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Thermoemission of Singlet Oxygen and Chemical Structure of Copper Oxides

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Abstract—Thermal treatment of copper oxides (CuO, Cu_2O) is accompanied by large-scale emission of singlet oxygen molecules ($^1\Sigma^+_g$). Electron spectroscopy for chemical analysis (ESCA) and electronic and IR spectroscopy were used to show that the thermoemission of electronically excited molecules results from dark generation of electronically excited states which contain in their structure isolated metal–metal bonds and oxygen associates. The anomalous diamagnetic response of the samples and reduced thermoemission activity (Cu_2O) are associated with cooperative interaction of electronically excited states.

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Copper oxide occupy a special place in contemporary solid state chemistry and technology of catalysts, semiconductors, and high-temperature superconducting complex oxide ceramics. As known [1, 2], CuO and Cu_2O are a typical example of ionic crystals possessing semiconductor properties, they show tendency for forming free electronically excited states and feature appreciable charge inhomogeneity. To find out the chemical structure of electron and hole components of intrinsic defects of this type, as well as the chemical structure of labile compounds providing their mobility is among the most urgent theoretical and applied problems.

We compared in the present work the thermoemission activities of copper oxides, their electronic and vibrational structures, and magnetic susceptibilities, aiming at gaining insight into the structural and chemical features of thermal generation of electronically excited states.

Gas chromatographic analysis [3] of oxygen thermoemitted by copper oxides in the temperature range 20–1000°C showed that the major component (50–75%) is the electronically excited form of molecular oxygen in the $^1\Sigma^+_g$ state ($E_{ex} \approx 2$ eV). As seen from Fig. 1, CuO exhibits enhanced activity, and the maximum emission is registered about 573 K. The observed effect suggests uniform defects in copper oxides and a mechanism favoring large-scale transformation of thermal perturbations into the energy of electron excitation is operative. The concentration of excited states, estimated from the quantity of emitted oxygen, is about 1018 cm^{-3}; such concentration level ensures initiation of association of structural defects [4]. The thermal (dark) energy source suggests the following sequence of process stages: local structural deformations, vibrational excitation, vibronic interactions, electron excitation and its structural chemical consequences .

The estimated strength of interaction of electronic and vibrational degrees of freedom in molecular and condensed systems [5] allows us to conclude that, in

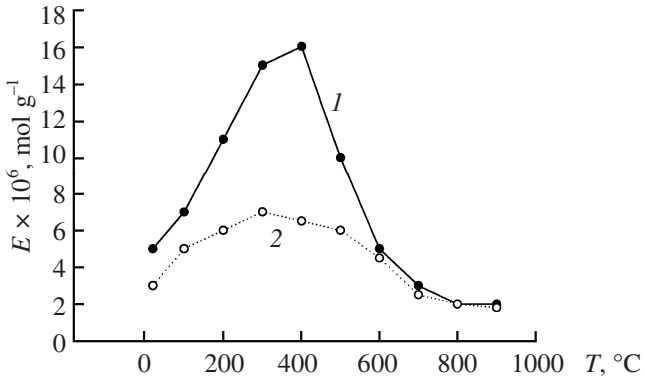

Fig. 1. Thermemission (TE) of singlet oxygen ($^1\Sigma^+_g$) by copper oxides: (*1*) CuO and (*2*) Cu_2O.

the absence of an outer resonance excitation source, the intrinsic resources of a condensed system can provide, due to interaction of elementary oscillators, generation for excited states and their existence as dimers. From the chemical viewpoint, this is a redox reaction [2] which forms a Mott exciton, i.e. two atoms with opposite excess charges. In the M^+O^- oxide lattice, state M corresponds to electron and state O, to hole. The transformation potential is given by the Hilsch–Pohl empirical formula which provides the best fit to experiment [6].

