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SEMICONDUCTORS AND DIELECTRICS

Band Structure and Chemical Bonding in Cu_2O and Ag_2O Oxides

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Abstract—The band structure, total and projected densities of states, and distributions of the valence and difference electron densities for copper and silver oxides are calculated in the framework of the density functional theory in the local approximation with ab initio norm-conserving pseudopotentials in the basis set of pseudoatomic orbitals. The results obtained are compared with the experimental data and calculations performed by other authors. The energy spectrum and spatial distribution of electrons in crystals are similar to each other. Metal ions are bonded to each other through charge density channels with a weakly pronounced maximum at the center of the empty tetrahedron.

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1. INTRODUCTION

The electronic structure of copper and silver oxides has been the subject of numerous investigations as a result of their considerable importance from both the practical and theoretical standpoints. Cuprous oxide Cu_2O has been extensively studied with the aim of elucidating the role of this compound in the generation of high-temperature superconductivity [1]. In this respect, it is important to understand the mechanisms responsible for the formation of Cu–O bonds and possible direct Cu–Cu bonds. Silver oxide Ag_2O has also been considered a possible candidate for unusual superconductors [2]. However, this oxide has found wide use as a necessary component of conducting glasses in the Ag_2O–AgI–P_2O_5 [3], Ag_2O–AgI–V_2O_3 [4], Ag_2O–AgI–MoO_3 [5], and Ag_2O–AgI–TeO_2 [6] systems. Dutta and Chosh [7] established that, in $xAg_2O–(1-x)TeO_2$ glasses, the concentration of mobile silver ions is lower than the concentration of all silver ions and decreases with increasing concentration of silver oxide. With knowledge of the electronic structure, it is possible to determine the type of chemical bonding between Ag and O atoms, which is necessary for understanding the local structure of glass and the mechanism of ionic conduction.

In order to gain a deeper insight into the chemical bonding in copper and silver oxides, it is necessary, above all, to consider the hybridization of the *d* states of the metal not only with the *p* states of the anion but also with the *s* and *p* orbitals of the metal itself. The elucidation of the mechanisms responsible for the *s–d* and *p–d* hybridizations is of particular importance in explaining the mechanisms of chemical bonding between atoms with filled *d* shells. In actual fact, crystals of copper and silver oxides have a cuprite structure (space group $Pn\bar{3}m$) in which oxygen atoms are in the tetrahedral environment formed by metal atoms, whereas the metal atoms themselves are linearly coordinated to the oxygen atoms. As was shown by Pyykkö [8], the linear coordination of copper to oxygen and the short interatomic distances in crystals cannot be explained within simple models of interaction between the O^{2-} and Cu^{+} ions with the completely filled 4*d* shell and can be interpreted only if it is assumed that the copper atoms form a direct Cu–Cu bond.

The band structure of the Cu_2O oxide and a number of related parameters were calculated by Ruiz et al. [9] with the use of the periodic Hartree–Fock method. It turned out that the calculated values of the geometric characteristics, parameters of the energy spectrum, and effective masses are in good agreement with the experimental data available in the literature. For example, the width of the upper valence band, according to [9], is equal to 7.7 eV. The dominant contribution to this band is made by the Cu *d* states with a maximum in the density of states at 3.1 eV. The direct band gap (at the Γ point) is equal to 9.7 eV.

The electron charge distribution in the lattice of copper oxide was investigated using electron and x-ray diffraction by Zuo et al. [10]. These authors revealed a local maximum in the deformation electron density at the center of the empty Cu_4 tetrahedron and treated this maximum as proof of the direct Cu–Cu interaction. However, the result obtained in [10] was not confirmed by Lippmann and Schneider [11] and the above interpretation of the local maximum was later contested by

Laskowski et al. [12], who applied the augmented plane-wave plus local-orbital method to the theoretical investigation of the difference electron density maps obtained by subtracting the superposition of the Cu^+ and O^{2-} electron densities from the electron density map of the crystal. The presence of the local maximum in the deformation electron density was confirmed by calculations with a specially chosen set of basis functions; however, this maximum was not uniquely assigned to the metal–metal bonding. Thus, the question as to the character of the hybridization of the filled *d* shells with other metallic and anionic states remains open.

