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The electronic structure and chemical bonding mechanism of silver oxide

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Abstract. The electronic structure and the chemical bonding mechanism of silver oxide (Ag_2O) are studied on the basis of band-structure calculations, using the full-potential linearized augmented-plane-wave (FLAPW) method. Our calculations indicate that silver oxide is a metal (or a semi-metal). Total and partial densities of states and electron densities were calculated and are utilized to give an interpretation of the chemical bonding. The admixture of the Ag 5s states with the Ag 4d–O 2p bands proved to be essential for the covalent bonding effect, since pure 4d–2p bands, with bonding and antibonding states fully occupied, do not lead to a covalent energy gain. It is found that there are significant deviations from a simple ionic picture due to the depletion of the valence band of the Ag 4d electrons, leading to non-spherical charge density around the silver.

1. Introduction

The compound silver oxide (Ag_2O) has interesting properties because of its role in fast-ion-conducting glasses of the type AgI–Ag_2O–B_2O_3. A detailed study of the electronic structure of silver oxide is necessary to the understanding of the chemical bonding between silver and oxygen in the glasses. This facilitates the understanding of the local structure of the glasses and the mechanism of ionic conduction. In addition, silver oxide has the same crystal structure as cuprous oxide. The crystal structures of silver oxide (Ag_2O) and cuprous oxide (Cu_2O) are rather unusual among those of metallic oxides because they each have a low coordination number of the metal atom with oxygen. Silver oxide has a highly symmetrical cubic structure, where silver atoms are linearly coordinated with oxygens and oxygen atoms are tetrahedrally coordinated with silver atoms. The unit cell of silver oxide (Ag_2O) is shown in figure 1. One might expect silver oxide to be a simple ionic compound consisting of Ag^+ cations with the [$4d^{10}$] configuration, and O^{2-} anions. Such an ionic model, however, can explain neither the low coordination number, 2, of silver nor the short Ag–O distance, which is not compatible with the sum of any pair of ionic radii for Ag^+ and O^{2-}.

Previous theoretical and experimental work done on silver oxide includes an x-ray absorption spectroscopy study by Czyzyk *et al* [1] and a Compton profile study on silver oxide by Bandyopadhyay *et al* [2]. Czyzyk *et al* have measured x-ray absorption spectra and also made band-structure calculations using the atomic sphere approximation with an extended basis set. Though they did not study the bonding mechanism in silver oxide and

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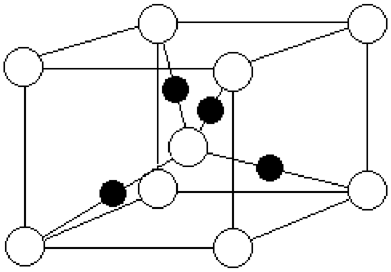


Figure 1. The unit cell of silver oxide. The large circles represent the oxygen atoms; small dark circles represent silver atoms.

the structure of the valence states of silver oxide in detail, they found that the valence states consist mainly of O 2p and non-closed Ag 4d states, and also a small significant contribution of Ag 5s states throughout the valence bands. On the other hand, Bandyopadhyay *et al* [2] made an experimental Compton profile measurement on a polycrystalline sample of silver oxide using 59.54 keV gamma radiation. The experimental data were compared with renormalized free-atom (RFA) model calculations.

In fact, the above-reported calculations show significant differences in their results. Therefore, we here performed new band-structure calculations with the emphasis on chemical bonding.

This paper is organized as follows. In section 2, we describe the calculation of the band structure. Then we present the density of states in section 3, and the electron densities in section 4. The chemical bonding is analysed in section 5, while the discussion and conclusions are given in section 6.

