Oxygen and vacancies in silver: A density-functional study in the local density and generalized gradient approximations

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The insertion of oxygen atoms in silver and their interaction with vacancies are studied with density-functional theory calculations using a plane wave basis set. Oxygen atoms are found to be preferentially inserted in octahedral interstitial sites and to have strong interactions with monovacancies as well as with divacancies. An original configuration is evidenced for the oxygen–divacancy complex where the oxygen atom is located halfway between the two nearest-neighbor vacancies, whereas the oxygen–vacancy pair reduces in fact to an oxygen atom in the available substitution site. Quantitative estimates of the formation energies of silver mono- and divacancies, solution energies of oxygen in various sites, and binding energies of oxygen with one or two vacancies are calculated either with local density or generalized gradient approximations. Both functionals lead to the same qualitative results but the calculated energies differ significantly. It is not possible to conclude, from comparison with available experiments, which functional is the most accurate.

I. INTRODUCTION

The diffusion and dissolution of oxygen in silver have been frequently studied[1–6] because they are important in many technological fields. These phenomena may indeed lead to the damage of silver intrinsic properties. They are also relevant when silver is considered as a cathode material for solid oxide fuel cell or as a substrate for electrodeposition of high temperature superconducting ribbons.[7] Recently, it has been discovered that a silver film deposited onto a nickel substrate dewets at high temperature under oxygen pressure.[8,9] The latter effect is believed to be related to the transport of silver vacancies during the diffusion of oxygen through the silver film. There is indeed some experimental evidence for a strong binding between vacancies and oxygen atoms in silver.[10]

The purpose of the present paper is to study from a theoretical point of view the insertion of oxygen atoms in silver and their interactions with vacancies. We focused on the atomic scale calculation of the associated energetics. We used the framework of density-functional theory (DFT) in the plane wave pseudopotential approach. All calculations have been carried out using either the local density approximation (LDA) or the generalized gradient approximation (GGA), which enables a detailed comparison of the results of the two types of functionals. Thermodynamical energies relevant to the insertion of oxygen atoms in silver and their interaction with vacancies have been calculated: formation energies of silver mono- and divacancies, solution energies of oxygen in various sites of silver, and binding energies of oxygen with one or two vacancies.

The first part presents the technical details of the calculations and introduces the notations. Results are presented in the following part: for each defect, the formulas used to obtain the thermodynamical energies from the calculations are specified. The discussion focuses on the comparison with available experiments and on the differences between LDA and GGA results.

II. METHODOLOGY

A. Technicalities

The calculations have been performed using the PWSCF package[11] based on a plane wave basis and pseudopotentials. In the LDA calculations we used the common Perdew–Zunger[12] functional. For the GGA calculations, we chose the functional proposed by Perdew, Burke, and Ernzerhof.[13] The LDA and GGA pseudopotentials for oxygen are of the ultrasoft type;[14] they are taken, respectively, from Ref. 15 and from the PWSCF pseudopotential library.[11] The latter is generated following the recipes of Rappe, Rabe, Kaxiras, and Joannopoulos (RRKJ).[16] The LDA and GGA pseudopotentials for silver are of the norm-conserving type; they have been generated with the FHI98PP code[17] using the Troullier–Martins scheme.[18] The generation parameters (core radii and reference energies) are kept to the values suggested in the FHI98PP code except for the reference energy of the $5p$ states which has been fixed 11 eV above their eigen-energy in order to improve the matching of the logarithmic derivatives of their real and pseudo wave functions. With this set of pseudopotentials, the energy cutoff was fixed to 40 Ry.

The validity of the pseudopotentials was checked on the silver and silver oxide structures. Silver crystallizes in the fcc structure. The experimental value of the lattice parameter is 4.09 Å and its bulk modulus is 100 GPa.[19] We determined the cell size and bulk modulus. For LDA (respectively, GGA) calculations we found a value of 4.03 Å (respectively, 4.17 Å) for the lattice parameter and of 134 GPa (respectively, 90 GPa) for the bulk modulus. Silver oxide (Ag_2O) crystallizes in the cuprite (Cu_2O) structure with an experimental lattice parameter of 4.74 Å.[20] Lattice parameters obtained within LDA and GGA are 4.65 and 4.87 Å, respectively. Thus, no functional appears to lead to more accurate results for the bulk properties. Our calculations exhibit the commonly observed trends: cell parameters are slightly underestimated within LDA whereas they are slightly overestimated within GGA and conversely for the bulk modulus.

