Electronic structure of mixed-valence silver oxide AgO from hybrid density-functional theory

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Mixed-valence AgO has attracted attention due to its utility in battery technologies. Despite this, a nanoscopic understanding of its electronic structure has been lacking and there has been considerable controversy about the formal oxidation states of silver in the system. In this Rapid Communication we study the electronic structure of AgO using density functional theory:generalized gradient approximation (GGA) and a screened hybrid density functional (HSE). GGA is found to be unable to model the mixed valence of the material, resulting in an $Ag^{II}O$ symmetric structure. We show conclusively using HSE that the oxidation states of silver in AgO are Ag^I and Ag^{III}, and *not* Ag^I and Ag^{II} with holes on neighboring oxygen ions as had previously been predicted.

I. INTRODUCTION

Mixed-valence silver oxide AgO (also known as Ag_4O_4) is an *n*-type semiconductor which has primary commercial applications in battery technology, where it is used with Ag_2O in Zn silver-oxide batteries.[1–3] It has also gained interest for possessing bacteriostatic properties,[4,5] and has been tested for applications in the treatment and cure of dermatological skin conditions.[6] Although not as widely studied as Ag_2O, several structural and spectroscopic studies have been carried out on AgO in an effort to elucidate the geometry and electronic structure of the material.[7–12]

AgO crystallizes in a monoclinic structure (space group $P12_1/c1$) with Ag ions in two distinct coordination environments.[7] Neutron-diffraction experiments have indicated that it is composed of linearly coordinated Ag ions (denoted Ag^{lin}) and Ag ions in a slightly distorted square planar coordination with four oxygens[8] (denoted Ag^{sq}), as shown in Fig. 1. It has been suggested that Ag^{lin} can be attributed to Ag with an oxidation state of +1 (Ag^I) and that Ag^{sq} can be attributed to Ag with an oxidation state of +3 (Ag^{III}).[8] AgO has been reported to be diamagnetic,[9] which is consistent with spin paired configurations of linearly coordinated $4d^{10}$ Ag^I, and square planar $4d^8$ Ag^{III}.[13] The coordination environments around the Ag ions in AgO are also consistent with the coordination environments of Ag^I in Ag_2O (Ref. 14) and Ag^{III} in Ag_2O_3.[15]

Early theoretical calculations carried out using local-density approximation (LDA) within the full-potential linearized augmented-plane-wave method have challenged the view that Ag^I and Ag^{III} are present in AgO.[12] The authors predicted that the cation valences are Ag^I and Ag^{II} with holes present on the oxygen ions.[12] This oxygen-hole theory was postulated due to the small O *p*-Ag *d* energy separation.[12] X-ray photoelectron spectroscopy (XPS) studies of AgO have reported two O 1*s* core levels despite the fact that only one inequivalent oxygen site exists in the structure.[10] The presence of these two core levels is attributed to oxygen in −2 and −1 valences,[10] consistent with the theory of Park *et al.*[12] Another study of AgO using XPS and electron energy-loss spectroscopy cast doubt on the presence of Ag^{III} in AgO. They stated that it was difficult to understand how Ag^{III}

forms due to the fact that no other Ag compound with the Ag^{III} valence had been reported,[11] despite the fact that the crystal structure of Ag_2O_3 had been reported five years earlier.[15]

The presence of two O 1*s* core-level peaks had been previously noted in other photoemission spectroscopy (PES) studies of AgO, but has been attributed to Ag carbonates or bicarbonates, hydroxyl groups, and adsorbed water, and *not* to oxygen holes.[11] Carbonate impurities are probably present in *all* AgO samples as their removal by sample calcination has been reported to be very difficult due to Ag_2CO_3 being more thermally stable than AgO.[16] Contrary to the PES studies of Bielmann *et al.*[10] and Hoflund *et al.*,[11] the XPS and x-ray adsorption spectroscopy study by Lützenkirchen-Hecht and Strehblow[17] support the theory that the Ag valences in AgO are Ag^I and Ag^{III}. An x-ray absorption near-edge structure (XANES) study has also supported the Ag^I/Ag^{III} theory.[18] The authors considered both Ag L_1 and L_3 XANES spectra for a range of binary oxides and silver containing compounds with the trends in the data clearly supporting an Ag^I and Ag^{III} mixed oxidation state rather than Ag^I and Ag^{II}.