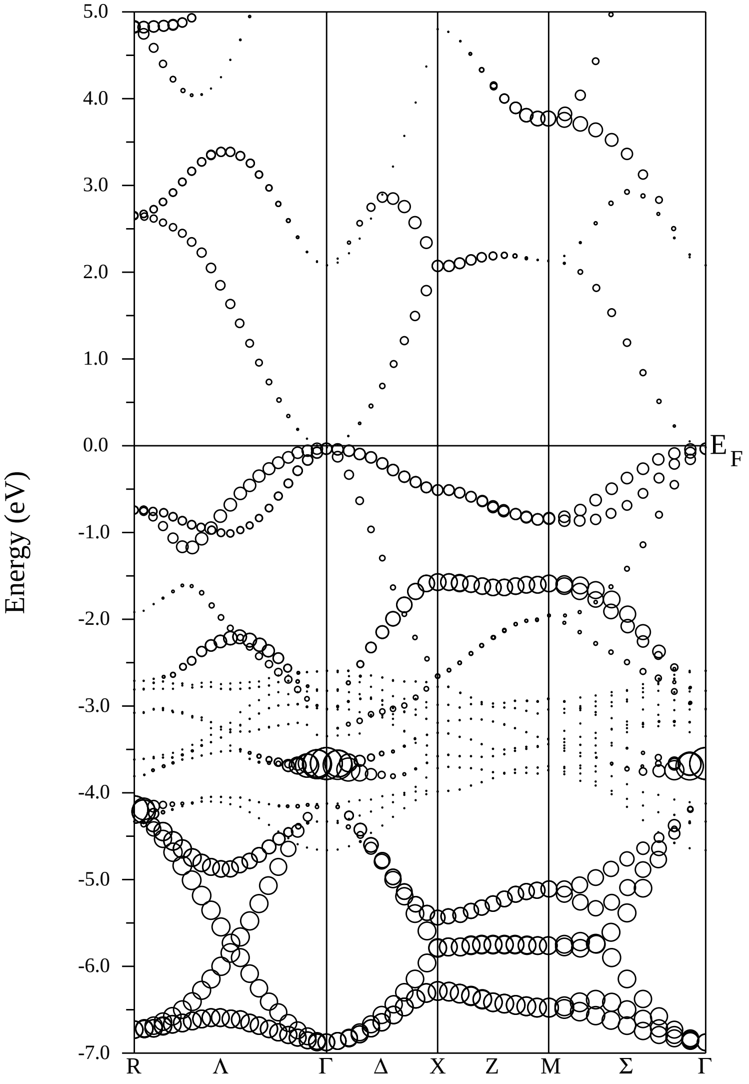
2. Band-structure calculations

A self-consistent band-structure calculation was carried out using the scalar relativistic full-potential linearized augmented-plane-wave (FLAPW) method [3]. Exchange and correlation were treated within the local spin-density approximation (LSDA), where we applied the Perdew and Wang parametrization [4].

In the FLAPW calculation, the origin of the cell was chosen, in contrast to the case in figure 1, to lie at the Ag site, in order for there to be inversion symmetry which allows us to have all matrix elements real.

We have distinguished between the Ag 1s, 2s, 2p, 3s, 3p and O 1s inner-shell electrons and the valence band electrons from the Ag 4d, 5s, 5p and O 2s, 2p shell. The extended Ag 3d, 4s, 4p states were taken as semi-core bands. The crystal wave functions were expanded into nearly 500 non-symmetrized plane waves in order to achieve energy eigenvalues converged to a few mRyd. In the muffin-tin spheres, the l-expansion of the wave functions was carried out up to $l_{max} = 12$, whereas $l_{max} = 6$ was chosen for the charge density and for the potential expansion. A mesh of 20 equally distributed k-points was used for the Brillouin zone integration in its irreducible wedge. A total of 16 iterations were necessary to achieve self-consistency, where the eigenvalues of the last two iterations generally differ by less than 0.1 mRyd. At the end, the eigenvalues and wave functions were calculated at 35 k-points using the self-consistent potential.

