The pressure-induced insulator-metal transition of solid oxygen - band-structure calculations

The pressure-induced insulator–metal transition of solid oxygen—band-structure calculations

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Abstract. The pressure-induced insulator–metal transition in molecular solid oxygen is investigated by calculating the electronic band structures as a function of volume. At large volumes (low pressures) an insulating antiferromagnetic state is the most stable. On decreasing the volume (increasing the pressure) an antiferromagnetic metallic state is realized by band overlapping and finally a paramagnetic metallic state becomes the most stable.

1. Introduction

Quite excitingly, superconductivity has been discovered recently in solid oxygen under pressures higher than $\simeq 100$ GPa [1]. Evidence for metallization of solid oxygen above ~ 95 GPa had already been provided by a couple of experimental observations: in measurements of optical absorption spectra [2] and electrical resistivity [4]. From x-ray diffraction measurements, Akahama *et al* [3] suggested that the metallization is realized in a molecular phase and proposed that the crystal structure of the metallic molecular state is of monoclinic type (called the ζ-phase) which is isostructural with the ε-phase.

If the insulator–metal (IM) transition in oxygen truly occurs in the molecular phase, several interesting questions arise. What is the driving force of the IM transition? Is the mechanism the same as for the IM transition of other diatomic molecular solids such as halogens? Does the spin of the oxygen molecules remain even in the metallic phase or does it disappear before the IM transition occurs? As the first step in seeking for answers to these questions, we have performed first-principles calculations of band structures of molecular solid oxygen as a function of volume. Preliminary results of our present calculations are reported in reference [5].

2. Calculational procedure

At low pressures and low temperatures, molecular solid oxygen has a monoclinic crystal structure called α-phase (space group $C2/m$). With increasing pressure at low temperatures, successive structural phase transitions occur: from the α-phase to the orthorhombic δ-phase (space group $Fmmm$) at about $P \simeq 3$ GPa, and from the δ-phase to the monoclinic ε-phase at about $P \simeq 8$ GPa [6]. It is reported [3] that the crystal structure after metallization above ~ 95 GPa is of monoclinic type, called the ζ-phase, which is isostructural with the ε-phase.

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We have carried out band-structure calculations for three types of crystal structure of the molecular phase by changing the volume: monoclinic α-phase, orthorhombic δ-phase and monoclinic ζ-phase. As the magnetic states, we have considered antiferromagnetic (AF), ferromagnetic (F) and non-magnetic (NM) states. The crystal structure parameters of these three phases observed experimentally at a particular pressure are given in table 1. While changing the molecular volume V_M, we have fixed the mutual ratio of the lattice constants and the angle β of the monoclinic structure to the values determined from table 1. Furthermore, the intramolecular atomic distance has been kept to 1.2 Å, which corresponds to that at ambient pressure.

Table 1. The crystal structure parameters of the α-, δ- and ζ-phases at a particular pressure. The data were taken at $T = 22$ K for the α-phase and at room temperature for the δ- and ζ-phases. V_M denotes the molecular volume, i.e. the volume per molecule.

	P (GPa)	a (au)	b (au)	c (au)	β (deg)	V_M (au^3)
α-phase [7]	0	10.21	6.480	9.611	132.3	235.2
δ-phase [8]	9.6	7.965	5.588	12.64	122.2	140.6
ζ-phase [3]	116	6.487	4.191	6.297	116.4	76.67

The method of band-structure calculation that we have used is the FP-LMTO method [9] based on the usual local spin-density approximation (LSDA). The calculational procedures are the same as those described in reference [5] except as regards the number of sampling k-points and the LMTO basis set. We have used 68 sampling k-points (compared with 32 sampling k-points in reference [5]) in the irreducible Brillouin zone for the k-space integration. We have used a 3κ sp LMTO basis set (12 LMTO/atom): $\kappa^2 = 0.102$, $\kappa^2 = -1.002$ and $\kappa^2 = -2.000$ Ryd (a 2κ sp LMTO basis set (with 8 LMTO/atom) was used in reference [5]).
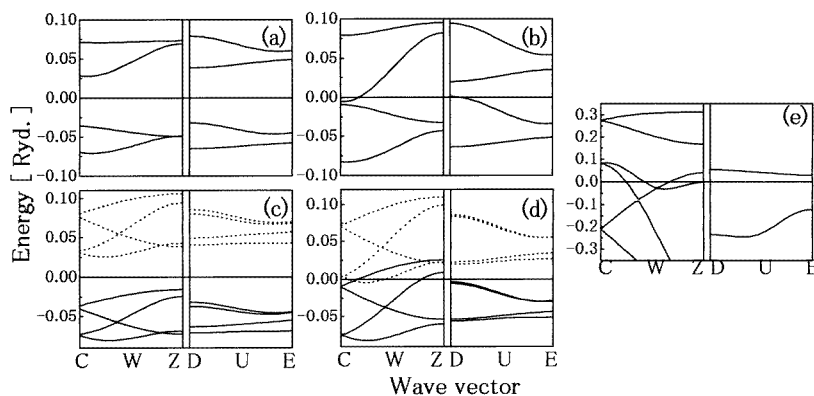

