Electronic structure of ε-oxygen at high pressure: GW calculations

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The pressure-induced metallization and its possible role in the phase transformation of ε-oxygen at high pressure are examined with density-functional theory with the generalized gradient approximation (GGA) and GW theory. The self-energy corrections to the GGA Kohn-Sham eigenvalues are computed. The GW-corrected electronic band structures show that the experimental $C2/m$ structure of ε-oxygen is an indirect band-gap semiconductor up to nearly 100 GPa. The present finding agrees with the experimental observation suggesting that metallization of the $C2/m$ structure should occur near 100 GPa.

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INTRODUCTION

Oxygen is a major component of both the earth's crust and its atmosphere. It is an essential material in both natural and industrial processes. Recently the crystal structure of the ε phase was finally resolved using single-crystal[1] and powder x-ray diffractions.[2] Crystalline ε-oxygen adopts the $C2/m$ space group.[1,2] A unique feature of this structure is the presence of $(O_2)_4$ molecular units. Details on the nature of chemical bonding in this cluster are still unclear.[3] At 96 GPa, ε-oxygen was found to transform to a metallic ζ phase.[4–8] Moreover, ζ-oxygen becomes a superconductor with a critical temperature of 0.5 K at 110 GPa. The structure of the ζ phase,[5,7] however, remains elusive. A recent theoretical study based on density-functional theory (DFT)-generalized gradient approximation (GGA) calculations has proposed that the $\varepsilon \rightarrow \zeta$ phase transition is isosymmetric where the $C2/m$ space group remains invariant.[8] However, in the calculations, the $C2/m$ structure is predicted to be metallic at about 50 GPa (Ref. 8) which is in substantial disagreement with the observed pressure of 96 GPa.[4] Although, it is well known that the GGA often underestimates the band-gap energy, the discrepancy between calculation and experimental transition pressure of about 45 GPa is unusually large. To improve the estimation band-gap energies of semiconductors, a quasiparticle theory is needed. In this study, the GW method[9] is applied to correct for the DFT Kohn-Sham eigenvalues by adding the self-energy corrections to several high-symmetry points in the Brillouin zone. The GW approximation has been successfully applied to many materials such as oxides and other inorganic materials where there were questions regarding their optical properties.[10] Previously, the pressure-induced metal-insulator transition of Si in the diamond structure has been investigated with this approach.[11] In this work, the GW approximation (GWA) is used to characterize the electronic band structure of ε-oxygen at high pressure in order to estimate the pressure for band-gap closure and possible implications for suggested phase transformations.

COMPUTATIONAL DETAILS

Calculations were performed using the first-principles electronic structure code ABINIT.[12] A Hartwigsen-Goedecker-Hutter pseudopotential with Perdew-Burke-Ernzerhof GGA for oxygen atom[13] together with a plane-wave energy cutoff (E_{cut}) of 110 Ry was used in all calculations. Fully optimized crystal structures and electronic band structures were obtained with Monkhorst-Pack k-point meshes[14] up to $6\times6\times8$ to check for convergence. The GW calculations were performed with the ABINIT code[12] based on the formulation of Schindlmayr *et al.*[15] Self-energy corrections to DFT-GGA Kohn-Sham eigenvalues at selected high-symmetry points were obtained for comparison with the GGA eigenvalues. The computational procedure is as follows. A converged ground-state calculation on an optimized structure was first performed. In essence, these calculations were carried out to first obtain a self-consistent density and potential Kohn-Sham eigenvalues and eigenfunctions at the ground electronic state. Calculations were performed on grids of reciprocal space points (k points) that included band points at extrema. This was followed by computation of the independent-particle susceptibility matrix at two frequencies and a calculation of the susceptibility matrix, the dielectric matrix, and its inverse. The self-energy matrix elements were then evaluated at selected k points which then used to derive the GWA eigenvalues for the selected states around the highest occupied states. Adhering to the experimental $C2/m$ space group for the ε phase,[1,2] high-pressure structures were optimized at 49, 69, 88, and 112 GPa. GW corrections to the Kohn-Sham energies obtained from GGA calculations are evaluated as described above for these four pressures. Typically, 30 electronic bands were used to generate the Kohn-Sham band structure and 26 bands were used in the screening calculations. An energy cutoff of 10 hartree was used in the calculation of the screening matrix. For the calculations of the self-energy matrix elements, 150 bands with an energy cutoff of 25 hartree, to represent the wave functions, were used. Using these parameters, the convergence in the calculated energy gaps is better than 0.05 eV. GW corrections are often quite linear with the energy; in this case, we examine k points along the high-symmetry directions where the GGA band structure indicates significant band overlap at 49 GPa since these are the points that will most affect the determination of the metallic or semiconducting nature of ε-oxygen. GW corrections for a proposed $C2/c$ structure[8] at 110 GPa were also calculated using the same procedure.

