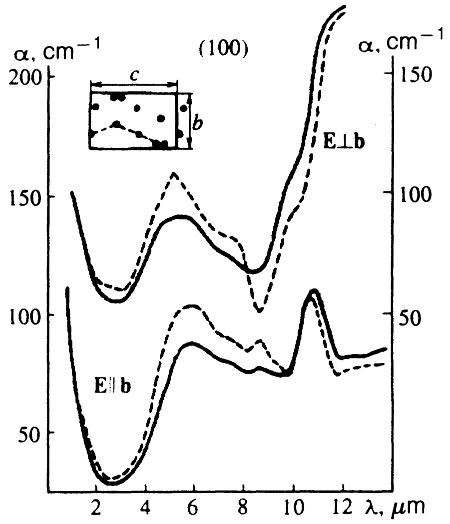

FIG. 9. Dispersion of the absorption coefficient for polarized light in a CuO single crystal [k⊥ (100)]. $T=300$ K (solid line) and 80 K (dashed line).

note that the character of the absorption anisotropy $(\alpha_{\parallel} \geqslant \alpha_{\perp})$ is identical to the character of the electric-conductivity anisotropy $(\sigma_{\parallel} \geqslant \sigma_{\perp})$.[6]

Under normal incidence of light on the (010) plane (Fig. 7) the form of the absorption dispersion as a whole remains the same, but the [$\bar{1}$01] direction is the distinguished axis: absorption is maximum for light polarized along this axis (see Fig. 8). The Cu and O atoms, projected on the (010) plane, and the [$\bar{1}$01] direction, making an angle of ~30° with the c axis, are shown in the inset in Fig. 7. Chains with the antiferromagnetic bond lie in the [$\bar{1}$01] direction. The angle between the Cu–O–Cu ions in the plane is ~146°, and the copper atoms lying in the same plane and the oxygen atoms lie alternately above and below the Cu plane. Relatively weak ferromagnetic exchange occurs between the chains.

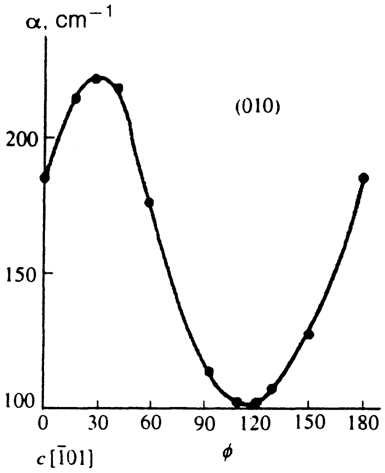

FIG. 8. Absorption coefficient for light with $\lambda=5$ μm [k⊥ (010)] in CuO as a function of the angle ϕ of the orientation of the intensity vector of the electric field E of the wave in the (010) plane.

The minimum at 0.140 eV in the absorption spectrum becomes much deeper on cooling, as in the case of unpolarized light, especially for **E**∥ [$\bar{1}$01]. The temperature dependence of the absorption in this region has an inflection point at ~190–200 K, similarly to the temperature dependence of the electric conductivity $\sigma(T)$.[6] The form of the angular dependence $\alpha(\phi)$ of the absorption coefficient on the orientation angle of the vector E in the (010) plane with $\lambda=5$ μm (Fig. 8) agrees qualitatively with theoretical notions about the polarization characteristics of electric-dipole transitions $^1A_{1g}$–^1E_u observed in the $[\mathrm{CuO}_4^{5-}]_{JT}$ (or $[\mathrm{CuO}_4^{7-}]_{JT}$) clusters only in E⊥ C_4 polarization. The existence of strong optical anisotropy makes it difficult to perform a detailed quantitative analysis of the polarization characteristics of the IR absorption spectrum of CuO.

In the case of light incident on the (100) plane (Fig. 9) a wide band with a maximum at 0.240±0.005 eV for E∥ c or 0.210±0.005 eV for E⊥ c, as well as a band at 0.113±001 eV, is observed. In the case of the polarization E∥ b a pronounced maximum is observed in the spectrum at 0.14 eV; this maximum can be associated with a transition whose intensity increases as the temperature decreases from room to liquid-nitrogen temperature. This transition is practically not observed in the case of the polarization E∥ c; this is indicated by the minimum in the absorption spectrum at 0.14 eV, which is especially deep at the temperature of liquid nitrogen. The temperature dependence of the absorption coefficient at 0.14 eV has a singularity in the form of a break at $T\sim 190$–200 K, similarly to the electric conductivity.[6] With the exception of this feature the temperature dependence of the absorption spectrum in the region 2–12 μm is, on the whole, relatively weak. We also note that we have not observed any appreciable effect of an external magnetic field (up to 80 000 A/m) on the spectrum.