$$W = (e^2/na)\mu + E - I. \quad (1)$$

Comparative calculation of the energy of Wannier–Mott excitons (W_n) as a function of their size (na) shows that with KCl the exciton energy tends to zero and acquires small negative values, starting from n 17 only (W_1 7.50 → W_{17} –0.02 eV). With CuO, the energy becomes negative already at n 2 (W_1 2.57 → W_2 –1.83 → W_{18} –5.75 eV), after which it fast approaches the limiting value ($W_{n\to\infty}$ –6.25 eV). This result suggests that the formation of excitons of a larger radius ($n \geq 2$) in copper oxides may involve exoenergetic stages. The energies of the latter stages are high enough to induce large-scale transformations of deformations of structural polyhedra into electron excitations of the exciton type. The activation energy of the process is determined by the sum of the first two terms in Eq. (1) and spans the range 1.5–15 eV. The minimum value is close to the electron affinity of oxygen atoms. The barrier is obviously overcome on stretching of the M–O bond and deformation of the structural polyhedron. Thus electron-vibrational excitation of the oxygen ion occurs, whose energy may reach threshold values high enough for electron abstraction and transfer. Overcoming the energy barrier comparable with the electron affinity of oxygen atoms (~1.47 eV) in CuO may be favored by vibronic enhancement of vibrational perturbations in the framework of the exoenergetic cooperative Jahn–Teller effect [7] and in Cu_2O (collinear bond structure), Paierls instability relaxation [8]; in both cases, the multiphoton mechanism of energy accumulation is a favorable factor. The probability of the latter contribution is increased by hindered rotation in deformed elements of a condensed structure, i.e. by slowed down *V–R–T* relaxation of the vibrational perturbation energy.

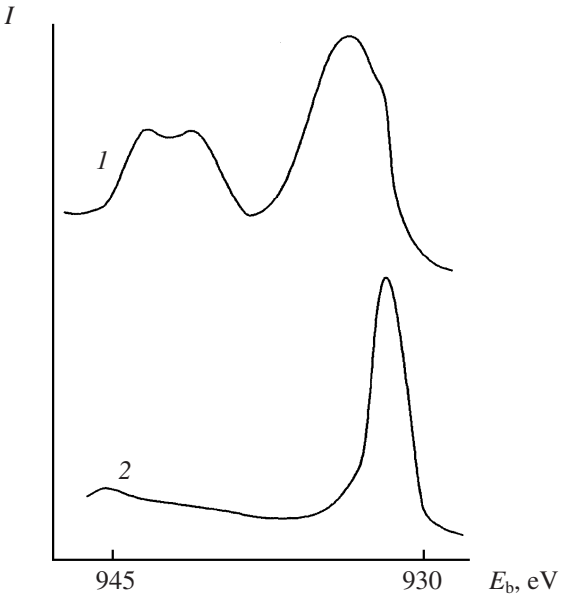

Fig. 2. X-ray electron (ESCA) spectra of copper oxides: (*1*) CuO and (*2*) Cu_2O; $Cu2p_{3/2}$ level.

It follows from the probabilities of one-electron transfer in Cu(I) and Cu(II) oxides, estimated from the standard redox potentials of the corresponding pairs: $Cu^+ + e = Cu$ (E^0 0.52 V) and $Cu^{2+} + e = Cu+$ (E^0 0.153 V), that, all other factors being equal, in Cu_2O this process is more probable.

The ESCA spectra (Fig. 2) obtained by excitation of the $Cu2p_{3/2}$ core level in CuO and Cu_2O contain only one peak for univalent copper Cu^{1+} in Cu_2O at the binding energy of about 932 eV, which is assignable [9] to the final state $Cu2p^53d^{10}$, i.e. to a hole in the $2p$ zone. The strongest peak of divalent copper Cu^{2+} is observed at 933 eV ($Cu2p^53d^{10}O2p^5$ state). The fact that the latter peak is located close to the base peak in Cu_2O can be explained by shielding of the hole state in the $Cu2p^5$ zone due to charge transfer from $O2p^6$ [9]. A broadened satellite peak at 943 eV is also observed. Its shape (weakly split doublet) is associated with mutliplet splitting of the $3d$ state. The shift of the satellite peak by 9 eV reflects Coulomb repulsion of two holes. The ratio of the peak areas (1 : 2) of the satellite and base peaks allows us to estimate the degree of charge transfer from oxygen to copper. The shift of the base peak of Cu_2O to lower energies ($\Delta E_b \approx$ 1 eV) and the shape of this peak point to prevalence, among the final states, of the $Cu2p^53d^{10}4s^1$ state, which, too, is formed by one-electron transfer. The shape of the base peak (low-energy shoulder at 932 eV) in the spectrum of CuO suggests existence of a low-energy component which has the same energy as the final state in Cu_2O, which corresponds to a large-scale appearance of two-electron transfer.

The gas permeability specific surface areas (S_{sp}) [10] of CuO and Cu_2O were found to be 5.6 and 12.8 $m^2\ g^{-1}$, respectively. Since these values are inversely related to thermoemission activity, we can conclude that the active centers responsible for thermoemission are localized in the bulk structures.