Figure 1. The energy dispersion curves of the α-phase along some symmetry lines in the first Brillouin zone: (a) AF state, $V_M = 235.2$ au^3; (b) AF state, $V_M = 175.1$ au^3; (c) F state, $V_M = 235.2$ au^3; (d) F state, $V_M = 190.7$ au^3; (e) NM state, $V_M = 76.67$ au^3. In (c) and (d), the full curves denote the up-spin bands, and the dotted curves the down-spin bands. Note that in the AF state the up-spin and down-spin bands are degenerate.

3. Results of calculations

In the case of the AF state of the α-phase, for volumes larger than 180.1 au^3 insulating states are realized and the full magnetic moments are induced. However, for $V_M < 180.1$ au^3 metallic states are realized by band overlapping and the magnetic moments are reduced from the full moments. On decreasing the volume further, for $V_M < 95.38$ au^3 the AF solution has not been obtained. Figures 1(a) and 1(b) show the energy dispersion curves of the AF state calculated for $V_M = 235.2$ au^3 (insulating) and $V_M = 175.1$ au^3 (metallic), respectively. As for the F state, we obtain insulating states for $V_M > 212.4$ au^3 and metallic states for $V_M < 212.4$ au^3. For $V_M < 95.38$ au^3 we could not obtain a self-consistent solution also for the F state, i.e. we obtain only the NM state for $V_M < 95.38$ au^3. Figures 1(c) and 1(d) show the energy dispersion curves of the F state obtained for $V_M = 235.2$ au^3 (insulating) and $V_M = 190.7$ au^3 (metallic), respectively, and figure 1(e) depicts the energy dispersion of the NM state obtained for $V_M = 76.67$ au^3 corresponding to the molecular volume of the ζ-phase at 116 GPa. It should be emphasized here that the NM state is also metallic. It is also noted that, from comparison of the total energies, the AF state is seen to be more stable than the F state over the whole volume range of $V_M < 95.38$ au^3. Finally, for the details of the volume dependence of the magnetic moments in both the AF and the F states, see figure 1 in reference [5].

For the δ- and the ζ-phases we have carried out the same calculations as for the α-phase. The results are essentially the same as those obtained for the α-phase. From comparison of the total energies we have found that the most stable state among the α-, δ- and the ζ-phases changes as $\alpha \rightarrow \delta \rightarrow \zeta$ with decreasing volume (increasing pressure). It should be noted, however, that we cannot discuss quantitatively the relative stability among the three phases or the transition pressures between them, because in the present calculations the ratios of the lattice constants, the monoclinic angle β and the intramolecular atomic distance are not optimized.

In order to explore the possibility of the observed metallization [2–4] being realized in a monatomic phase of solid oxygen, we have performed band calculations for the monatomic phases for the volume corresponding to that of the ζ-phase at 116 GPa ($V_M = 76.67$ au^3). As the crystal structures, we have chosen β-Po-type ones, because it is the monatomic structure that is realized first under high pressures in other group VIb elements. The β-Po-type structure is rhombohedral and can be described as a simple cubic lattice deformed along the [111] direction keeping the edge length unchanged. We have calculated the total energy as a function of c/a and obtained the minimum energy at $c/a = 1.04$, and found that it is higher than the total energies of the α-, δ- and ζ-phases obtained for the same volume. Therefore, judging from all the results of our present calculations it is strongly suggested that a paramagnetic metallic state is realized in molecular solid oxygen under high pressures—higher than about 100 GPa. It is noted here that a theoretical prediction of metallization in molecular solid oxygen under high pressures is also given in reference [10].

It is thought that the present calculations underestimate the energy gap and the magnetic moments, because our calculations have been done within the framework of the usual LSDA. Further LSDA calculations may not predict correct behaviours of the insulator–metal transition and the disappearance of magnetic moments. Therefore we have constructed a model multi-band Hubbard Hamiltonian relevant to molecular solid oxygen and are investigating correlation effects on the magnetism and the insulator–metal transition of solid oxygen. The preliminary results have been reported in reference [11].

Acknowledgments

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