In a qualitative discussion of the observed features of the absorption spectra of CuO in the middle-IR range it appears completely natural to relate the LE band with a maximum near 0.1 eV to $[\mathrm{CuO}_4^{5-}]_{JT}$ hole Jahn–Teller centers and the HE band with a maximum near 0.2 eV to $[\mathrm{CuO}_4^{7-}]_{JT}$ electronic Jahn–Teller centers. However, comparing the corresponding energies of transitions in CuO and in an entire series of copper-oxygen high-T_c superconductors shows that it is more reasonable to conclude that both lines (0.1 and 0.2 eV) in the IR absorption spectrum of CuO belong to the transitions ${}^1A_{1g}$–${}^1E_u'$ and ${}^1A_{1g}$–${}^1E_u''$ in the $[\mathrm{CuO}_4^{5-}]_{JT}$ hole centers, forming the overall LE band. The corresponding transitions are marked in Fig. 6 by the thick arrows.

In this case the absence of an HE band in the IR absorption spectrum of CuO is a unique indication of a triplet ${}^3E_u$ ground state of the $[\mathrm{CuO}_4^{7-}]_{JT}$ electronic center in CuO. The above correlation effect of the "soft" anionic core[25] can stabilize the ${}^3E_u$ term as the ground state; this effect can contribute to the relative lowering of the energy of the E_u terms quite differently for hole and electronic centers because of the difference in the O_{2p} hole density. Apparently, it is the triplet electronic centers that are manifested in the wide band of the density of states observed in point-contact spectra of CuO in the region $E \geqslant 0.7$ eV.[5),6]

The supposition that the ground state of electronic $[\mathrm{CuO}_4^{7-}]_{JT}$ centers is a triplet state agrees very well with the existing experimental observations of strong paramagnetic contribution to the paramagnetic susceptibility[4] as well as the direct observation of EPR in different CuO samples.[43] Indeed, the internal triplet centers, surrounded by singlet nonmagnetic hole centers, are paramagnetic resonance centers. The virtual absence of an angular dependence in the EPR spectra and the fact that the g-factor is close to the purely spin value [$g=2.095$ (Ref. 43)] indicate that the spin anisotropy of the center is weak. The concentration of paramagnetic centers, according to Ref. 43, for different CuO samples fluctuates from 10^{19} cm^{-3} up to extremely high values $\sim 10^{21}$ cm^{-3}. These same concentrations, according to our model, must also be characteristic for hole centers in CuO.

For internal centers in a nucleus the effect of the magnetic state of the main matrix is characteristically weak, and hence the change in the spectral characteristics accompanying a transition through the temperature range (213–231 K) where the magnetic order in CuO changes is weak. The temperature effects will then be of the usual character, determined mainly by the structure of the lower vibronic levels. The adiabatic potential and energy spectrum of the internal and boundary centers can be significantly different. Actually, in the case of boundary centers we are dealing not only with an ordinary (dielectric) polaron, in terms of which an internal center can be conventionally represented, but also with a polaron-type state with strong mixing of electronic, vibrational, and magnetic spin modes. In addition, it is also necessary to take into account the possible existence of different boundary centers differing by their "matrix" environment. Boundary centers must be appreciably affected by the state of the magnetic environment via a change in both the transition energy and the transition probability. The participation of $e_u(\pi)$ orbitals in the formation of a vibronic shell of electronic and hole centers can result in strong ferromagnetic exchange of boundary centers with the nearest $[\mathrm{CuO}_4^{6-}]_{JT}$ centers when the geometry of the superexchange bonds is almost rectangular (interchain exchange). It is interesting that by virtue of the orthogonality of the wave functions of the E_u' and E_u'' states of the boundary centers strong interchain ferromagnetic $e_u - b_{1g}$ exchange and strong intrachain antiferromagnetic $b_{1g} - b_{1g}$ exchange should be observed for one of them, while relatively weak interchain exchange and competition between ferromagnetic $e_u - b_{1g}$ and antiferromagnetic $b_{1g} - b_{1g}$ exchange within chains should be observed for the other center. Strong interchain exchange for the boundary centers will cause the spectral characteristics of the boundary centers to depend strongly on the interchain magnetic correlations so that, in particular, their spectrum will be restructured in the temperature range of the three-dimensional magnetic ordering, T_{N_1} and T_{N_2}.