The band structure of the Ag_2O oxide was calculated using the augmented-localized-spherical-wave method by Czyzyk et al. [13], who also measured the x-ray absorption spectra. It was established that the width of the valence band is equal to 18.76 eV and the band gap is 0.40 eV. The upper valence band is characterized by the O_{2p}–Ag_{4d} hybridization. The Ag 4*d* band is located in the energy range from –4.5 to –2.5 eV. By analyzing these data, as well as the electron energy-loss spectra and x-ray photoelectron spectra, Hoflund et al. [14] proposed a model for the electronic band structure of silver oxide.

Earlier [15], we investigated the electronic (photochemical) properties of the Ag_2O oxide within the empirical pseudopotential approach and made a number of assumptions regarding the mechanism of chemical bonding. As far as we know, spatial distributions of the electron charge have not been studied in detail. In this respect, we performed ab initio calculations of the electronic structure of Cu_2O and Ag_2O oxides within a unified approach.

2. COMPUTATIONAL TECHNIQUE AND PARAMETERS OF THE CALCULATIONS

The electronic structure of copper and silver oxides was calculated within the framework of the density functional theory in the local approximation with ab initio norm-conserving pseudopotentials [16, 17]. The Kohn–Sham equations were solved using the basis set of pseudoatomic orbitals [18] obtained from the pseudoatomic equations on a radial grid, followed by determination of the parameters of their analytic representation [19]. The basis set of localized orbitals has the advantage that the local characteristics can be calculated by methods similar, in many respects, to those traditionally employed in quantum chemistry [20]. Moreover, as was shown in our previous papers [21, 22], the relatively small extension of the minimum valence basis set of pseudoatomic orbitals with functions of the ionized excited states of pseudoatoms makes it possible to obtain results that, in terms of accuracy, are on par with those calculated in the basis set of plane waves.

In our calculations, the basis set of pseudoatomic orbitals involved the set of *s*, *p*, and *d* functions of cations and oxygen atoms. In order to simplify the calculation of the multicenter integrals, these functions were expanded into a Fourier series in terms of plane waves with a maximum energy of 28.2 au. The electron density was calculated using the special points method on a $4 \times 4 \times 4$ grid in reciprocal space. The total and projected densities of states were determined by the improved tetrahedral method, for which the energy spectrum and the wave functions were calculated on a **k** grid containing of the order of 30000 points. The lattice constants for the structures of Cu_2O and Ag_2O were taken equal to 4.2696 and 4.7180 Å, respectively.

3. BAND STRUCTURES AND DENSITIES OF STATES

The band structures of Ag_2O and Cu_2O oxides are shown in Fig. 1. The energy is reckoned from the last filled state. Figure 1 also depicts the experimental photoelectron spectra taken from [23] and the densities of states *N*(*E*) in which the partial contributions of the *d* states of the metals are shown in dark gray.

The total widths of the valence bands for Cu_2O and Ag_2O oxides are equal to 15.82 and 16.65 eV, respectively. The lower valence bands are formed by the O 2*s* states. The width of these bands is approximately equal to 1.0 eV, which is considerably larger than that for oxides and halides of alkali metals. High energies of the interaction between the fragments constituting crystals with a cuprite structure were noted by Ruiz et al. [9].