The previous comparative X-ray diffraction, electron microscopy, and electron-diffraction study [11] of crystals of copper oxides established that the aggregates several thousand angstroms in size consist of blocks 300 Å in diameter, which, in their turn, consist of smaller aggregates 40 Å in diameter. These findings suggest different size conditions for the realization of stable exciton states in the structure of copper oxides.

The fundamental absorption spectra (Fig. 3) show that the absorption edge of CuO is formed by indirect allowed charge-transfer transitions in CuO_4^{6-} clusters from the ground Cu3*d*–O2*p* hybride states into purely oxygen $e_u(\pi)$ states, which corresponds to E_g 11700 cm^{-1}. Intrinsic defects, hole CuO_4^{5-}, and electronic CuO_4^{7-} pseudo-Jahn–Teller polar centers are associated with transitions at ~1750 and ~6500 cm^{-1}. The strong absorption at ~10500 cm^{-1} is assigned [1] to surface plasmon resonances produced by association and cooperative interactions of polar centers. As seen (Fig. 3), the spectrum of cuprite shows absorption in the range of defects and enhanced absorption (ν 1750 cm^{-1}) of their hole components.

Analysis of the vibrational spectra showed that the fundamental absorption edge of copper oxide looks like a band broadened on the low-frequency side and havind a well-defined maximum at 630 cm^{-1} which virtually coincides with the transition frequency in the ground electron state ($^2\Pi_{3/2}$) of the "free" molecular oscillator Cu–O [12]. In the range 630–557 cm^{-1}, bands of vibrational transitions in the electronically excited state of the "free" oscillator Cu–O (E_{ex} ~3 eV) are observed. Thus, we deal here with a high-frequency anomaly which was previously observed in a series of oxides [13]. This anomaly is associated with the effect of longitudinal vibrations [14], which relates to the presence of Coulomb excitons in a 2D quantum well.

The low-frequency region contains well-resolved lines at 505, 350, 302, 280, 276, 265, and 252 cm^{-1}. The first three lines were assigned, from a comparison with the Raman spectra of copper oxide ceramics [15], to totally symmetric vibrations of the labile part of the oxygen sublattice. Therewith, the first line relates to stretching vibrations of bridging oxygen atoms, whereas the second and third, to out-of-plane vibrations of oxygen in CuO_2 layers.

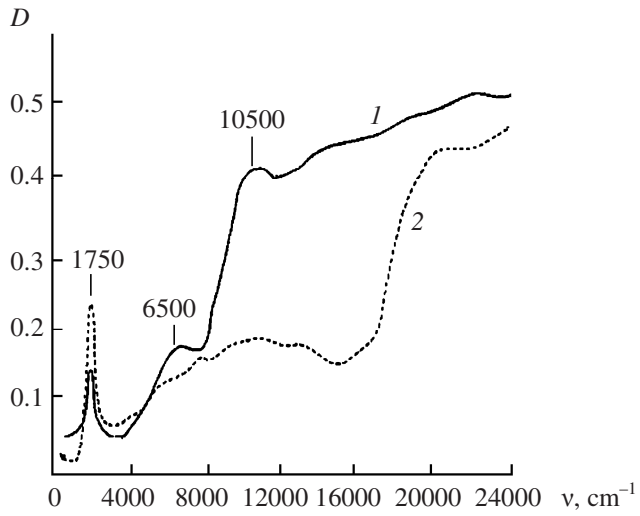

Fig. 3. Optical density spectra of copper oxides: (*1*) CuO and (*2*) Cu_2O.

The low-frequency bands in the range 250–300 cm^{-1} might be assigned to bending vibrations of the Cu–O–Cu bond, but the position of the band at 265 cm^{-1} almost completely coincides with the frequency of the fundamental vibrational transition of the free molecular oscillator Cu–Cu ($^1\Sigma_g^+$) [12]. The high intensity of the doublets at 280, 276, and 252, 255 cm^{-1} suggests that these modes relate to charge-transfer processes and correspond to high transition dipole moments. The Zeeman splitting of these bands (*H* 1–4 kG) allows them to be assigned to transitions in a system of localized exciton states, which are analogous to the levels of donor and acceptor admixtures in semiconductors [16]. The maximum electron–hole bond energy corresponds to the highest frequency band of the series (ν 505 cm^{-1}).

