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Structurally induced insulator-metal transition in solid oxygen: A quasiparticle investigation

Duck Young Kim,[1,*] S. Lebègue,[2] C. Moysés Araújo,[1] B. Arnaud,[3] M. Alouani,[4] and Rajeev Ahuja[1,5,†]
[1]*Condensed Matter Theory Group, Department of Physics, Uppsala University, P.O. Box 530, SE-751 21 Uppsala, Sweden*
[2]*Laboratoire de Cristallographie et de Modélisation des Matériaux Minéraux et Biologiques, UMR 7036, CNRS-Université Henri Poincaré, Boite Postale 239, F-54506 Vandoeuvre-lès-Nancy, France*
[3]*Institut de Physique de Rennes, UMR UR1-CNRS 6251, Universite de Rennes1, Bat 11A Campus de Beaulieu, F-35042 Rennes Cedex, France*
[4]*Institut de Physique et de Chimie des Matériaux de Strasbourg, UMR 7504 CNRS-ULP, 23 rue du Loess, 67034 Strasbourg, France*
[5]*Materials Science and Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden*
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Structural phase transition of solid oxygen has been investigated by using ab initio calculations based on density functional theory. We found sudden jumps in structural parameters at the transition pressure, which confirm that the epsilon (ϵ) phase undergoes a first-order isostructural phase transformation to the zeta (ζ) phase. In particular, this happens without any molecular dissociation. Using the *GW* approximation to calculate the band-gap closure under high pressure, we show that the structural transition is accompanied by an insulator-metal transition, contrary to a standard density functional calculation which predicts a metallization at a much lower pressure in the ϵ phase.

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Solid oxygen shows many structural phase transitions induced by both pressure and temperature,[1,2] which are either accompanied or driven by magnetism[3,4] or metal-nonmetal transitions.[5,6] At low temperature and high pressure, even a superconducting state has been observed.[7] More specifically, at room pressure and below 24 K, oxygen crystallizes into a monoclinic structure (α phase) with space group $C2/m$, which shows an antiferromagnetic ordering.[8] Above 24 K (up to 44 K), the α phase transforms into the nonmagnetic rhombohedral (β-phase) structure, which belongs to the space group R-3m. By raising the temperature and pressurizing the system, we have the following scenario; at room temperature and around 5.4 GPa, oxygen solidifies into the β phase and it transforms into the δ phase (orthorhombic) at 9.6 GPa, which displays antiferromagnetic ordering.[9] Thus, a magnetic transition takes place again. The subsequent structural transformation occurs at 10 GPa from δ to ϵ phase.[10] This is found to be a strong first-order transition as observed from the significant volume discontinuity.[5,11] This transition leads also to the following changes: appearance of a strong infrared absorption, new Raman and infrared modes, and a magnetic collapse. The full determination of the ϵ phase has only recently been performed.[12,13] This structure displays $C2/m$ symmetry with associations into units containing four O_2 molecules (O_8 units). The knowledge about the positions of the molecules in the unit cell has helped the atomic modeling of the physical properties of this structure.

The ϵ phase undergoes a structural phase transition at 96 GPa to the so-called ζ phase[5] and the previously observed metallic state of solid oxygen[1] was ascribed to this transition. This structure was proposed to be isostructural with the monoclinic unit cell of the ϵ phase. However, in a more recent work, through x-ray diffraction and Raman measurement, it was shown that the metallization of solid oxygen is associated with a continuous displacive phase transformation where the structure was suggested to be not isostructural with the ϵ phase,[6] raising a controversy about the nature of this phase transition. They have also shown that the metallic oxygen might be molecular up to at least 120 GPa. In another Raman measurement, a moderate decrease of vibron mode at the transition confirmed the molecular characteristic of metallic oxygen.[14] Most recently, a theoretical investigation of the ζ phase based on *ab initio* evolutionary methodology for crystal structure prediction supported the isostructural nature of the ϵ-ζ transformation.[15] In that paper, the ζ phase remained as a molecular solid and there was no further structural transition in the pressure range of 100–250 GPa. While molecular nature of the metallic solid oxygen appears to be a common conclusion among all the above studies, the following questions are still prompting to further investigations. Is the ζ-phase isostructural with the ϵ phase? Does the insulator-metal (IM) transition accompany with the structural phase transition?