An analysis of the eigenvectors allows us to extract information about the orbital character of the bands. The low-lying band coming mainly from O 2s states will be called the ‘s band’, the next one mainly due to O 2p states the ‘p band’ and the band which originates predominantly from Ag 4d states will be called the ‘d band’. The main results



(a)

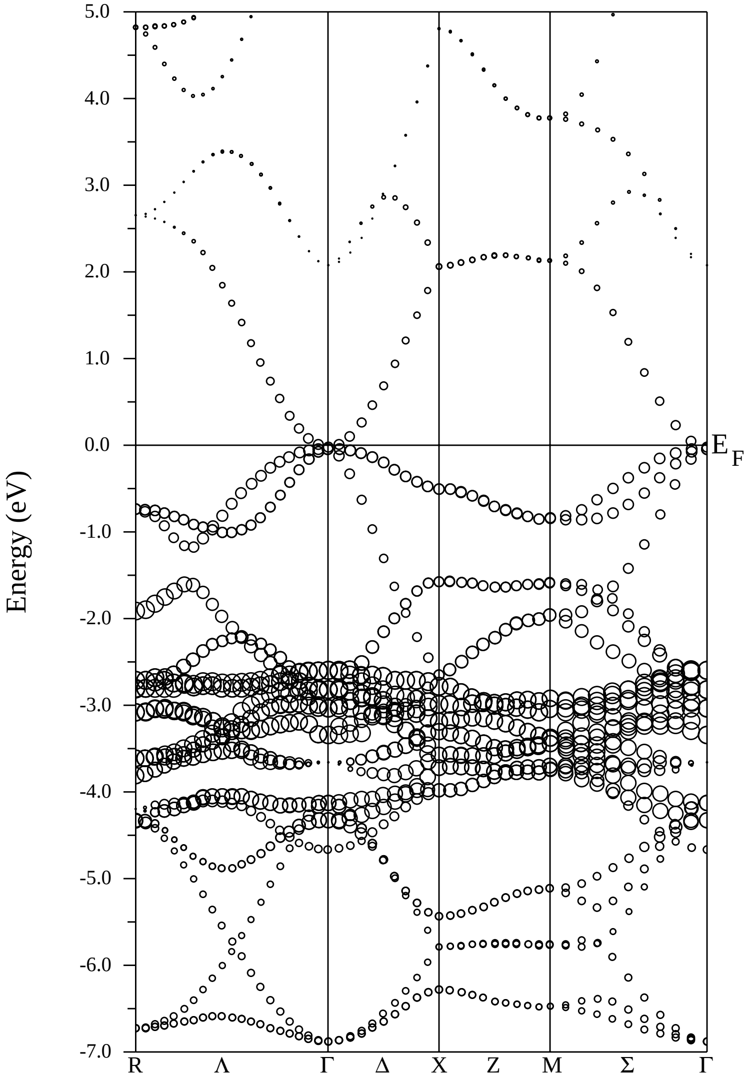
Figure 2. The FLAPW band-character plot for silver oxide: (a) O 2p, (b) Ag 4d, (c) Ag d_{z^2}. The symbol size indicates the strength of the orbital character of the bands.

of this analysis are displayed in figures 2(a) to 2(c). An analysis of these figures indicates that the main contribution comes from the Ag 4d states and O 2p states, in the d band and p band respectively.

3. Total and partial densities of states

The densities of states (DOS) $g(E)$ are given by

$$g(E) = \Omega \sum_n \int_{BZ} \delta(E - E_{n\boldsymbol{k}}) A_{n\boldsymbol{k}} \, \mathrm{d}^3\boldsymbol{k}. \tag{1}$$