The spectrum of CuO at elevated temperatures (Fig. 4) shows enhanced characteristic bands of Cu–Cu bonds and peroxide groups (668 cm^{-1}, see table), as well as sharply enhanced absorption bands of hydroxyls perturbed by ozone (3645 cm^{-1}, Fig. 5) [17]. A series of strong hydroperoxide absorption bands appears (3615 cm^{-1}, Fig. 5). The hydroperoxide and peroxide bands were identified by spectrophotometry of samples with applied hydrogen peroxides. Therewith, the spectrum preserves strong absorption bands of molecular oxygen in the ground (1557 cm^{-1} – $^3\Sigma_g^-$) and

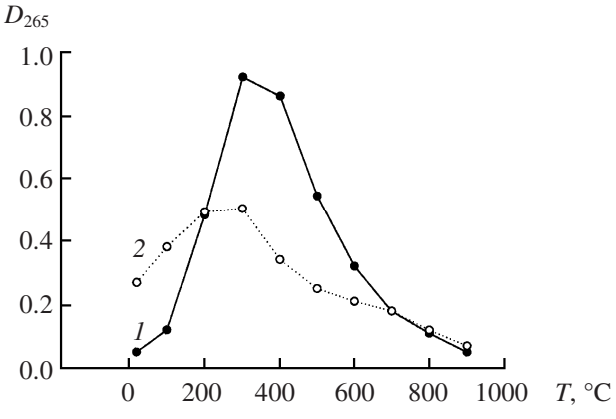

Fig. 4. Temperature dependence of optical density (D_{265}) for the Cu–Cu free oscillator band ($^1\Sigma_g^+$): (*1*) CuO and (*2*) Cu_2O.

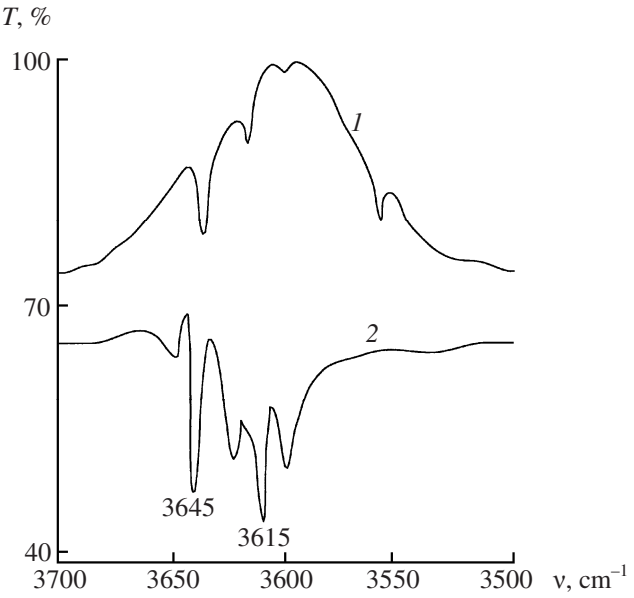

Fig. 5. IR spectra of (*1*) Cu_2O and (*2*) CuO in the range of stretching vibrations of hydroperoxide groups at 573 K (T is transmission).

singlet states (1456–1340 cm^{-1}; $^1\Delta_g$, $^1\Sigma_g^+$) (see table), as well as of ozone (1040–1060, 2005 cm^{-1}) [17].

As a result of discussion on the physical nature of the medium IR absorption bands (MIR bands) of copper oxides and high-temperature superconductivity, such bands were treated as the "optical portrait" of Jahn-Teller hole polaron centers (correlated small polaron model) [1], which define mobility of structural defects.

From the IR spectra of CuO at a temperature corresponding to a maximum thermoemission activity with respect to oxygen (573 K) we can assess the chemical structure of defects. At that temperature, the strong broad structured absorption band in the range 1150–850 cm^{-1}, whose center of gravity at 1020–1000 cm^{-1} (see table) contains a series of narrow strong bands reaches a maximum. The latter bands most probably belong to superoxide groups (O_2^-) in the electronically excited state ($a\ ^4\Pi_u$ ~1020 cm^{-1}, E_{ex} ~12 eV), since simultaneously we observe bands of the ground (X $^2\Pi_{gi}$ – 1072 cm^{-1}) and excited states ($a\ ^2\Pi_u$ – 560, $b\ ^4\Pi_u$ ~1290 cm^{-1}). Of no doubt is the presence of highly excited free O_2 oscillators (E_{ex} ~15 eV), since their vibrational activity clearly reveals itself in the ranges 760–730 and 1150–1020 cm^{-1}, as well as a single band at 2015 cm^{-1} [12]. The conclusion that the oxygen dimers O_2, O_2^-, and O_2^{--} are the chemical structure of the polaron states allows us to estimate, from the bond energy of the hole polaron $E_p = h\nu_{max} = 2E_u$ [1], the activation energy of oxygen mobility E_u at ~5–6 kJ mol^{-1}. The latter value is nicely consistent with the kinetic results.