TABLE I. Values of the vacancy formation energy in silver in the unrelaxed configuration (in electron volts). Present results (pw-UR) are compared with previous calculations. The experimental value is 1.10 eV.

	pw-UR	Other calc. (UR)
LDA	1.15	1.08 [a], 1.24 [b]
GGA	0.86	0.80 [a]

[a]FP-KKR-GF, Ref. 22.
[b]FP-LMTO, Ref. 23.

B. Simulation cell

The periodically repeated cell, in which point defects are introduced, is built from the duplication, in three directions, of the simple cubic cell of silver. In the perfect crystal it contains 32 atoms. The irreducible Brillouin zone is sampled by a set of 10 special k points generated following the Monkhorst and Pack scheme.[21] An Hermite–Gaussian smearing with a width of 0.02 Ry is applied. The introduction of point defects (oxygen atoms, silver vacancies, etc.) in the box sometimes decreases its symmetries and results in a larger number of k points especially for complex oxygen–vacancy clusters. All defect calculations are carried out at constant volume. Atomic relaxations are taken into account thanks to the calculated forces acting on the atoms. Due to computer limitations only atomic displacements that preserve the symmetries present before relaxation are allowed in the calculations. This limitation may cause a small overestimate of the energies of the high symmetry configurations.

C. Notations

The total energies directly resulting from the electronic structure calculations are denoted with a capital E. The number of silver and oxygen atoms in the cell are indicated in the superscript. In the subscript the nature of the defect is specified (vacancy, oxygen interstitial, etc.). For instance the energy of the box containing 32 silver atoms and an oxygen interstitial in octahedral position is denoted $E_{O_{oct}}^{32Ag+O}$. The thermodynamic energies deduced from these calculated energies are denoted with an ε. In the superscript the nature of the quantity (formation energy F, solution energy sol, binding energy B, etc.) is indicated. In the subscript the nature of the defect is specified. For instance ε_V^F is the formation energy of a vacancy in silver.

TABLE II. Formation energies of mono- and divacancies in silver, ε_V^F and ε_{V-V}^F, and divacancy binding energy $\varepsilon_{V-V/2V}^B$ (in electron volts).

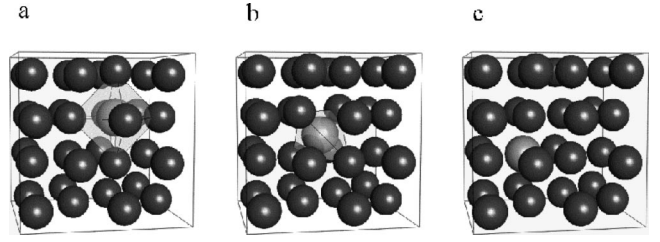| Functional	ε_V^F	ε_{V-V}^F	$\varepsilon_{V-V/2V}^B$
LDA	1.09	2.18	−0.01
GGA	0.82	1.59	0.05

FIG. 1. Insertion sites of oxygen in silver: (a) octahedral interstitial, (b) tetrahedral interstitial, and (c) substitution sites. The spheres correspond to the positions of the atoms in the simulation cell after relaxation: oxygen atoms in gray and silver atoms in black.