In this Rapid Communication we investigate the geometry and electronic structure of AgO using state of the art first-principles approaches. We show: (i) generalized gradient approximation (GGA) is *incapable* of modeling the mixed-valence structure of AgO, predicting a structure with equivalent Ag sites, (ii) hybrid density functional (HSE) results in a structure consistent with experiment with two distinct Ag coordinations, and (iii) Bader charge analysis and comparison with Ag_2O and Ag_2O_3 indicates that Ag^I and Ag^{III} are present in AgO.

All our DFT calculations were performed using the VASP code[19] with the projector augmented wave approach.[20] The calculations were performed using both the GGA of Perdew, Burke, and Ernzerhof (PBE) (Ref. 21) and the hybrid functional as proposed by Heyd *et al.*[22] with the inclusion of spin polarization in all calculations. Difficulties in evaluating the Fock exchange in a real-space formalism are caused by the slow decay of the exchange interaction with distance. In the HSE06 hybrid functional approach, this problem is addressed by separating the description of the exchange interaction into long- and short-range parts.[22] Thus, a percentage ($\alpha=25\%$) of exact nonlocal Fock exchange is added to the
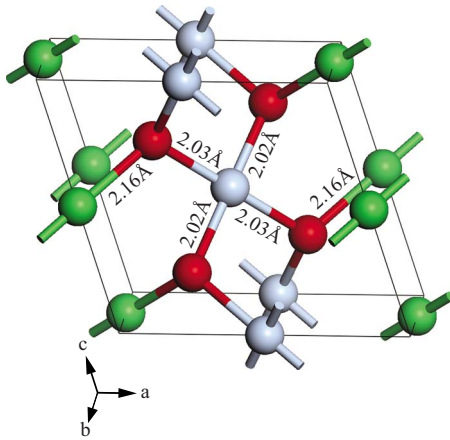
FIG. 1. (Color online) (a) Experimental crystal structure of AgO (Ref. 7). Green (medium gray) spheres denote linearly coordinated Ag^{lin}, light blue (light gray) spheres denote square planar coordinated Ag^{sq}, and red (dark gray) spheres represent oxygen.

PBE functional and a screening of $\omega = 0.11$ bohr^{-1} is applied to partition the Coulomb potential into long-range (LR) and short-range (SR) terms. Thus the exchange and correlation terms are

$$E_{xc}^{HSE}(\omega) = E_x^{HSE,SR} + E_x^{PBE,LR} + E_c^{PBE}, \qquad (1)$$

where

$$E_x^{HSE,SR} = \frac{1}{4}E_x^{Fock,SR} + \frac{3}{4}E_x^{PBE,SR}. \qquad (2)$$

Hartree-Fock (HF) and PBE exchange are therefore only mixed in the SR part with the LR exchange interactions being represented by the PBE functional.[22] HSE has been shown repeatedly to produce structural-data and band-gap descriptions that are more accurate than LDA/GGA and meta-GGA data.[23–31] Cutoffs of 500 eV were used for the GGA and 400 eV was used for the more computationally expensive HSE calculations. Gamma centered k-point meshes of $4 \times 6 \times 4$ were found to be sufficient for all methods. Calculations were deemed to be converged when the forces on all the atoms were less than 0.01 eV A^{-1}.

The GGA and HSE calculated structural parameters for AgO are presented in Table I. It is clear that minimization of

TABLE I. Lattice constants, interatomic distances, and angles for AgO, calculated using GGA and HSE methods, and the corresponding experimental values. All distances are in Å and angles are in degrees.

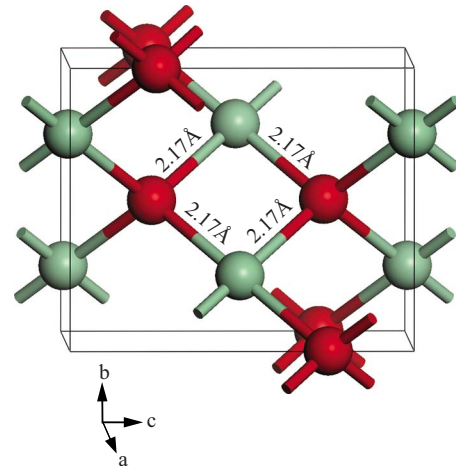|	GGA	HSE	HF	Expt. (Ref. 7)
a	4.74	5.97	5.96	5.86
b	4.62	3.55	3.69	3.48
c	5.60	5.57	5.53	5.50
Ag^{lin}-O	2.17	2.15	2.31	2.16
Ag^{sq}-O	2.17	2.01, 2.02	1.99, 1.99	2.02, 2.03
Angle (β)	90.31	107.33	102.85	107.56

