

Electronic structure of β -PbO₂ and its relation with BaPbO₃

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Self-consistent calculations of the electronic structure of β -PbO₂, using the augmented-spherical-wave method and the *ab initio* pseudopotential method, are presented. The band structure consists of a set of nonbonding oxygen 2*p* bands and a very broad band, formed by strong hybridization of Pb 6*s* and O 2*p* orbitals. The calculations indicate that β -PbO₂ is a semimetal, with holes of O 2*p* character and electrons of mixed Pb 6*s*-O 2*p* character. The relation with the electronic structure and the properties of BaPb_{1-x}Bi_xO₃ is discussed.

Lead dioxide occurs in an orthorhombic α , a tetragonal β , and a high-pressure γ modification.^{1,2} A mixture of α - and β -PbO₂ is used as the active material of the positive electrode of the lead-acid battery.³ Although PbO₂ is a technologically important material, little is known about its electronic structure and physical properties. The reason is that it is difficult to obtain pure and stoichiometric phases of PbO₂. The electrical conductivity of PbO₂ is large.⁴⁻⁶ Optical measurements of β -PbO₂ show a large free-carrier absorption, and a strong increase of the absorption at about 1.5 eV.^{4,5,7} These data have been taken as evidence that PbO₂ is a semiconductor with an energy gap of 1.5 eV.

Robertson has reported tight-binding calculations of the electronic structure of PbO₂ and the related compounds GeO₂ and SnO₂.⁸ However, these calculations are semiempirical. In this paper, we present self-consistent *ab initio* calculations of the electronic structure of β -PbO₂, which indicate that β -PbO₂ is a semimetal. The available optical data are consistent with this conclusion.

β -PbO₂ crystallizes in the tetragonal rutile structure, space group $P4_2/mnm$; the lattice parameters at 300 K are $a = 0.49556$ nm and $c = 0.33867$.¹ The lead atoms occupy (2*a*) positions at (000) and (1/2, 1/2, 1/2), the oxygen atoms (4*f*) positions at $\pm(u, u, 0)$ and $\pm(1/2+u, 1/2-u, 1/2)$, with $u = 0.3066$. Each lead atom is surrounded by a distorted octahedron of six oxygen atoms, two at a distance $R_1 = 0.2149$ nm, and four at $R_2 = 0.2169$ nm.

Self-consistent band-structure calculations were per-

formed with the augmented-spherical-wave (ASW) method,⁹ and with the pseudopotential method.^{10,11}

In the ASW calculation, exchange and correlation were treated with the local-density approximation.¹² Scalar relativistic effects (mass velocity and Darwin terms) were included.¹³ Spin-orbit interaction was treated by adding a term λLS and incorporating it within the self-consistent loop. The value of the spin-orbit parameter λ was taken from photoelectron spectra of Pb: $\lambda(5d) = 1.04$ eV, $\lambda(6p) = 1.20$ eV.¹⁴ The basis functions were Pb 5*d*, 6*s*, and 6*p*, and O 2*s* and 2*p*. In the ASW method the crystal is subdivided into Wigner-Seitz spheres, surrounding the atoms. The sphere radii R are chosen in such a way that the overlap is well balanced. Moreover, for open crystal structures like rutile, it is necessary to include empty spheres in the calculation. For the rutile structure we chose eight empty spheres, at positions (4*d*) (0, 1/2, 1/4), and (4*g*) (0.3118, 0.6882, 0), with radius $R = 0.100$ nm. The calculated band structure of β -PbO₂ obtained for Wigner-Seitz radii $R(\text{Pb}) = 0.146$ nm and $R(\text{O}) = 0.112$ nm is shown in Fig. 1.

It was found that the band structure and, in particular, the energy gap of β -PbO₂ calculated with the ASW method, depends strongly on the Wigner-Seitz radii (see Table I). The most reliable result is expected for radii for which the values of the internal pressure (3*PV*, see Ref. 9) is small. This is the case for $R(\text{Pb}) = 0.146$ nm. We remark that in α - and β -PbO the calculated energy gap is nearly independent of the chosen Wigner-Seitz radii.¹⁵

In view of the uncertainty about the Wigner-Seitz radii in the ASW calculations, we have also calculated the