III. RESULTS

A. Vacancies in silver

The formation energies of vacancies and divacancies in silver and the binding energy of the divacancy made of two nearest-neighbor vacancies versus two isolated vacancies were calculated as follows:

$$\varepsilon_V^F = E_V^{31Ag} - \tfrac{31}{32} E^{32Ag}, \tag{1}$$

$$\varepsilon_{V-V}^F = E_{V-V}^{30Ag} - \tfrac{30}{32} E^{32Ag}, \tag{2}$$

$$\varepsilon_{V-V/2V}^B = E_{V-V}^{30Ag} + E^{32Ag} - 2E_V^{31Ag} = \varepsilon_{V-V}^F - 2\varepsilon_V^F. \tag{3}$$

The values we obtain for the formation energy of a monovacancy in silver before structural relaxations are compared in Table I with previous unrelaxed values from the literature.[22,23] It can be seen that our results compare fairly well with the previous ones. The effect of structural relaxation is rather small, as expected for a compact structure (see the first column of Table II). In the following all figures are given for relaxed configurations.

The values of mono- and divacancy formation energies as well as the binding energy of the latter are given in Table II. The experimental value of the formation energy of a monovacancy in silver is 1.10 eV. The LDA formation energy is very close to the experiment, whereas the GGA result deviates notably from it. Both functionals predict that no energy is gained upon association of two vacancies, i.e., the formation energy of a divacancy is simply twice that of a monovacancy.

B. Oxygen insertion in silver

Three sites were considered for the insertion of oxygen in silver: the octahedral O_{oct} and tetrahedral O_{tet} interstitial positions and the substitution for a silver atom O_{sub} (see Fig. 1). The solution energies of oxygen in silver were calculated using the di-oxygen molecule as a reference state for oxygen outside silver. For the interstitial sites the solution energy is given by

$$\varepsilon_{O_{oct}}^{sol} = E_{O_{oct}}^{32Ag+O} - E^{32Ag} - \tfrac{1}{2}E_{O_2}, \tag{4}$$

TABLE III. Solution energies of atomic oxygen in silver for the octahedral interstitial, tetrahedral interstitial, and substitutional sites (in electron volts).

Functional	$\varepsilon_{O_{oct}}^{sol}$	$\varepsilon_{O_{tet}}^{sol}$	$\varepsilon_{O_{sub}}^{sol}$
LDA	0.34	0.74	0.62
GGA	0.65	0.93	1.09

where E_{O_2} is energy of the di-oxygen molecule. E_{O_2} has been calculated including spin-polarization and using an 8-Å side simple cubic box.

For the substitution case the decrease in the number of silver atoms upon introduction of an oxygen atom must be taken into account. This leads to

$$\varepsilon_{O_{sub}}^{sol} = E_{O_{sub}}^{31Ag+O} - \frac{31}{32}E^{32Ag} - \frac{1}{2}E_{O_2}. \qquad (5)$$

The LDA and GGA results, reported in Table III, show some discrepancies but both functionals predict that the octahedral interstitial site is the most stable site for the insertion of oxygen in silver.

C. Oxygen interactions with vacancies

Due to computer limitations, only two configurations were considered for the oxygen–vacancy pair. In the first one the oxygen atom occupies an octahedral interstitial site with one vacant apex. The second one is simply the substitution–insertion configuration; it can be viewed as a configuration where an oxygen atom occupies an empty silver site, thus filling a vacancy. These geometries are denoted $V-O_{oct}$ and O_{sub}, respectively. The binding energy of a pair, ε^B, is defined as the reaction energy of the pair formation, starting from isolated defects:

$$\varepsilon \begin{vmatrix} B \\ V-O_{oct} \\ O_{sub} \end{vmatrix} = E \begin{vmatrix} 31Ag+O \\ V-O_{oct} \\ O_{sub} \end{vmatrix} + E^{32Ag} - E_V^{31Ag} - E_{O_{oct}}^{32Ag+O}. \qquad (6)$$

The calculated values, reported in Table IV, show that the substitution–insertion configuration is the most stable one.

For defect clusters made by an oxygen atom and two vacancies the calculations were restricted to two sets of positions, denoted, respectively, $V-O_{sub}$ and $V-O-V$ (see Fig. 2). In the first configuration the second vacancy is placed on a nearest-neighbor site of an oxygen substitutional atom. In the second configuration the oxygen is placed halfway be-

TABLE IV. Binding energies of the oxygen–monovacancy pairs and of the oxygen–divacancy clusters relative to isolated point defects (in electron volts). For a description of the atomic configurations see the text and Fig. 1.