In this Brief Report, we address these questions by employing first-principles theory. We confirm that the ϵ phase undergoes a first-order isostructural transformation to the ζ phase without molecular dissociations. This is demonstrated by abrupt changes of lattice parameters and internal degrees of freedom obtained directly from the optimization of the ϵ phase. Most importantly, by using quasiparticle *GW* calculations, we show that the IM transition accompanies the structural transformation. The band gap, in the ϵ phase, decreases with pressure and eventually goes to zero at the transition point. However, the metallic phase is found only at the ζ phase. To clarify the IM transition, we maintain the ϵ phase up to the pressure at which the ζ phase is already stabilized, by constraining the geometry optimization, and calculate the electronic structure to show this structure to be a semimetal state. In the following, we provide the details of our theoretical calculations and discussions of our results.

The geometry optimization has been performed within the framework of the generalized gradient approximation (GGA)[16] to density functional theory (DFT)[17,18] using the projector augmented wave (PAW) method,[19] as implemented in the Vienna *ab-initio* simulation package (VASP).[20] The PAW potential with the valence states $2s^2 2p^4$ for O has been employed. All results reported here have been successfully tested for convergence with respect to both cutoff energy and number of *k* points in a mesh generated by the Monkhorst-Pack scheme.[21] In all calculations, self-consistency was achieved with a tolerance in the total energy of at least 0.01 meV. Ionic positions and cell parameters were relaxed with respect to minimum forces and stress using either conjugate-gradient or quasi-Newtonian method.

To look at the metallization of solid oxygen, one has to go beyond a standard DFT in order to get well defined excited state properties. For this, we have chosen to use the so-called *GW* approximation to the self-energy Σ.[22–24] In this approximation, the self-energy (the proper exchange-correlation potential acting on an excited electron or hole) is written as the product of the one-electron Green's function times the screened Coulomb interaction: $\Sigma = iGW$. The latter has been calculated within the plasmon-pole approximation, which is computationally less expensive and provides similar results as the full *GW* when it is applied for *sp* bonded materials. By using a perturbation theory starting from a DFT calculation, the quasiparticle eigenvalues $E_n(k)$ can be written as

$$E_{nk} = \epsilon_{nk}^{GGA} + Z_{nk} \times [\langle \Psi_{nk}^{GGA} | \Sigma(\mathbf{r},\mathbf{r}',\epsilon_{nk}^{GGA}) | \Psi_{nk}^{GGA} \rangle - \langle \Psi_{nk}^{GGA} | V_{xc}^{GGA} | \Psi_{nk}^{GGA} \rangle], \qquad (1)$$

with the renormalization factor written as

$$Z_{nk} = \left[1 - \left\langle \Psi_{nk} \middle| \frac{\partial}{\partial \omega} \Sigma(\mathbf{r},\mathbf{r}',\omega = \epsilon_{nk}) \middle| \Psi_{nk} \right\rangle \right]^{-1}. \qquad (2)$$

More details about the implementation could be found in Refs. 25 and 26.

We start the calculations by optimizing the monoclinic structure (space group $C2/m$) of the ϵ phase at different points in the pressure range of 7–140 GPa. We have found that when optimizing the ϵ phase above 51.7 GPa, it undergoes spontaneously a structural phase transition in good agreement with the previous theoretical work[15] where the structure of the ζ phase was predicted. The disagreement between this calculated transition pressure and the experimental findings (about 96 GPa) could be explained by the deficiency of DFT to describe weak intermolecular covalent interactions of the ϵ phase as discussed by Ma *et al.*[15] Molecular solids also tend to have big hysteresis along their thermodynamic paths. Degtyareva *et al.* reported that some group VI elements such as S and Se maintain their molecular characteristics up to a high pressure and are quenchable to a very low pressure.[27] In that paper,[27] it is clear that phases are overlapped in wide-ranged pressures. When it comes to oxygen, a recent study showed that the difference in energy between two phases is very small[28] and in another work, a big hysteresis has been observed.[14]