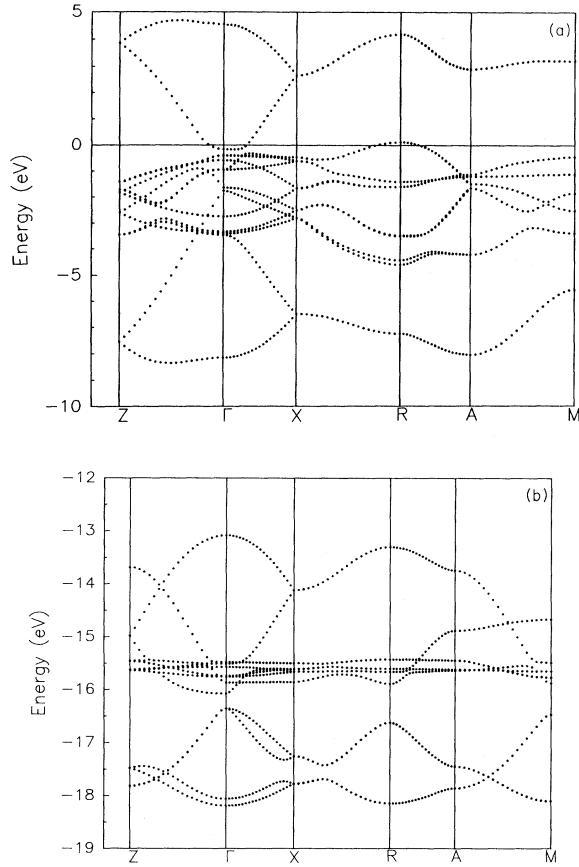


FIG. 1. Energy bands of β -PbO₂ calculated with the ASW method.

band structure of β -PbO₂ with the *ab initio* pseudopotential method, using the local-density approximation for the exchange-correlation function.^{16,17} The atomic potentials were represented by Kleinmann-Bylander-type scalar-relativistic pseudopotentials.^{18,19} The integration in k space was replaced by a summation over six special k points in the irreducible part of the Brillouin zone. The Kohn-Sham states were occupied according to Fermi statistics with $k_B T = 0.025$ eV. The plane-wave basis set already converged with a 64-Ry cutoff. As the electronic structure is closely related with the atomic geometry, it is important to determine the equilibrium positions of the atoms. Therefore, we optimized also the atomic degrees

TABLE I. Dependence of the internal pressure $3PV$ (in Rydberg) and the energy gap E_g (in eV) on the Wigner-Seitz radii R (Pb) and R (O) (in nm) for ASW calculations of the band structure of β -PbO₂.

R (Pb)	R (O)	$3PV$ (Pb)	$3PV$ (O)	E_g (eV)
0.1077	0.1392	8.67	1.17	0.87
0.1149	0.1351	6.06	0.88	0.24
0.1223	0.1329	3.86	0.60	0.01
0.1299	0.1272	2.16	0.47	-0.12
0.1458	0.1118	-0.71	0.55	-0.33

of freedom, using the Car-Parrinello scheme.¹⁰ A code based on the fhi93cp was used, according to Ref. 10. The equilibrium lattice parameter a at 160-Ry cutoff was 2.2% larger than the experimental value, at 64 Ry the difference was 3%. The c/a ratio was 0.68, in good agreement with experimental value. The calculated parameter $u = 0.308$ of the equilibrium configuration is in excellent agreement with the experimental value $u = 0.3066$. The band structure, obtained with the pseudopotential method, is in good agreement with the ASW calculation for $R(\text{Pb}) = 0.146$ nm and $R(\text{O}) = 0.112$ nm (Fig. 2).

The total and partial densities of states (DOS), deduced from the ASW calculations, are shown in Fig. 3. The valence band between energy +0.1 eV and -4.4 eV (energies are with respect to the Fermi energy) consists mainly of nearly nonbonding oxygen 2*p* bands. In addition there is a half-filled set of energy bands, formed by strong hybridization between Pb 6*s* and O 2*p* orbitals. The calculated band structure of β -PbO₂ is that of a semimetal, with holes of oxygen 2*p* character in a valence band with a doubly degenerate maximum at point R in the Brillouin zone, and electrons near Γ in a nondegenerate conduction band of strongly mixed Pb 6*s*-O 2*p* character. The Fermi level is about 0.1 eV below the top of the valence band. The calculated number of electrons and holes in β -PbO₂ is $n = p = 1.8 \times 10^{20}$ cm⁻³, i.e., 0.008 per Pb atom. Using the calculated band structure, it is possible to obtain an estimate of the effective masses of electrons and holes at the Fermi energy. The results are $m_{na}^* = 0.3m_0$, $m_{nc}^* = 0.2m_0$, $m_{pa}^* = 0.7m_0$, and $m_{pc}^* = 1.2m_0$, where n and p refer to electrons and holes,