FIG. 2. (Color online) GGA symmetric structure of AgO with equivalent Ag sites. The light green (light gray) spheres represent the Ag and red (dark gray) spheres represent O ions.

the AgO structure using GGA yields a structure in disagreement with the experimentally known crystal structure. GGA predicts a structure with only one inequivalent Ag site, which is fourfold coordinated with Ag-O bond lengths of 2.17 Å, Fig. 2. On closer inspection, this bonding environment is very similar to that seen in CuO, where Cu^{II} is the only cation present.[32] Thus it seems that GGA is unable to relax to the experimental structure with two different Ag sites but rather predicts an AgO structure with equivalent Ag (presumably Ag^{II}) sites. The band structure for the GGA AgO structure with equivalent Ag coordinations indicates that the material is metallic (Fig. 3), which is at variance with the experimentally known semiconducting nature.[33,34]

Considering the fact that our GGA calculations predict AgO to be a metallic material with equivalent Ag coordinations, it is puzzling that the LDA calculations of Park *et al.*[12] yielded two distinct Ag coordinations with a small indirect band gap of 0.03 eV. We have calculated an *unrelaxed* GGA bandstructure for the material, which yielded a small indirect
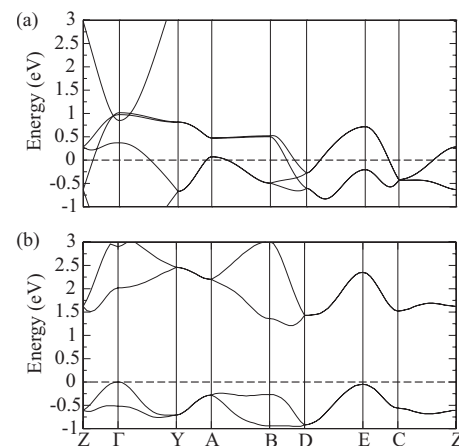

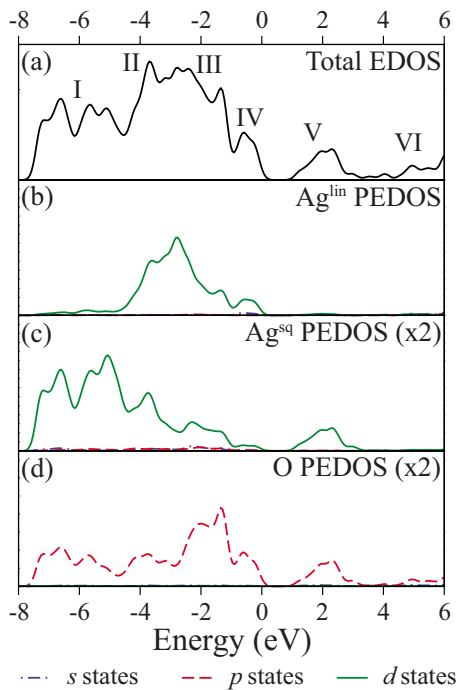FIG. 3. (a) GGA and (b) HSE calculated band structures for AgO.

FIG. 4. (Color online) Electronic density of states for AgO. (a) Total EDOS, (b) Ag^{lin} PEDOS, (c) Ag^{sq} PEDOS, and (d) O PEDOS, as calculated using the HSE method. For (b)–(d), the s, p, and d states are colored blue (dots dashes), red (dashes), and green (solid), respectively.

band gap of 0.2 eV. This indicates that the previous LDA calculations did not involve ionic relaxation.[12]

Minimization of AgO using HSE yields a structure very similar to the experimental structure. The lattice vectors are all within <1.9% of the experimental values (Table I) and the differing coordination around both Ag sites is maintained. We have also examined the structure with full HF and find a similar result to the HSE approach, albeit with a slightly expanded lattice. Analysis of the HSE band structure reveals that the valence band (VB) maximum appears at Γ with the conduction-band minimum occurring on the line from B to D, Fig. 3. Thus AgO has an indirect band gap of 1.2 eV, and a smallest direct band gap of 1.6 eV which occurs between B and D, which are consistent with the experimentally measured optical band gaps of 1–1.1 eV.[33,34]