Figure 1(a) shows the variations of the volume (per atom) as a function of pressure. It is observed that, starting from the value of 8.74 Å^3, the volume of the ϵ phase (blue line with dots) decreases monotonically down to 6.56 Å^3 where a first-order structural phase transition occurs. After the transition, a different phase (red line with dots) belonging to the same space group as the ϵ phase is stabilized. The inset graph shows the magnified volume-pressure relation around the phase transition pressure. The transformation from the ϵ phase to the different phase at 51.7 GPa shows a small, but noticeable, volume collapse by 1.0%, which is comparable to the experimental data.[5] They[5] have reported a small volume collapse by less than 1.4% in ϵ-ζ phase transition with no molecular dissociation.

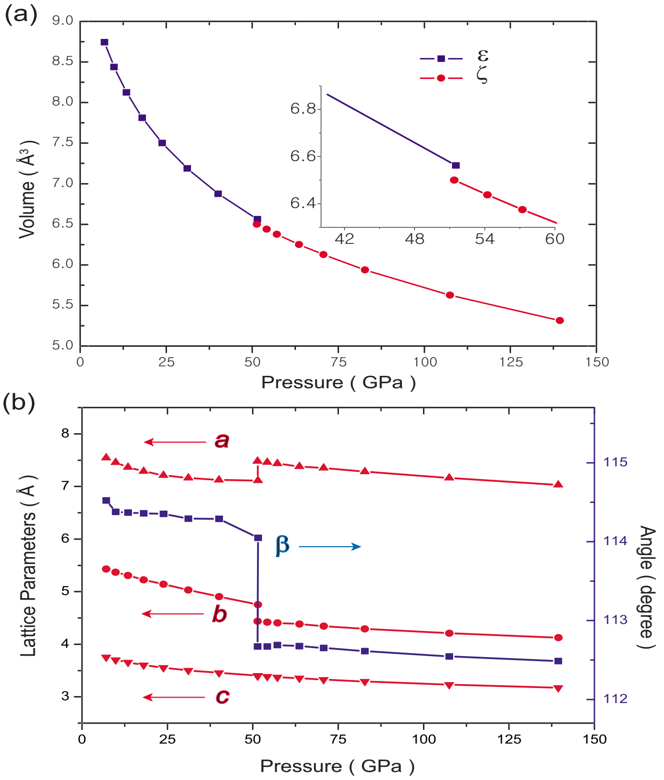

FIG. 1. (Color online) Pressure dependence of structural parameters. (a) Pressure dependence of the atomic volume of O_2 solid. The blue solid squares with line as guide for the eyes are for the ϵ phase and the red circles for the ζ phase. The inset shows a discontinuity of volume at the transition pressure. (b) Pressure dependence of the lattice parameters: *a*, *b*, *c*, and β (lines are guides for the eyes).

In Fig. 1(b), the changes of lattice parameters are shown as a function of pressure. As can be seen, all lattice parameters display similar decreasing behaviors in the beginning of the compression (up to 14.5 GPa), showing an isotropic process, at the ϵ phase. As the transition pressure is approached, trends of changes in lattice parameters are different for each parameter. The lattice parameter *a* becomes nearly constant, while *b*, *c*, and β keep decreasing with pressure. At the transition pressure, an abrupt change of *a*, *b*, and β takes place while *c* keeps decreasing slightly, which indicates that the phase transition happens in the *ab* plane. Since O_2 molecules are aligned along the *c* axis, there is no molecular dissociation with this structural transformation. The elongation of *a* and the contraction of *b* at the transition were shown in previous x-ray diffraction experiments,[5,6] which is consistent with this work. The sudden change of β by around 1.5° at the transition has also been reported in the recent experiment[13] and calculation,[15] which is a precursor for the transition to the ζ phase.