As we have already mentioned above, comparing the IR-absorption and Raman scattering spectra can give important information about the character of the nuclei and, especially, about the states of the boundary centers. The strongest lines in the Raman scattering spectrum of boundary singlet centers will be the lines corresponding to the transitions ${}^1A_{1g} \to {}^3E_u'$, ${}^3E_u''(M_s = 0)$, which are allowed because of the exchange interaction with the matrix, mixing these states with different spin multiplicity and parity. These "forbidden" transitions will also be observed in the IR absorption spectrum of boundary hole centers, but their intensity will be determined mainly by the exchange interaction, mixing the terms ${}^3E_u$ and ${}^1E_u$. The exchange interaction does not mix singlet terms and it cannot remove the exclusion of the singlet-singlet transition ${}^1A_{1g} \to {}^1E_u'$, ${}^1E_u''$, which is most active in IR absorption, in the Raman scattering spectra.

The triple electronic boundary centers $[\mathrm{CuO}_4^{7-}]_{JT}$, like the internal centers, are not manifested in either IR-absorption or Raman-scattering spectra, with the exception of the relatively weak magnetic-dipole transition between the Zeeman components of the ground spin triplet, split by the exchange field of the matrix (see Fig. 6).

Two wide ($\leqslant 200$ cm^{-1}) intense bands with maxima at 630 and 1150 cm^{-1} as well as a relatively weak narrow line, whose frequency and intensity are appreciably temperature-dependent (238 cm^{-1} and $T = 100$ K and 234 cm^{-1} at $T = 150$ K; the intensity drops sharply as the temperature increases to $T \approx T_{N_2}$), are observed, in addition to the clearly identified phonon peaks at 299, 346, and 630 cm^{-1}, in the experimental Raman scattering spectrum of CuO single crystals.[4]

It is natural to associate the wide bands at 630 and 1150 cm^{-1} with the transitions ${}^1A_{1g} \to {}^3E_u'$ and ${}^3E_u''(M_s = 0)$, and for them, as expected, interchain exchange plays a significantly different role. Indeed, the intensity of the band at 1150 cm^{-1} remains virtually unchanged as the temperature decreases from room temperature to $T \approx 100$ K, while the intensity of the band at 630 cm^{-1} increases by a factor of 2 or 3 (Ref. 44), indicating that interchain exchange makes a strong contribution to mixing of the corresponding $^3E_u'$ state with the ground singlet $^1A_{1g}$. The transition $^1A_{1g} \rightarrow {}^3E_u''$ with a maximum at $\hbar\omega = 1150$ cm$^{-1} \approx 0.14$ eV is observed in the IR absorption spectra (see Fig. 9), its intensity increasing with the transition through the region of three-dimensional magnetic ordering ($T \sim 213$–231 K). This shows that interchain exchange makes a strong contribution to the mixing of $^3E_u''$ and $^1E_u''$ states, which is responsible for the allowance of the electric-dipole transition $^1A_{1g} \rightarrow {}^3E_u$.

The singlet-triplet splittings that we obtained for the E_u terms of the $[\mathrm{CuO}_4^{5-}]_{JT}$ boundary centers on the basis of our interpretation of the IR-absorption and Raman-scattering data (≈ 0.03 eV—lower branch and ≈ 0.08 eV—upper branch) agree very satisfactorily with the value $E(^1E_u) - E(^3E_u) \approx 0.04$ eV which we computed in the cluster model for the hole center $[\mathrm{CuO}_4^{5-}]_{JT}$. This is an important additional indication of the reliability of the model developed.

Judging from the polarization characteristic and the temperature dependence of the frequency and intensity, the line at 238 cm^{-1} ($T = 100$ K) in the Raman scattering spectrum of CuO is associated with a transition between the two lower Zeeman components of the boundary triplet electronic center $^3E_u'(M_s = 1) \rightarrow {}^3E_u'(M_s = 0)$. Its frequency will reflect more the effects of the short-range magnetic order and the intensity will reflect the long-range magnetic order.