Analysis of the partial electronic densities of states (PEDOS) reveals that the Ag positions have considerably different features, Fig. 4. The PEDOS of the Ag^{lin} site reveals that the VB is dominated by Ag 4d states with a central peak at ~-3.5 eV. This is consistent with PEDOS previously calculated for Ag_2O, where Ag is also in the +1 oxidation state.[35] For the Ag^{sq} site, the PEDOS is very different. The Ag 4d states straddle the entire VB with two large peaks situated at ~-7 and ~-4.5 eV. States with Ag 4d character can also be seen at the bottom of the conduction band, which is consistent with Ag having a valence higher than Ag^{lin}. Indeed the Ag^{sq} PEDOS for AgO is consistent with the PEDOS for Ag^{III} in Ag_2O_3.[36]

To understand the oxidation states present in AgO, it is instructive to analyze the Bader[37] charges of the material, and compare them to the charges on Ag in Ag_2O and Ag_2O_3.

TABLE II. Bader charges for Ag and O in Ag_2O, Ag_2O_3, and AgO. The charge for O_1 in the Ag_2O_3 structure refers to an average over oxygen atoms O_1, O_{1a}, and O_{1b} (Ref. 15). Quoted values are HSE and GGA values are in parenthesis.

Structure	Ag charge	O charge
Ag_2O	+0.52 (+0.47)	−1.04 (−0.94)
Ag_2O_3	+1.23 (+1.10)	O_1: −0.85 (−0.74)
		O_2: −0.77 (−0.72)
AgO	Ag^{lin}: +0.65 (+0.83)	−0.91 (−0.83)
	Ag^{sq}: +1.17 (+0.83)	

The corresponding GGA and HSE computed Bader charges are listed in Table II. The HSE charges for Ag^{sq} in AgO are very similar to those of Ag^{III} in Ag_2O_3. Similarly the charges of Ag^I in Ag_2O are consistent with those of Ag^{lin} in our HSE minimized AgO. It is also clear that the GGA charges for AgO are at variance with those for Ag_2O and Ag_2O_3. The Bader charge analysis therefore strongly supports the suggestion that the Ag is present as both +1 and +3 oxidation states. It also indicates that the oxidation state of Ag in the GGA minimized AgO structure is between that of Ag^I and Ag^{III}, indicating that GGA has predicted an $Ag^{II}O$ structure, similar to CuO.

The reported diamagnetism of the AgO structure[9] is also not consistent with the Ag^I/Ag^{II} theory, as Ag^{II} would be formally $4d^9$, and thus have a magnetic moment similar to Cu^{II} in CuO. It is widely known that CuO is an antiferromagnetic semiconductor.[38] Therefore the absence of magnetism in AgO is a valid indicator that a valence of Ag^{II} is most likely not present. Similarly the oxygen hole argument is highly questionable. In most oxides with O 2p dominated VBs, p-type defect formation results in *localized* oxygen holes (polarons), bound to strong lattice distortions.[39,40] There has been no evidence presented for strong structural distortions in AgO. In addition to this, the presence of Ag^I in the AgO system (which is not in doubt), would mean that any holes formed would most likely reside on the Ag ions, similar to hole formation in Cu_2O.[27,41] In fact, alloying wide band gap oxides with formally $d^{10}(Ag^I, Cu^I)$ metal oxides is currently the most effective way to form p-type transparent conducting oxides, in an effort to stop the formation of localized oxygen holes that limit conductivity.[28,42] Thus the formation of Ag^{II} with synergistic oxygen holes in AgO is chemically unlikely.

The failure of GGA to describe the mixed valence of AgO is not surprising, as GGA has been shown to fail to capture the structure, valence (Bi^{III} and Bi^V) or semiconducting properties of $BaBiO_3$.[43,44] An explanation for this problematic failure of GGA is that standard semilocal exchange-correlation functionals, such as LDA or GGA predict a too small charge disproportionation, resulting in a metallic description of known semiconductors.[45]

In conclusion we have carried out GGA and state of the art HSE calculations on mixed-valence AgO. Minimization

of the AgO structure with GGA highlighted the abject failure of GGA/LDA methods at handling materials with a cation that displays multiple oxidation states. The HSE calculations have captured the different coordinations of the Ag ions. Analysis of the HSE calculated EDOS/PEDOS and Bader charges point to the fact that the Ag valences present are in fact Ag^I and Ag^{III}, and not Ag^I and Ag^{II} with synergistic oxygen holes.

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