Figures 2(b) and 2(c) present schematically the atomic

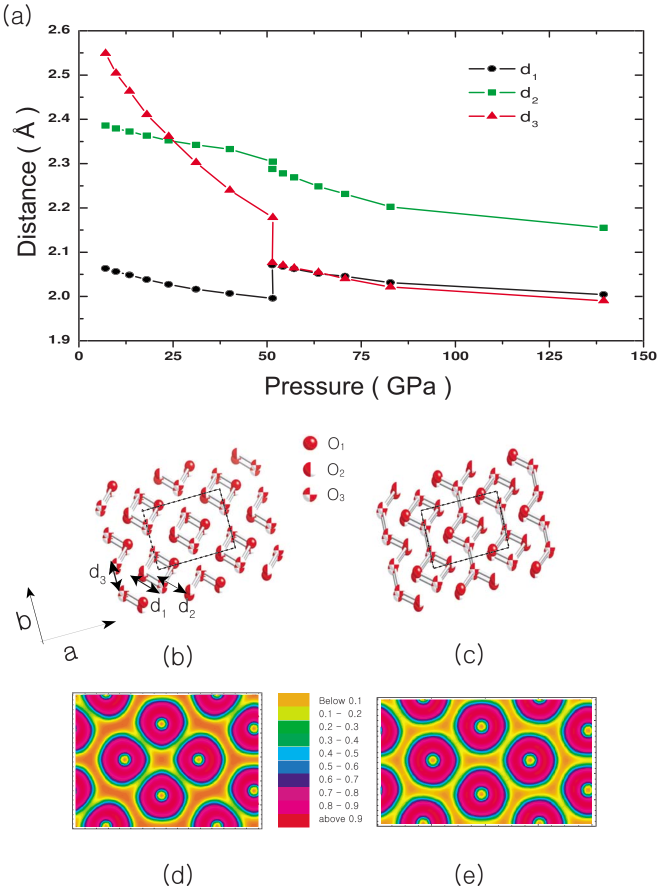

FIG. 2. (Color online) Pressure dependence of interatomic distance. (a) Pressure dependence of d_1 [intradistance of $(O_2)_4$ cluster], d_2 [interdistance of $(O_2)_4$ clusters in the *ab* plane], and d_3 (the distance of O_3-O_3 between clusters), as schematically shown in (b). The structure as viewed perpendicular to the *ab* plane (b) at 7 GPa (ϵ phase) and (c) at 51.7 GPa (ζ phase). The dashed square line shows the boundary of unit cell. The electron localization function image in the *ab* plane of the unit cell of (b) and (c) is shown in (d) and (e), respectively.

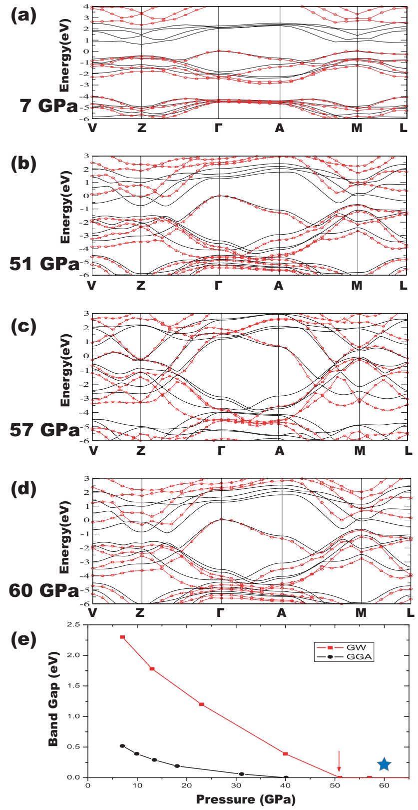

FIG. 3. (Color online) The band structures at [(a) and (b)] two ϵ phases and (c) one ζ phase of solid oxygen. The corresponding band-gap and pressure relations are plotted in (e). At the pressure pointed by an arrow (51.7 GPa), the indirect gap is closed, but direct gap still remains (semimetallic). For higher pressures, the direct gap is also closed. The blue colored solid star points out the pressure of an artificial structure, which exists as an ϵ phase in ζ-phase regime, and its band structure is shown in (d).