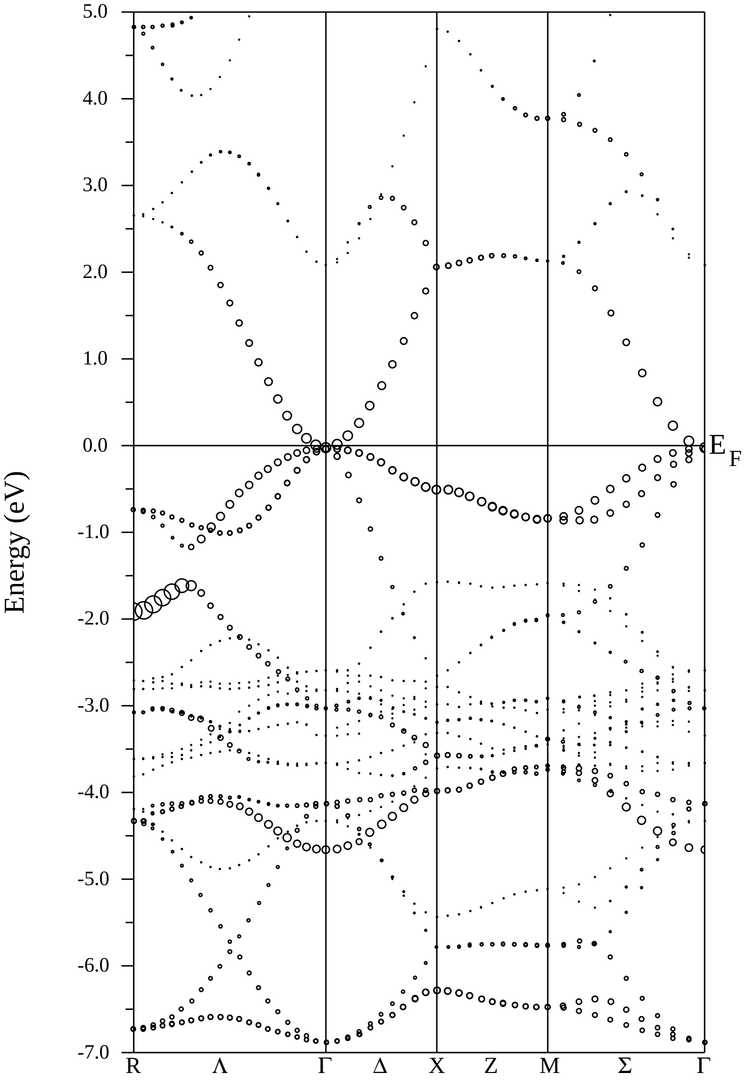


(b)

Figure 2. (Continued)

In (1), Ω is the volume of the Brillouin zone and $E_{n\boldsymbol{k}}$ is the nth eigenvalue at the point $\boldsymbol{k}$. The total density of states (DOS) is obtained with $A_{n\boldsymbol{k}} = 1$, while the partial DOS $A_{n\boldsymbol{k}}$ is set equal to the local (inside sphere t) partial (l-like) charge $q_l^t(E_{n\boldsymbol{k}})$. For the Brillouin zone integration in (1), the tetrahedron method of Lehman and Taut [5] was employed.

The partial charges q_l^t and consequently the partial densities of states can be further decomposed according to the irreducible representations of the point group of site t. The silver d_{z^2} wave functions transform like $\mathrm{A}_{1\mathrm{g}}$, while the d_{xz} and d_{yz} as well as the d_{xy} and $\mathrm{d}_{x^2-y^2}$ functions transform like E_g. The partial charges q_l^t and their contributions are listed in table 1.



(c)

Figure 2. (Continued)

The partial density of states of O p and Ag d are shown in figure 3, and the latter is decomposed according to symmetry in figure 4. The main contributions to the DOS of the conduction band are shown in figure 5. From the analysis of figure 4 it is revealed that the $d_{x^2-y^2}$, d_{xy} states show negligible admixture with the bonding and antibonding bands.

The valence band is dominated by the Ag 4d states, while the contribution of the Ag 5p states is practically zero. However, the 5s Ag states show a small significant contribution to the valence band. This indicates an s–d hybridization at the metal atoms, to explain the linear coordination of Ag^+.

The only contribution of the O atoms to the valence band comes from the 2p states, while the s-state and d-state contributions are negligible.