As we have already mentioned above, the relatively small magnitude of the total exchange field of the matrix for the lower branches of the triplet $^3E_u'$ states of boundary centers ($\Delta_{\mathrm{Zee}} = 238$ cm^{-1}—electronic center, $\Delta_{\mathrm{Zee}} < 630$ cm^{-1}—hole center) indicates the existence of very strong total exchange fields for the upper branches of the $^3E_u''$ triplet states of boundary centers, manifested, in particular, in the unexpectedly strong temperature dependence of the conductivity of CuO.[5,6] Indeed, the strong effect of the three-dimensional magnetic ordering on the activational character of the hole conductivity of CuO (Ref. 6) indicates that the upper triplet $^3E_u''$ states of the boundary hole centers play the predominant role in carrier transfer. Hole transfer between the hole center $[\mathrm{CuO}_4^{5-}]_{JT}$ and the initial center $[\mathrm{CuO}_4^{6-}]_{JT}$ of the matrix is most efficient along chains consisting of triplet states ^3E_u with the spin parallel to the spin of the neighboring center $[\mathrm{CuO}_4^{6-}]_{JT}$ ($s = 1/2$).6) The numerical value of the conduction activation energy (0.12–0.16 eV) for $T > T_{N_1}$ (Ref. 6) is close to the average energy of the upper triplet state $^3E_u''$ (0.14 eV), which, evidently, provides the main channel for transfer of the hole carriers. This triplet level is subjected to very strong $e_u - b_{1g}$ ferromagnetic exchange between chains, which will lead, as the temperature decreases below T_{N_1} and T_{N_2}, to a strong increase in the energy of the Zeeman sublevel with spin orientation most favorable for hole transfer and hence a significant increase in the hole-conduction activation energy. The experimental value of the activation energy at temperatures $T < T_{N_2}$ [0.28–0.30 eV (Ref. 6)] indicates that the exchange splitting of the triplet state $^3E_u''$ is comparable to its average energy.

The existence, in our model, of carriers of both signs as well as internal and boundary centers in CuO makes it more difficult to perform a detailed analysis of conduction, and it is apparently responsible for the anomalously low values of the Hall effect and magnetoresistance[6] as well as the characteristic features of the temperature dependence of the thermo-emf.[5] It is still difficult to draw any conclusions about the role in transport effects played by internal centers, the sizes and shapes of nuclei, and the nonuniformity of the distribution of electronic and hole centers in CuO, i.e., factors which, in our opinion, also play an important role in the formation of the superconducting state in similar nuclei in high-T_c superconducting materials.

5. CONCLUSIONS

Cluster calculations of the electronic structure and energy spectrum of the square complexes $[\mathrm{CuO}_4^{6-}]_{JT}$ and $[\mathrm{CuO}_4^{5-}]_{JT}$ shows the existence of electronic quasidegeneracy in the ground state of the two-hole complex $[\mathrm{CuO}_4^{5-}]_{JT}$—closeness of the energies of the terms $^1A_{1g}$ and $^{1,3}E_u$ of the configurations b_{1g}^2 and $b_{1g}e_u$, respectively. This indicates the possibility of a weak-strong pseudo-Jahn–Teller effect transition accompanying the addition of a hole into the $[\mathrm{CuO}_4^{6-}]_{JT}$ complex with the formation of a $[\mathrm{CuO}_4^{5-}]_{JT}$ hole Jahn–Teller center. Such a center is, in turn, a center of localization of an S-boson—two electrons in a completely filled b_{1g} shell which are paired by the interaction with the vibronic shell. The hole center $[\mathrm{CuO}_4^{5-}]_{JT}$ with an S-boson forms an electronic center $[\mathrm{CuO}_4^{7-}]_{JT}$, which differs significantly from the ordinary center Cu^{1+} with a completely filled $3d$ shell. The formation of polar Jahn–Teller centers results in a decrease of the threshold of the disproportionation reaction. The penetration of a hole or an electron into the lattice of $[\mathrm{CuO}_4^{6-}]_{JT}$ clusters, photoexcitation of the lattice, and the presence of strongly polarized defects can result in the formation of nuclei of a new phase—a system of $[\mathrm{CuO}_5^{5-}]_{JT}$ and $[\mathrm{CuO}_4^{7-}]_{JT}$ polar Jahn–Teller centers. The new phase can be regarded as an S-boson liquid in a reservoir consisting of a lattice of $[\mathrm{CuO}_4^{5-}]_{JT}$ centers.

The nuclei are manifested optically as absorption bands at energies $\hbar\omega_{\pm} \approx 4E_{JT}^{\pm}$ in the middle-IR range. The structure of the bands and the effect of the magnetic state of the matrix are determined by quite subtle details of the electronic structure of the centers as well as the size and shape of the nuclei and the relative concentration of internal and boundary centers.