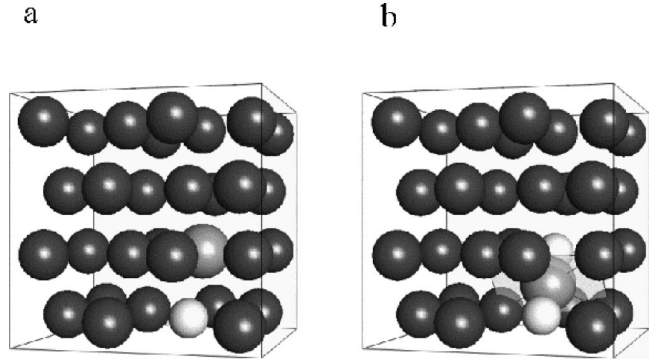|	Oxygen–vacancy		Oxygen–divacancy	
	$\varepsilon_{O_{sub}}^{B}$	$\varepsilon_{V-O_{oct}}^{B}$	$\varepsilon_{V-O-V/O_{oct}+2V}^{B}$	$\varepsilon_{V-O_{sub}/O_{oct}+2V}^{B}$
LDA	−0.81	−0.10	−1.15	−0.86
GGA	−0.39	−0.11	−0.69	−0.10

FIG. 2. Oxygen–divacancy clusters: (a) $V-O_{sub}$ and (b) $V-O-V$. Oxygen and silver atoms are indicated in gray and black, respectively. Vacancies are shown as light gray spheres.

tween two nearest-neighbor vacancies. Starting from a divacancy one can see that the oxygen atom is located on one side of a divacancy in the first case and in the middle of it in the second case. After relaxation of the atomic positions, the second configuration is found to have the lowest energy. The binding energies of these defect clusters can be defined relative to either (i) the three separated defects, (ii) the substitutional oxygen and vacancy defects, or (iii) the divacancy and oxygen interstitial defects. From one binding energy one can easily deduce the other ones. The values of case (i) are reported in Table IV. Approximately the same amount of energy is gained upon the oxygen–vacancy pairing and by the subsequent binding of a second vacancy.

LDA and GGA energies are once again very different. LDA seems to lead to systematically higher binding energies than GGA.

IV. DISCUSSION

A. Oxygen in silver

Based on the ratio between their respective atomic radii, Hägg's rule[24] predicts that oxygen lies in octahedral interstitial position in silver. Our calculation confirms this prediction: the octahedral site has the lowest solution energy. This result is quite robust in view of the rather large energy difference with the solution energies of the other sites (0.3 eV or more, see Table III). Our values can be compared to the solution energy deduced from experiments on the solubility of oxygen in silver.[1,2,5] It can be described by

$$[O_{Ag}] = \sqrt{P_{O_2}} \times 0.072 \exp(-0.50 \ \text{eV}/k_B T). \qquad (7)$$

In this expression, $[O_{Ag}]$ is the oxygen concentration and P_{O_2} is the oxygen partial pressure in the outer gas. The variation of oxygen concentration as the square root of pressure proves that oxygen atoms are dissolved as opposed to dioxygen molecules. Our calculated values of the solution energy are in overall agreement with the experimental value (0.50

eV): it is underestimated in the LDA case (0.34 eV) and overestimated in the GGA case (0.65 eV). Both functionals lead to similar deviations from the measured value.

Concerning the interactions between oxygen atoms and vacancies, we found that the oxygen–vacancy pair of lowest energy is simply the oxygen in substitution for silver. The fact that the energy decreases when an oxygen atom goes from an interstitial to a vacant site is not in contradiction with the fact that the interstitial configuration has the smallest solution energy. The solution energy of the substitution site indeed includes the formation energy of a vacancy which, according to our results, is larger than the energy gained by putting an interstitial oxygen in a vacant site.