Table 1. Local partial charges q_l^t in electrons per unit cell. For the symmetry analysis of the Ag d charges, the z-axis is chosen to lie in the [111] direction.

	s band	p band	d band	Total
O s	3.434	0.030	0.040	3.504
O p	0.001	6.658	1.533	8.191
O d	0.000	0.000	0.064	0.064
Ag s	0.030	0.217	0.298	0.552
Ag p	0.050	0.120	0.080	0.250
d_{z^2}	0.060	0.880	5.236	6.176
$d_{xy}^{x^2-y^2}$	0.000	0.050	13.556	13.606
d_{xz}^{yz}	0.010	1.080	13.020	14.100
Outside spheres	0.415	2.965	6.173	9.547
Total	4.000	12.000	40.000	56.000

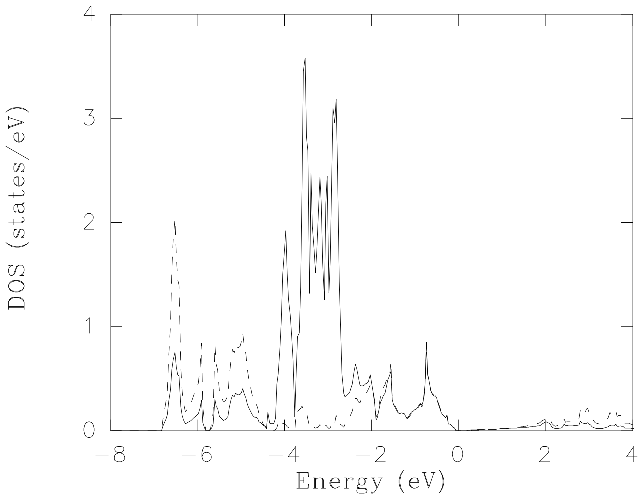


Figure 3. Ag d (full line) and O p (small-dash line) local partial densities of states in states per eV per unit cell.

4. Electron densities

For convenience, the electron density is represented as a linear combination of real spherical harmonics inside the atomic spheres, and as a Fourier series outside. A detailed calculation of the charge densities within the FLAPW formulation is given by Blaha and Schwarz [6].

Electron-density maps were calculated for silver oxide in the (110) plane. Figure 6 shows the difference between the crystalline charge density and the superposition of the spherical atomic densities. An analysis of figure 6 reveals that there are oxygen atoms at the corners and in the centre, and silver atoms between the central oxygen and the oxygen atoms at the bottom. The electron densities decrease in the region close to the silver atom in the Ag–O bond direction, while an increase of the electron density appears at the O atom. The charge densities of the ions were calculated by a modified Hermann–Skillman