Optical densities of characteristic bands of structural defects of copper oxides

Sample	T, K	D_{265} Cu–Cu	D_{668} ^-O–O^-	D_{1040} O_3	D_{1456} $^1O_2$ ($^1\Delta_g$)	D_{1400} $^1O_2$ (Σ_g^+)	D_{1020} O_2^-
CuO	298	0.05	0	0.07	0.18	0.18	0
Cu_2O		0.22	1.39	0.70	0.06	0.10	0.13
CuO	573	0.92	0.26	0.40	0.13	0.06	4.60
Cu_2O		0.48	1.12	0.53	0.09	0	0.69
CuO	973	0.06	0.34	0.14	0.12	0.07	0.21
Cu_2O		0.08	0.38	0.12	0.12	0.09	0.23

Essential distinguishing features of cuprous oxide are the presence of high-intensity luminescence bands at 532 and 418 cm^{-1}, as well as the lack of accentuated absorption at 600–500 cm^{-1}. The anomalously high optical density of the band at 668 cm^{-1} (see table), as well as the presence of a series of medium-intensity bands in the range 800–700 cm^{-1} point to increased concentration of peroxide groups. The observation of a series of bands at 1456, 1435, 1417, and 1400 cm^{-1} is indicative of prevalence of singlet forms among oxygen dimers (see table). A characteristic feature is the presence of bands due to O_2^+ radical cations (1010, 1870 cm^{-1}) [12].

The resulting data allow the formation of electronic excitations of the exciton type to be related to the presence of metal clusters and molecular states of oxygen in the cationic and anionic copper oxide sublattices. Evidence for this conclusion comes from the observation of a series of medium-intensity bands in the Cu_2O core absorption range 630–500 cm^{-1}, as well as from the virtually lacking accentuated absorption of a "free" Cu–O molecular oscillator (630 cm^{-1}). These findings are consistent with the concept that in the structure in question Coulomb excitons correspond to zero-valent states of copper and oxygen.

Comparison of the optical densities of the absorption bands of neutral and charged oxygen dimers and trimers shows that cuprous oxide has the strongest characteristic absorption maxima of peroxide groups and ozone (see table). Since peroxide groups and metal–metal bonds can be considered as forms of respectively hole and electron associates, the obtained result points to increased content in Cu_2O of localized associates of exciton defects.

Comparison of the temperature dependences of the optical densities of the bands of isolated Cu–Cu oscillators (see Fig. 4 and table) and peroxide and hydroperoxide groups shows that the observed peculiarity persists until the initiation temperature of a strong $Cu_2O \rightarrow CuO$ transition is attained (200–300°C).

The realization of the "hole" state as a heavy species (oxygen atom) predetermines an m_h/m_e ratio of much higher than 10, along with the steady-state formation of biexcitons (O_2) at a fairly high concentration (~1018 cm^{-3}), and creates conditions for formation of an exciton condensate in the copper oxide structure [18]. The condensation energy at T_c 300 K, estimated from the relation $\Delta E \sim 10kT_c$, is ν 2000 cm^{-1}. From this it follows that the IR luminescence activity in the spectra of Cu_2O and CuO can be associated with the formation of the exciton condensate. The latter characteristically shows a diamagnetic response on an outer magnetic field, and in strongly inhomogeneous systems this response can be anomalously high (superdiamagnetism).

Comparing the temperature dependences of the magnetic susceptibilities of copper oxides (Fig. 5), we should mention that CuO is a quasi-unidimensional antiferromagnetic and has a high Neel temperature (T_N 230 K) [19]. Below T 213 K, a collinear antiferromagnetic structure is realized in the oxide structure, while in the 213 K < T < T_N range, spiral. Strong spin correlations of Cu^{2+} ions along the [101] direction persist much higher than the Neel temperature.