The upper valence band with a width of 5.30 eV for copper oxide can be separated into three bands. The lower band from –5.00 to –3.00 eV is predominantly formed by the O_{2p} states. However, the Cu_{3d} states also make a noticeable contribution. To this band there correspond two maxima in the density of states at ~–3.50 and –5.00 eV. This is in agreement with the location of the peak at an energy of –5.00 eV, which was assigned in [23] to the O_{2p} state. In what follows, for convenience of comparison, the data taken from [23] will be reduced to the energy origin taken at the top of the valence band. The Cu_{3d} band is located in a sufficiently narrow energy range of ~1.50 eV. This band corresponds to the maximum with a barycenter at –1.93 eV in the density-of-states curve *N*(*E*) (at –2.5 eV according to the experimental data). The electronic states in the vicinity of the valence band top exhibit a mixed anion–cation nature. The density of states in this energy range has maxima at –0.40, –0.75, and –1.25 eV.

The energy band spectrum of The Ag_2O oxide has a similar structure. However, the effects of the hybridization of the Ag_{4d} states with the O 2*p* states are more pronounced. As a result, the width of the upper valence band increases to 6.76 eV and the maxima in the density of states *N*(*E*) are shifted toward the low-energy range to –6.41 and –4.96 eV. The Ag_{4d} bands are also characterized by a higher energy with a barycenter at –3.43 eV (–3.90 eV [23]). In the upper region of the