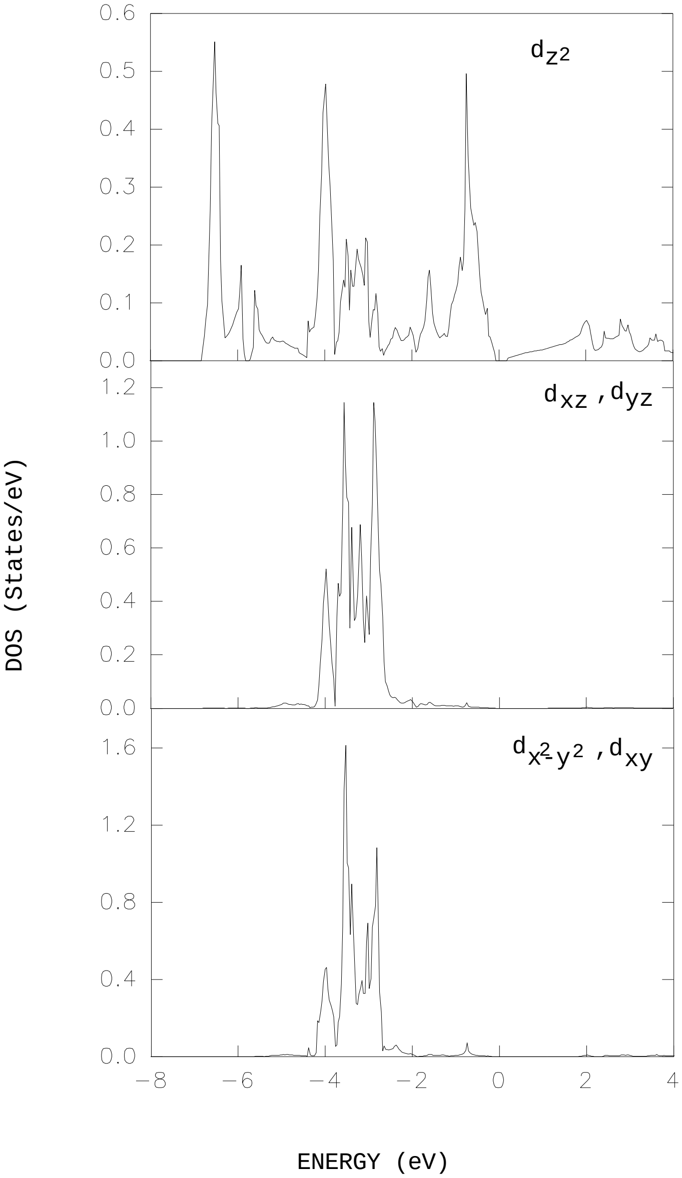


Figure 4. The symmetry decomposition of the Ag d local partial density of states shown in figure 3.

atomic program [7] using the Perdew and Wang [4] approximation for the exchange and correlation.

5. Chemical bonding

As mentioned earlier, one expects Ag_2O to show an ideal ionic behaviour, and it consists of Ag^+ cations with filled d shells and O^{2-} anions. To a certain extent, such an ionic model is a

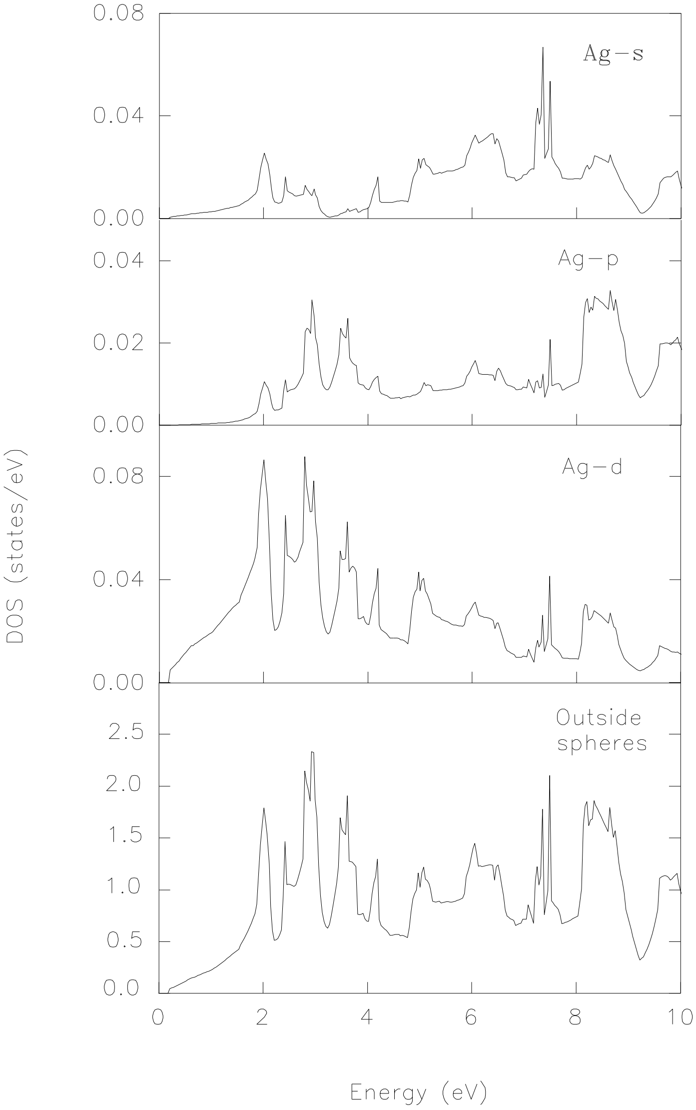


Figure 5. The main contributions to the density of states of the conduction band; the DOS labelled ‘outside spheres’ contains contributions from the interstitial region and all empty spheres.