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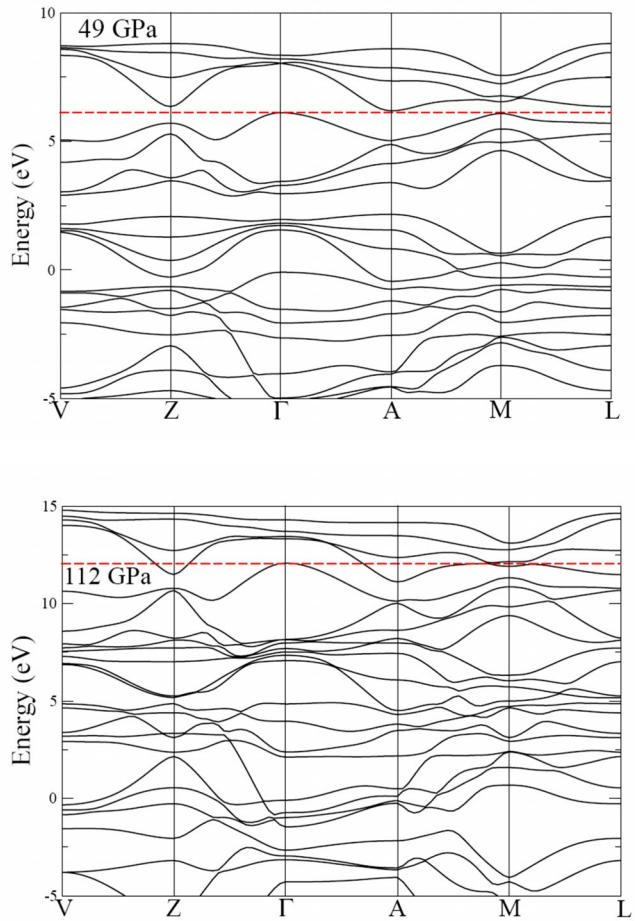

FIG. 1. (Color online) Calculated GGA electronic band structures of $C2/m$ ε-oxygen at 49 and 112 GPa.

RESULTS AND DISCUSSION

Electronic and crystal structure of ε-O_2

Using the ABINIT code, the GGA optimized structural parameters of ε-oxygen at 49 GPa are $C2/m$, $\boldsymbol{a}=7.154$, $\boldsymbol{b}=5.048$, $\boldsymbol{c}=3.488$ Å, and $\beta=114.23°$ with O(1) (0.830, 0.0000, 0.1860); O(2) (0.2449, 0.0000, 0.1955); and O(3) (0.0374, 0.2732, 0.1903). At 112 GPa, the optimized structural parameters are $\boldsymbol{a}=6.867$, $\boldsymbol{b}=4.586$, $\boldsymbol{c}=3.268$ Å, and $\beta=113.74°$ with O(1) (0.3190, 0.0000, 0.6988); O(2) (0.2431, 0.0000. 0.2998); and O(3) (0.03790, 0.2304, 0.3009). The theoretical unit-cell parameters compare favorably with observed structural parameters at 50 GPa of $\boldsymbol{a}=7.184$, $\boldsymbol{b}=5.016$, $\boldsymbol{c}=3.459$ Å, and $\beta=115.6°$ and the extrapolated cell size at 110 GPa of $\boldsymbol{a}=6.768$, $\boldsymbol{b}=4.572$, $\boldsymbol{c}=3.258$ Å, and $\beta=114.9°$.[2]

The GGA electronic band structures for the $C2/m$ structure are shown in Fig. 1. At 49 GPa, the GGA band structure indicates that ε-oxygen is an indirect band-gap insulator. The predicted indirect band gap of 0.075 eV between the Γ and A points, however, is very small. In fact, when pressure is increased beyond 50 GPa, within the GGA, there is no longer an energy gap and ε-oxygen is then predicted to be metallic. These results are in agreement with the previous GGA calculation,[8] but both are in surprisingly large discrepancy with experiment where a metallization transition was observed at 96 GPa.[4–7] The large difference between theoretical and experimental metallization pressures undoubtedly can be attributed to a well-known defect of the GGA in underestimating the band-gap energies. To obtain a more realistic estimate of the band-gap energies, it is necessary to carry out correlated calculations. In this study, to correct for the deficiency of GGA, GW calculations were performed. Table I summarizes the results of calculations at selected pressure between 49 and 112 GPa. The predicted GGA and the corresponding GW-corrected indirect band-gap energies between Γ and A, M, and Z symmetry points are listed. The A, M, and Z points are chosen since they are the lowest energy points in the conduction band predicted by GGA calculations (Fig. 1). In Table I, E_{GGA} and E_{GWA} are the indirect band gaps for the GGA-Kohn-Sham and GW-corrected eigenenergies, respectively.