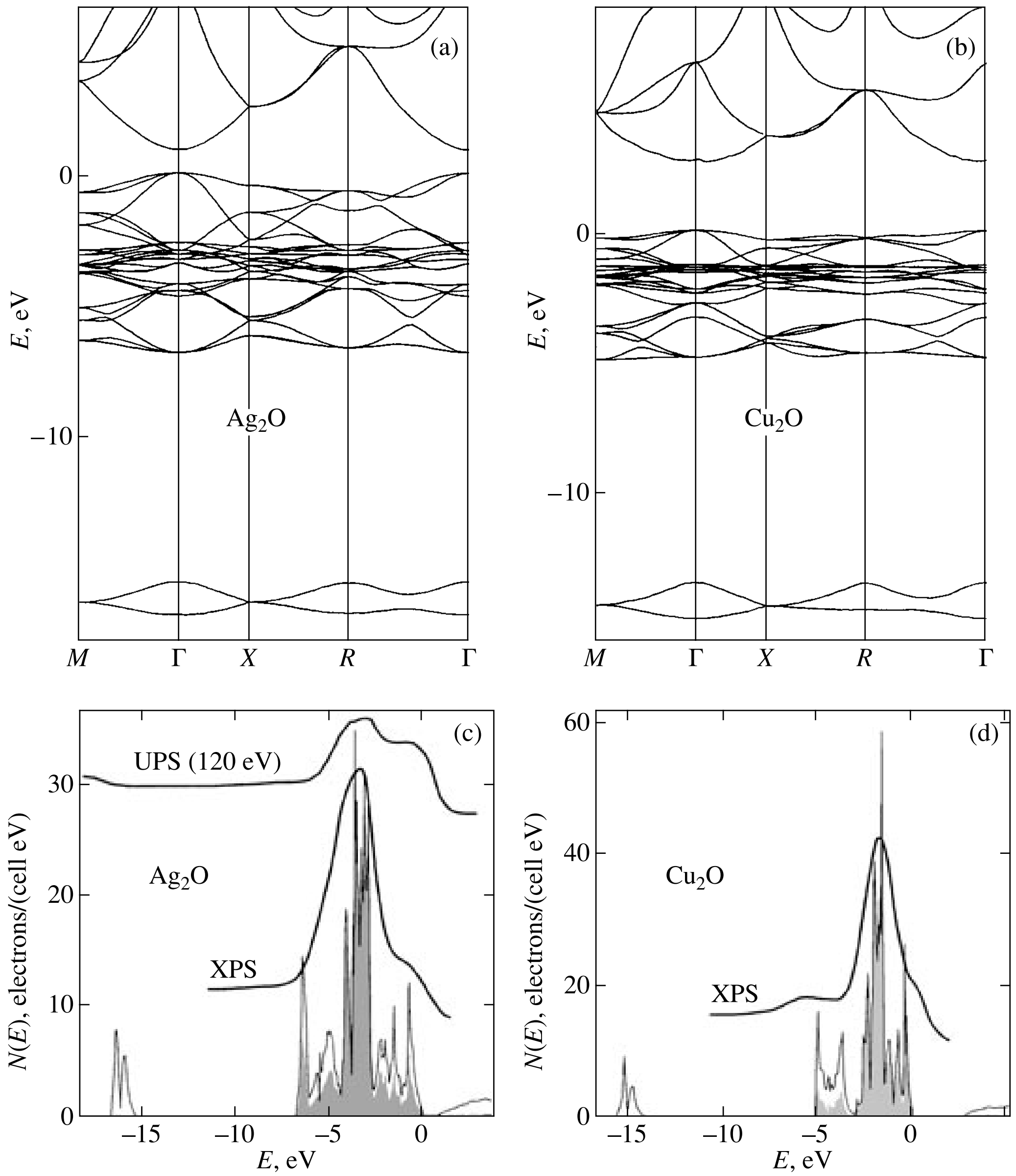

Fig. 1. (a, b) Band structures, (c, d) densities of states *N*(*E*), and photoelectron spectra taken from [23] for (a, c) Ag_2O and (b, d) Cu_2O oxides.

valence band, the contribution of the O_{2p} states is considerably larger than that for the Cu_2O oxide and the density of states has a pronounced maximum at –2.40 eV, which is in good agreement with the experimentally observed maximum at the same energy.

The top of the valence band, like the bottom of the empty band, is located at the Γ point for both compounds. In this case, the band gap is equal to 2.87 eV (2.17 eV according to the experimental data) for the Cu_2O oxide and 0.88 eV (1.30 eV according to the experimental data) for the Ag_2O oxide. Thus, the energy band spectra calculated in this work for copper and silver oxides are in good agreement with the experimental data and the results of calculations carried out by other authors.

4. ELECTRON DENSITY DISTRIBUTIONS AND CHEMICAL BONDING

The intra-atomic and interatomic hybridizations were investigated using three types of difference electron densities, which were obtained as the difference between the valence electron density of the crystal and the superposition of the electron densities of the neutral atoms ($\Delta\rho_a$) (as in [9]), the superposition of the valence electron densities of the metal and oxygen sublattices constituting the crystal ($\Delta\rho_s$) [24], or the superposition