good first approximation. However, there are strong indications that a purely ionic model is not quite adequate to describe the chemical bonding in the silver oxide compound. Instead, one has to suppose a combination of ionic and covalent bonding mechanisms. In a solid there have been different approaches to defining ionicity [8]. As usually defined, ionicity is the amount of charge transfer. A useful way to study the ionicity is via a comparison between the crystal charge density and the charge density of superposed free atoms or ions. Such an analysis has already been made for silver oxide—see figure 6. From this figure, it is seen that there is a small difference density around the oxygen site. Thus we are justified in speaking of an O^{2-} anion, but, due to the electroneutrality, this observation requires a Ag^{+} cation. It is interesting to note here, in the case of the superposition model, that a

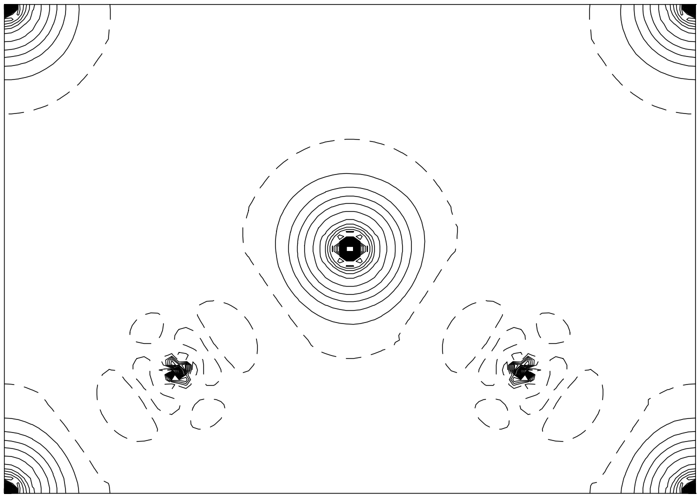


Figure 6. Electron-density maps obtained for silver oxide on a (110) plane. Density difference maps: bulk minus neutral-atom superposition; linear scale, in units of electrons Å^{-3}; negative values are indicated by dashed lines.

Ag$^+$[4d^{10}5s^1] configuration was taken into consideration, but figure 6 clearly demonstrates that there is a deviation from this configuration. The negative difference densities present around the Ag indicate that the d shell is not completely filled. Thus an ideal ionic model with a Ag$^+$ cation with a [4d^{10}] configuration is not quite an adequate description. We can also find in figure 4 that there is more charge in the interstitial region, suggesting a certain Ag 5s contribution in the crystal. These deviations from an ideal ionic model and the symmetry of the difference density around Ag suggest certain directed bonds between Ag and O. Even if one considers such bonds between nearest neighbours, electrostatic forces are essential to stabilize the silver oxide, because it consists of two interpenetrating sublattices which are not connected by Ag–O bonds. Starting with the oxygen atom at the centre of the unit cell, only four out of the eight oxygen atoms at the corners can be reached by directed bonds, while the other four belong to the second sublattice. These sublattices are forced into their respective places by electrostatic interaction. Thus this reflects that it is presumably easier to shift one sublattice than to vary the Ag–O bond length.