The identification of two bands in the IR-absorption spectrum of CuO at 0.1 and 0.2 eV with two allowed electric-dipole transitions with charge transfer in $[\mathrm{CuO}_4^{5-}]_{JT}$ singlet hole centers, as well as the conjecture that the ground state of the $[\mathrm{CuO}_4^{7-}]_{JT}$ electronic center is a triplet state, makes possible a unified description of the basic features of the optical spectra of CuO in the middle-IR range, including also the Raman scattering spectra and the characteristic features of the temperature dependences of the electric conductivity and magnetic susceptibility.

The existence of nuclei of a phase of polar Jahn–Teller configurations in CuO will result in a "pseudoimpurity" behavior of different physical characteristics. Thus, the existence of orbital magnetism of polar Jahn–Teller centers and spin magnetism of triplet electronic centers explains the low-temperature anomaly of the magnetic susceptibility[3,4] and magnetostriction[11] as well as, in principle, the recently observed[45] manifestation of magnetic metastability and magnetization fluctuations, increasing with increasing external magnetic field, in high-quality CuO single crystals. Structural instability in a system of Jahn–Teller centers in nuclei is manifested in the form of anomalies in the temperature dependence of ultrasonic absorption and temperature hysteresis of the sound speed.[10] The appearance of additional Mössbauer signals and μ-meson resonance can also be associated with the existence of nuclei.[12] We note here that there exists a correlation between the temperatures at which paramagnetic susceptibility,[3,4] magnetostriction and thermal expansion,[11] ultrasonic absorption coefficient,[10] and depolarization rate of μ-mesons[12] are observed. All this shows that the different "pseudoimpurity" effects are of the same nature and confirms our model of the formation of nuclei of a phase of Jahn–Teller centers in CuO.

The fundamental difference between CuO and copper-oxygen high-T_c superconductors in our model is the different character of the electronic $[\mathrm{CuO}_4^{7-}]_{JT}$ centers. The identical (singlet) ground state of hole and electronic centers in copper-oxygen high-T_c superconductors results in a low effective mass of S-bosons, while the different ground state of these centers in CuO results in their localization and a high effective mass of S-bosons. This fact limits significantly the prospects for obtaining high-T_c superconductivity in CuO.

We did not address the problem of making a comparative analysis of different alternative model descriptions (scenarios) of copper oxides, including, in particular, previous models of the absorption bands in the middle-IR range and the associated problem of the so-called mid-gap states (see, for example, Refs. 9, 14, 30, 33–35, and 40 as well as the recent work in Ref. 46). Such an analysis is still difficult to perform.

However, time the model proposed in present paper for the pseudoimpurity behavior of copper oxides includes many ideas and representations advanced in connection with the problem of high-T_c superconductivity.

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1) In addition, the effect under consideration will cause the absorption bands to have a complicated form associated with transitions with charge transfer. In the simplest model proposed by Hirsch[25] a $b_{1g}\rightarrow e_u$ transition should correspond to superposition of at least two (narrow and wide) absorption bands.

2) A short exposition of the basic model ideas elaborated in Sec. 3 is given in Ref. 26.

3) We note that the often employed comparison $\mathrm{CuO}_4^{6-}\rightarrow\mathrm{Cu}^{2+}$, $\mathrm{CuO}_4^{5-}\rightarrow\mathrm{Cu}^{3+}$, $\mathrm{CuO}_4^{7-}\rightarrow\mathrm{Cu}^{1+}$ is very arbitrary, especially considering the vibronic character of the polar centers. Thus, roughly speaking, an electronic Jahn–Teller center $[\mathrm{CuO}_4^{7-}]_{JT}$ formally corresponds to a $\mathrm{Cu}^{1+}(3d^{10})$ center only at the point $Q=0$ of configuration space.

4) The additional absorption band with a maximum at 0.4 eV, which we discovered in our first experiments,[42] is associated with the appearance of an ice film on the surface of the CuO single crystal.

5) Some terms (for example, ${}^{1,3}B_{2g}$; see Fig. 3) of a singlet hole center can also fall in the region $E\gg0.7$ eV.

6) Under otherwise the same conditions, purely spin effects alone give in this case a transfer probability that is four times higher than for the singlet state ${}^1E_u$ or the triplet state ${}^3E_u$ $(M_s=0)$.

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