positions in the *ab* plane and the bonds of oxygen before and after the transition. In this structure, there are three distinct symmetry sites for oxygen atoms labeled as O_1, O_2, and O_3. In Fig. 2(b), we define three distinct atomic distances (d_1, d_2, and d_3), which represent the characteristics of inter- and intradistances of the refined structure. For the ϵ phase, d_3 is significantly shorter than d_2 and d_3, as shown in Fig. 2(a), meaning that each $(O_2)_4$ cluster maintains its shape. The structure described in Fig. 2(b) exhibits isolated $(O_2)_4$ clusters in the ϵ phase. This is consistent with previous works[12,13] where it was proposed that the localized electrons in oxygen clusters spread out into the *ab* plane making the metallic ζ phase. The rapid downward slope of d_3 makes it overcomes d_1 at the transition pressure, which shows the change of bonding in the *ab* plane. The enhanced bonding along d_3 makes $(O_2)_4$ clusters connected to each other, as shown in Fig. 2(c). After overcoming d_1, d_3 goes almost parallel with d_1 and makes chainlike connection along the *b* axis. These trends in bonding with pressure between clusters become apparent with the help of electron localization function (ELF) images shown in Figs. 2(d) and 2(e). Figures 2(d) and 2(e) show the contour plots of the ELF for the dotted square area in Figs. 2(b) and 2(c), respectively. The images reveal the distortion of $(O_2)_4$ clusters and the bonding formation between the nearest O_3 atoms in the ζ phase contrary to the ϵ phase. It is obvious that the bonding between O_3 is the key feature of the structural phase transition.

To investigate whether the structural transition is accompanied by the IM transition, we have performed several *GW* calculations for various pressures. In Fig. 3(a), we show our calculated GGA (black full lines) and *GW* (red lines with dots) band structures at the pressure of 7 GPa. The correction appears to be crucial, since, for example, the minimum (indirect) band gap (between Γ and Z) has a value of 2.3 eV when using *GW*, whereas it has only a value of 0.6 eV when using DFT-GGA. In Fig. 3(b), the GGA and *GW*, band structures are presented for a pressure of 51.0 GPa, which correspond to the ϵ phase right before the structural phase transition. It is observed that although the GGA band structure is already fully metallic, the overlap between the bands is very weak with *GW*, therefore an electronic conductivity close to zero (owing to the precision of the *GW* approximation for *sp* materials, it could also be possible that a small band gap still exists). This is in opposition with the band structure of the ζ

phase at 57 GPa [see Fig. 3(c)], which is clearly metallic, even with *GW*. Therefore, one can see that the structural transition is accompanied by the IM transition. To comfirm further this effect, we have calculated the band structure of the ϵ phase at 60 GPa at which the ζ phase is already stabilized [see Fig. 3(d)]. We kept the shape constant and allowed only the changes of internal parameters of an ϵ phase. Clearly, the corresponding *GW* band structure still displays a poorly metallic behavior, contrary to the *GW* band structure of the ζ phase at 57 GPa, which is fully metallic. This confirms that the IM transition is strongly linked with the structural phase transformation.

Figure 3(e) shows the closure of the band gap with pressure using both GGA and *GW* methods. The band gap with GGA is estimated to be 0.6 eV in the ϵ phase under lower pressure and is closed at 40 GPa, which was also shown in the previous theoretical work.[15] However, the *GW* band gap is closed at 51.7 GPa exactly where the structural transformation takes place. Thus, *GW* corrections not only improve the quantitive estimations of band gap energies but also reveal that the IM transition is accomplished by the structural phase transition in solid oxygen.

In conclusion, we have presented a study of the ϵ-ζ phase transition of solid oxygen. Using density functional theory, we found a first-order transition presenting a noticeable volume collapse, but without the molecular dissociation. Using the *GW* approximation to the self-energy for band-gap calculations, we showed that the IM transition is strongly linked with the structural transformation, a result that cannot be obtained within DFT due to the usual underestimation of the band gap. Furthermore, this work opens the path toward the theoretical studies of the metallization under pressure of other molecular systems using appropriate theories beyond DFT.

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*duck.young.kim@fysik.uu.se
†rajeev.ahuja@fysik.uu.se

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