The temperature dependence of the magnetic susceptibility of bulk samples in the low-temperature range has a shape typical of low-temperature antiferromagnetic systems which undergo transition into the 3D state with decreasing temperature. The susceptibilities (χ) of polycrystalline samples are normally 1.5×10^{-6} cm^3 g^{-1}. Heterophase samples have lower values. Univalent copper ions have a closed 3*d* shell (3d10, S 0) and are nonmagnetic. The low-temperature susceptibility of Cu_2O is low and decreases with increasing temperature from χ 0.81×10^{-6} (80 K) to 0.23×10^{-6} cm^3 g^{-1} (290 K) [19]. Metallic copper has a diamagnetic, temperature-independent susceptibility χ -0.1×10^{-6} cm^3 g^{-1} (300 K) [19].

Magnetic susceptibility measurements at elevated temperatures (Fig. 6) show that the susceptibility of CuO decreases from χ 0.36×10^{-6} cm^3 g^{-1} (20°C) to χ -2.9×10^{-6} cm^3 g^{-1} (900°C). Diamagnetic transition is observed at 400°C. Cu_2O is diamagnetic at temperatures above 50°C. At about 500°C the patterns of the temperature dependences of both samples are almost coinciding, which is explained by the $Cu_2O \rightarrow CuO$ transition. The mean diamagnetic response of the samples is higher by almost an order of magnitude than that of metallic copper, which, accounting for the concentration of exciton states, allows us to conclude that we deal here with a "giant" diamagnetism.

Together our results allow the thermemission of singlet oxygen by copper oxides to be correlated with dissociation acts of electronically excited states of exciton type. Since the hole components of such states are formed by oxygen dimers and associates, the thermoemission of singlet molecular oxygen as its singlet forms is an obvious consequence of dissocia-

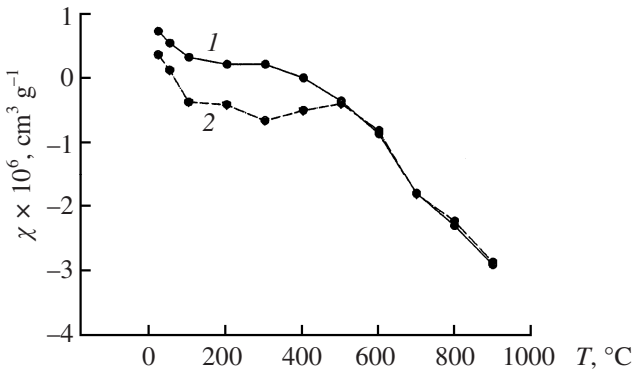

Fig. 6. Temperature dependence of magnetic susceptibility for copper oxides: (*1*) CuO and (*2*) Cu_2O.

tion. The fairly low activity of Cu_2O at a higher concentration in the cuprite structure of electronically excited states is an obvious consequence of the latter due to formation of strongly bound ionic associates (peroxide groups) and cooperative interaction (condensation). Experimental evidence for this suugestion comes from the observation of a series of luminescence bands (532, 418, and 302 cm^{-1}) and, at elevated temperature, of a very strong broadened luminescence band whose center of gravity (3615 cm^{-1}) (Fig. 6) coincides with the stretching vibration frequency of O–O–H groups. The resulting data allow us to identify as major two thermal redox transformations, namely homolytic bond rupture [reaction (2)] and intermolecular rearrangements [reaction (3).]

$$2\,[CuO_{4/2}]^{2-} \rightleftarrows [(O)_{3/2}\text{–}Cu\text{–}Cu\text{–}(O)_{3/2}]^{4-} + O_2\uparrow, \qquad (2)$$

$$2\,[CuO_{4/2}]^{2-} \rightleftarrows [\text{–}OO\text{–}(O)_{2/2}Cu\text{–}Cu(O)_{2/2}\text{–}OO\text{–}]^{4-}. \qquad (3)$$

At elevated temperatures they ensure stabilization of the chemical composition due to interaction of localized excitations.

EXPERIMENTAL

As objects for study we used polycrystalline CuO and Cu_2O of analytical grade. Structural identification was performed using a DRON-2.0 diffractometer (CrK_α radiation). The composition of gases thermoemitted by copper oxides was established by gas chromatography [3].

The X-ray electron spectra were taken on an HP ESCA-5950A spectrometer. The electronic and vibrational spectra of samples applied as dispersions on thin films of mica or polyethylene terephthalate (4–5 μm) with a surface density of ~2 mg cm^{-2} were measured on high-resolution instruments (IKS-25M, Chromex USA, Shimadzu-8400S, and Shimadzu-3101PC) which allowed reliable digital compensation for difference spectra.

The magnetic susceptibilities were determined by the magnetic compensation procedure, using Hall's detectors [20].

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