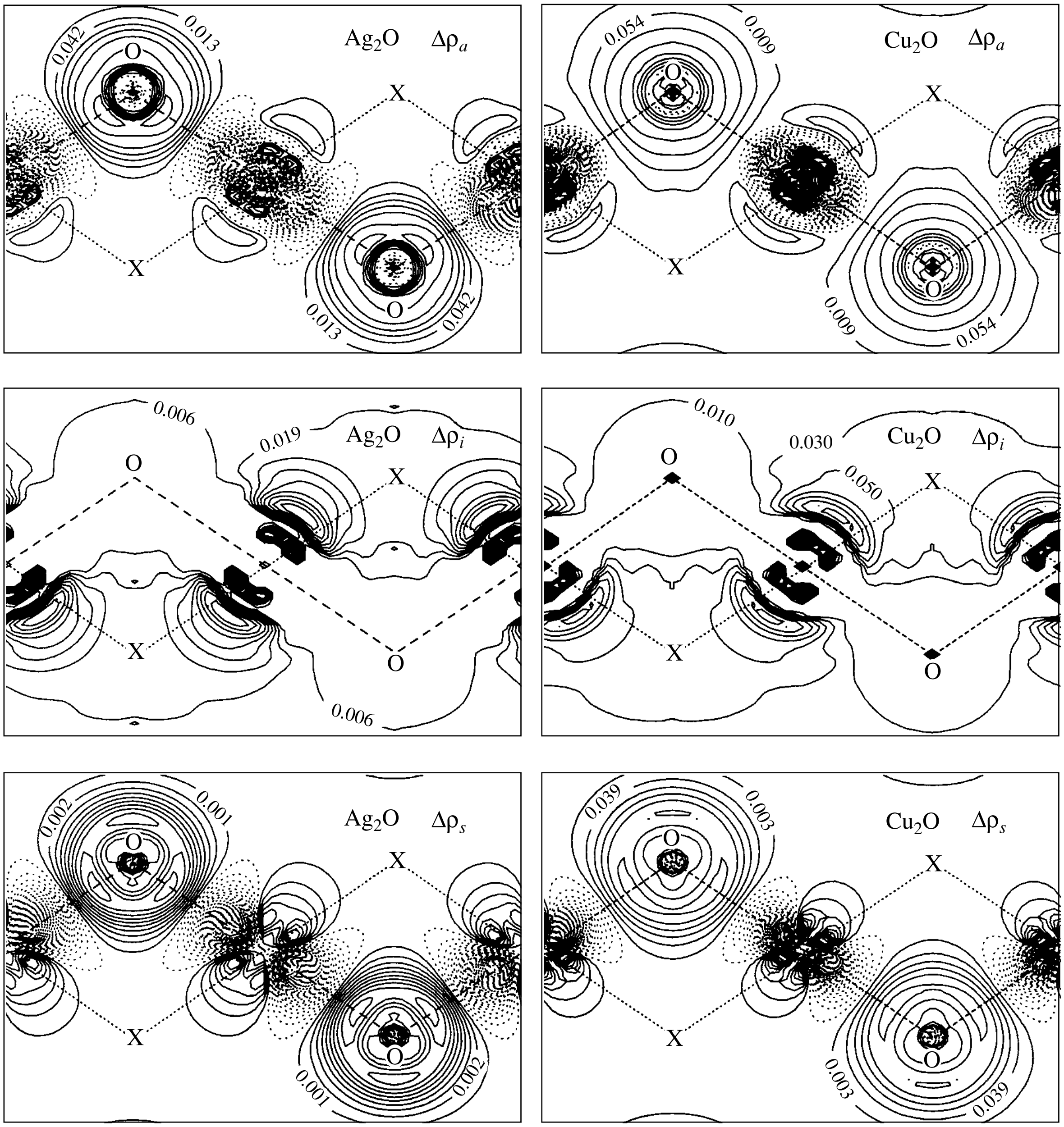

Fig. 2. Difference electron densities $\Delta\rho_a$, $\Delta\rho_i$, and $\Delta\rho_s$ for Ag_2O and Cu_2O oxides (only positive values of $\Delta\rho_i$ are given).

of the electron densities of the Cu^+ (Ag^+) and O^{2-} ions ($\Delta\rho_i$) (as in [12]). The valence density distributions for both crystals are qualitatively similar to each other and agree well with the data obtained in [9]. Figure 2 presents the difference electron densities for copper and silver oxides. The solid and dotted lines correspond to the positive and negative electron densities, respectively. The numerical values are given in units of e/Å^3 (where e is the elementary charge) with a constant step.

By definition, the difference electron density $\Delta\rho_a$ characterizes the charge transfer in the course of the interaction of neutral atoms. This difference density accounts for the hybridization between all atoms, including equivalent atoms. It can be seen from Fig. 2 that the charge is transferred from the region around the O–Cu–O bond to the region of oxygen atoms. Positive values of the difference electron density $\Delta\rho_a$ are also observed in the immediate vicinity of the metal nucleus and in the region symmetric with respect to the bond line at some distance from the nucleus. Such a complex redistribution of the electron charge inside the cation indicates the hybridization of the localized *d* states with the *s* states of the metal. This hybridization can be associated with the interaction between the d^{10} shells of the neighboring atoms.