TABLE I. Calculated indirect band gaps between Γ and selected Brillouin-zone points for $C2/m$ ε-oxygen with GGA (E_{GGA}) and GW corrections (E_{GWA}) at 49, 69, 88, and 112 GPa.

Pressure (GPa)	Indirect band gap	E_{GGA} (eV)	E_{GWA} (eV)
49	Γ→A	0.075	1.12
49	Γ→M	0.44	1.47
49	Γ→Z	0.21	1.46
69	Γ→A	−0.20	0.48
69	Γ→M	0.28	1.19
88	Γ→A	−0.62	0.29
88	Γ→M	0.03	0.91
112	Γ→A	−0.82	−0.105
112	Γ→M	−0.022	0.25
112	Γ→Z	−0.57	0.27

As it is expected, GW corrections widened the energy gaps. At 49 GPa, the indirect gap between Γ and A now has an energy of 1.12 eV. This is substantially larger than the GGA value of 0.075 eV. Calculated GGA Γ-to-A indirect band gaps are however negative at 69 and 88 GPa with band gap values of −0.20 and −0.62 eV, respectively. On the other hand, GW Γ-to-A calculated band gaps at these points are positive and therefore correctly predict that ε-oxygen at that pressure is an insulator. When pressure increases, energy of the conduction band at the M point decreases more rapidly than those at the A and Z points. At 112 GPa, the energy-band gap between Γ and A points becomes negative (−0.105 eV), indicating that the band gap has already been closed. Therefore, band-gap closure in $C2/m$ ε-oxygen is expected to occur at pressure slightly lower than 112 GPa. Additional calculations have been performed at the intermediate pressures of 69 and 88 GPa. The GGA band gaps for the Γ-to-A and Γ-to-M points was found to decrease monotonically to the 112 GPa values in Table I. The GW-calculated bandgaps for Γ to A and Γ to M remain positive, 69 and 88 GPa, and they decrease monotonically as for the GGA calculations. This result is clearly in good accord with the experimentally observed structural phase transition from ε-oxygen-to-ζ-oxygen at 96 GPa (Ref. 4), which is found to

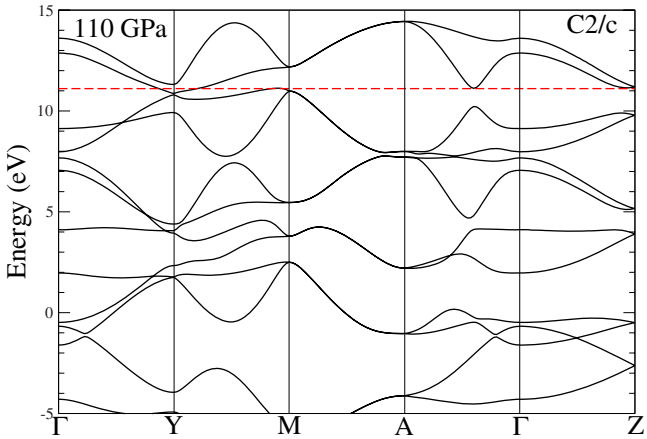

FIG. 2. (Color online) Calculated GGA electronic band structure of proposed $C2/c$ structure of oxygen at 110 GPa.

be associated with the closure of the band gap leading to a metallic phase.[5,6]

The present results indicate that a correlated treatment of the valence electrons is needed in order to describe properly the electronic structure of high-pressure ε-oxygen. The calculated results, in agreement with experiment, show a band-gap closure at 110 GPa (see Fig. 2). This may be the precursor to the observed phase transition to the ζ-phase. In a very recent paper that appeared after this work was submitted,[16] and which employed another code and the Projected Augmented Wave (PAW) potential for the GW corrections, the band-gap closure was found at much lower pressures than in experiment and in the present study. In the present study, the direct gap remains open to at least 88 GPa and the indirect gap is closed by 112 GPa. This compares with Ref. 16 where the direct gap is already closed at 57 GPa, which is significantly lower than that of experiment. In the earlier study,[16] it was found that the indirect gaps were closed along $A \rightarrow M$ and $\Gamma \rightarrow Z$. At 57 GPa, the energy at Γ is found to be substantially higher than at the Z and M points. As shown in Table I and as discussed above, we did not reproduce this trend in our GWA calculations. The lowest conduction-band energy at Z and M fall below Γ only near 100 GPa. The basic finding between the present and previous studies that the insulator-metal transition is strongly linked with the structural phase transition is however in complete accord with the present study.

CONCLUSIONS

Although it is not surprising that GGA underestimate the electronic band-gap energy, in this case, the predicted metallization pressure of ε-O_2 is much lower than the observed value by almost 50 GPa. The employment of the GW approximation to obtain self-energy corrections to GGA band-gap values has greatly improved the agreement with experiment. The results presented here indicate that calculations including electron correlation effect are needed in order to fully characterize the high-pressure metallic transitions in solid oxygen.

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