From resistivity measurements on silver submitted to various thermal treatments, Quéré evidences interactions between dissolved oxygen and vacancies.[10] He deduces a value of -0.35 eV for the binding energy of the pair. Mathieu *et al.* also cite an unpublished value of -0.45 eV obtained by Moya from calorimetric measurements.[4] The calculated GGA value of the binding energy of the substitution oxygen (-0.39 eV) is very close to these experimental estimates. On the contrary the LDA value (-0.81 eV) seems to be significantly too large.

The formation of an oxygen–divacancy cluster starting from a substitutional oxygen and a monovacancy decreases the energy by 0.3 eV (for both functionals). There is therefore an important interaction of oxygen with vacancies beyond the first pairing that creates the substitutional oxygen. At the opposite, the silver divacancy binding energy came out to be negligible or even slightly positive (see Sec. III). The presence of oxygen therefore greatly favors the formation of divacancies and increases the number of such defects by creating divacancies bonded to oxygen atoms.

B. LDA–GGA comparison

The qualitative trends predicted by LDA and GGA calculations are the same: (i) oxygen is predicted to insert preferentially in the octahedral interstitial site; (ii) its binding with a vacancy results in a substitution oxygen; and (iii) upon further association with a second vacancy the oxygen atom goes in the middle of the created divacancy.

However LDA and GGA calculations lead to quantitatively very different results. When comparing GGA to LDA results, the vacancy formation energy in silver is 25% smaller, the oxygen solution energy is 50% larger, and the various binding energies of the oxygen–vacancy pairs and clusters are about twice smaller. Quantities such as the temperature dependence of the amount of dissolved oxygen, oxygen vacancy pairs or clusters will differ by orders of magnitude depending on which figures they are deduced from. The differences between the two functionals are on the whole larger when complex defects are considered (see Tables II–IV). We suggest that this comes from the fact that more simulation cells are involved in the definition of the energy of the more complex defects.

Unfortunately the values that are closest to experiments are not always the same. Indeed, the LDA value is clearly in better agreement with experiment for the formation energy of

silver vacancies. GGA calculations highly underestimate this energy. For what concerns oxygen insertion in silver, the two functionals equally deviate from the experimental value with an overestimation for LDA and underestimation for GGA. Finally, GGA results are much closer to the available experiments on the binding energy of the oxygen–vacancy pairs.

In view of our results, no clear conclusion can be drawn on which functional is the most accurate for such defect studies. Results available in the literature are of little help on this point. Indeed, even for first-principles simulations, the values of defect energies depend on many aspects of the calculations (type of program, size of the basis set, type of pseudopotential, supercell size, etc.). If LDA and GGA approximations are routinely compared for bulk properties of perfect materials, we found very few papers comparing LDA and GGA calculations on defect energetics in bulk materials (for vacancies in metals see Refs. 25 and 26; for vacancies in SiO_2 polymorphs[27] and for Si self-interstitials.[28] In these papers, the differences between LDA and GGA defect formation energies range from 0.1 to 0.9 eV, which is the order of magnitude of the differences observed in our calculations.

The underestimation of GGA formation energies in metals has already been reported.[22,25] Carling *et al.*[25] suggest that this discrepancy of GGA can be analyzed as a surface effect.

V. CONCLUSION

We have studied the insertion of oxygen atoms in silver and their interactions with vacancies with DFT plane wave calculations. Our results confirm that oxygen atoms are preferentially inserted in octahedral interstitial sites and that they have strong interactions with vacancies. We predict that the geometry of the oxygen–vacancy pair is the oxygen on a substitution site. Interactions of the same order of magnitude are found for the subsequent binding energy of the pair with a second vacancy. For this cluster an original configuration is obtained, the oxygen atom being located in the middle of the divacancy.

We have systematically calculated all quantities with LDA and GGA approximations. The results are qualitatively the same but differ significantly quantitatively. The LDA value is in better agreement with experiment than the GGA value for the vacancy formation energy in silver. For oxygen solubility LDA and GGA have similar deviations from the measured solution energy. Finally for interactions with vacancies, the GGA result is much closer to experiment. From our results as from the literature, it does not seem possible, in the context of point defect studies, to ensure that one approximation works better than the other.

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