The nature of these bonds can also be interpreted via the analysis of the partial density of states, electron densities and partial charges. As is evident from figure 3, there is an extensive hybridization between Ag d and O p states. From figures 3 and 4, it is clearly seen that the p-band DOS shows mainly a four-peak structure and is dominated by O 2p states. The two peaks at lower energy contain mainly Ag d_{z^2} admixtures, and the two at higher energy mainly Ag d_{xz} and d_{yz}. It should be noted that the z-axis of the local coordinate system of the silver atoms points to the nearest oxygen neighbour. The d-band density of states can be best analysed from figure 4. In the lower-energy region of the d band the narrow DOS corresponds to the Ag $d_{x^2-y^2}$ and d_{xy} states, and it shows the least O p admixture. These results are also evident from our partial charge analysis, as shown in table 1.

In addition to this, the above hybridization can also be interpreted on the basis of the partial charge analysis and can be explained in terms of molecular orbital (MO) language. The O p and the Ag d_{z^2} states can form pdσ bonds and the O p and Ag d_{xz}, d_{yz} states can form pdπ bonds. The states which can hybridize form bonding and antibonding states in the case of the p band and d band respectively, while on the other hand the Ag $d_{x^2-y^2}$ and d_{xy} states remain non-bonding.

If the bonding and the antibonding states are both fully occupied, no energy is gained. However, in silver oxide there are considerable contributions from d_{z^2} states in the conduction band (figure 2(c)), so some Ag d_{z^2} antibonding states remain unoccupied. Consequently some Ag 5s-like states are found in the valence band. We have noted also from our calculation that the partial Ag 5s density of states is very small in the valence band and not very intense in the conduction band, but nevertheless these states are present, and the conduction band is dominated by them.

Finally, the depletion of the Ag d_{z^2} electrons in the valence band is the very feature which makes the ionic model not quite adequate to describe the electronic structure of silver oxide. An ideal Ag^+ ion will have a [d^{10}] configuration, and consequently will have a charge density which is spherically symmetric. One may interpret this deviation from ideal ionic behaviour as indicating a covalent contribution rather than polarization, since one can interpret the partial DOS in a molecular orbital picture in terms of bonding and antibonding states. It is noteworthy that the majority of the d states are non-bonding, and their interaction is weak.

This kind of s–d_{z^2} hybridization is not so surprising for metals, but is somewhat unusual for ionic semiconductors, for which the band gap is expected to separate the filled d band from the empty metal sp bands. Thus it is important to note that here, for silver oxide, the unusual linear coordination occurs due to a possible s–d_{z^2} hybridization.

6. Discussion and conclusions

We have carried out FLAPW energy band calculations in order to study the electronic structure and bonding mechanism of silver oxide compound. Czyzyk *et al* [1] also obtained a p band which is mainly contributed by the O p states, but, as compared to that obtained in the earlier work, our band-structure-character plot provides a clear idea of the contributions of the different states of silver and oxygen in the valence and the conduction bands respectively.

It has been demonstrated above that there would be no covalent bond in silver oxide if Ag and O ions had $4d^{10}$ and $2p^6$ configuration. Here it is important to note that the electric field gradient (EFG) is an observable which is very sensitive to electron-density distortion. We calculated the electric field gradient (EFG) for silver oxide which is equal to $1.71ea_{\mathrm{H}}^{-3}$, where a_{H} is the Bohr radius. Since at present there are no experimental results on the EFG of silver oxide available in the literature, we have here only reported our theoretical value.

A feature common to silver oxide and cuprous oxide is the linear coordination of the silver cations and the copper cations with oxygen anions. A detailed study of the electronic structure of cuprous oxide has already been reported in the literature by Marksteiner *et al* [9]. If we compare the results, it is evident that for both compounds there is a significant deviation from the simple ionic picture. For both compounds the p band is dominated by the O p states while the Ag d states and Cu d states dominate the d band.

Though the previous theoretical calculations by Czyzyk *et al* [1] indicate that silver oxide is a semiconductor with a band gap of 0.0297 Ryd, inspection of our band-structure plots does not show a gap. This is mainly due to the well-known shortcoming of the LSDA as regards describing narrow-band-gap semiconductors.

Finally, we found here that the FLAPW method has proved to be a very effective tool for analysing the bonding mechanism of silver oxide.

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