The difference electron density $\Delta\rho_s$ reflects the charge transfer caused by the interaction between the metal and oxygen sublattices [24]. The distribution of the difference electron density $\Delta\rho_s$ in the vicinity of the oxygen nucleus is similar to the distribution of the difference electron density $\Delta\rho_a$. This is especially true in regard to the Ag_2O oxide. In the vicinity of the metal nucleus, the charge is transferred from the toroidal region aligned with the bond line to the region located perpendicular to it. Therefore, the charge transfer inside the metal atom is also caused by the interaction between the metal and oxygen sublattices. Such a complex redistribution of the difference electron density $\Delta\rho_s$ in the vicinity of the metal nucleus suggests the occurrence of the *s*–*d* and *p*–*d* intra-atomic hybridizations. However, with allowance made for the spatial extension of positive values of the difference electron densities, the attraction should be toward the *s*–*d* hybridization mechanism: $2Ag^0(4d^{10}5s^1) + O^0(2s^22p^4) \longrightarrow 2Ag^+(4d^95s^1) + O^{2-}(2s^22p^6)$.

According to the estimates obtained by different authors (see [9, 12]), the effective charge of the cations varies from –0.07 to +0.97 e. This scatter in the estimates, as well as the maximum of the difference electron density in the vicinity of the oxygen nucleus, allows us to make the inference that the chemical bonding involves not only the ionic component but also the covalent component. For this reason, we calculated the difference electron density $\Delta\rho_i$, which is associated with the electron charge redistribution due to the exchange–correlation effects. As follows from the calculations performed in [9], the electronic interaction plays a significant role in the systems under consideration.

The analysis of the difference electron density $\Delta\rho_i$ obtained for the Cu_2O oxide (Fig. 2) revealed that the electron charge is transferred to the center of the empty Cu_4 tetrahedron where the difference electron density map has a rather flat relief. The maximum difference electron density is equal to 0.05 e/Å^3. This value is close to the difference electron density calculated in the local-density approximation [12]. Thus, we can infer that the cations are bonded to each other through the charge density "channels" at the center of the tetrahedron. This can be considered a tendency toward bonding. However, since the difference electron density is relatively low, the conclusion cannot be drawn that there is direct metal–metal bonding.

A comparison of the two compounds under investigation demonstrates that the Ag_{4d} orbitals are more diffuse than the Cu_{3d} orbitals. As was shown in [9], this difference leads to a stronger d^{10}–d^{10} interaction, which is governed, to a great extent, by the exchange–correlation effects because the relevant Coulomb integrals, according to [23], are larger for the Cu_2O oxide. However, the difference electron density corresponding to the last contour of the charge density channel, as well as the difference electron density $\Delta\rho_i$ at the center of the empty tetrahedron for the Cu_2O oxide, is somewhat higher than that for the Ag_2O oxide. Owing to the diffuse nature of the orbitals in silver oxide, the Ag_{4g}–O_{2p} hybridization should be more pronounced; however, this circumstance does not clearly manifest itself in the difference electron densities $\Delta\rho_a$ and $\Delta\rho_s$. Therefore, despite the qualitative similarity, the mechanisms of chemical bonding in structurally related compounds can differ significantly in terms of quantitative characteristics and this difference can have a determining effect on the physical properties.

5. CONCLUSIONS

Thus, the above calculations of the electronic structure of copper and silver oxides have established that the widths of the valence band and the upper valence band for the Ag_2O oxide are larger than those for the Cu_2O oxide, whereas the band gap of the Cu_2O oxide is larger than the band gap of the Ag_2O oxide. The *d* bands of the metal are located deeper with respect to the top of the valence band in the Ag_2O oxide. These differences are caused by the anion–cation hybridization associated with the more diffuse nature of the Ag 4*d* orbitals. The analysis of the difference electron density maps has demonstrated that the hybridization brings about a charge transfer from metal atoms to oxygen atoms and, what is especially important, the intra-atomic transition $d^{10}s^1 \longrightarrow d^9s^1$. The electron correlation effects are responsible not only for the covalent component of the Ag–O chemical bonding (and, to a lesser extent, of the Cu–O chemical bonding) but also for the electron density transfer to the center of the empty tetrahedron formed by the Cu^+ (Ag^+) cations.

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