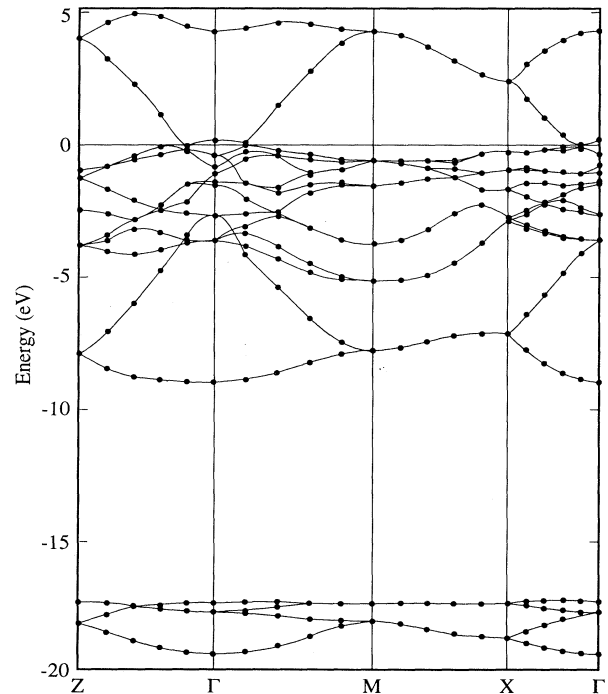


FIG. 2. Energy bands of β -PbO₂ calculated with the pseudopotential method (cutoff 64 Ry).

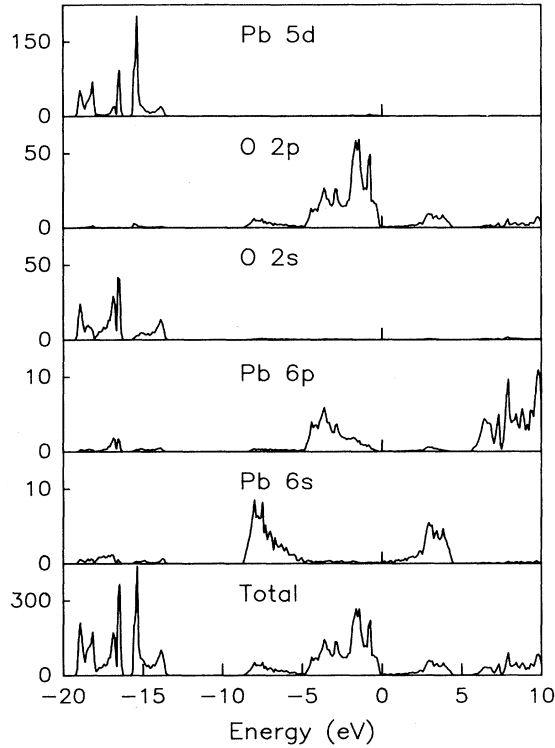


FIG. 3. Total and partial densities of states of β -PbO₂ obtained with ASW calculations.

and a and c to conduction along the crystallographic a and c axes, respectively.

The Pb 6s-O 2p broad bands can be fitted quite well with a simple tight-binding model, with a transfer (hopping) matrix element $t = \langle \text{Pb } 6s | H | \text{O } 2p \rangle = 2.2$ eV (we neglect the small difference between the values t_1 and t_2 for transfer to oxygen atoms at distances R_1 and R_2), and with orbital energies $\epsilon(\text{Pb } 6s) = -1.4$ eV and $\epsilon(\text{O } 2p) = -2.0$ eV. The low value of $\epsilon(\text{Pb } 6s)$ is caused by the relativistic stabilization of the Pb 6s orbitals. The calculated tight-binding Pb 6s-O 2p bands are shown in Fig. 4. The energy of the states at Γ is given by

$$E(1^+) = \epsilon(\text{O } 2p) + \frac{\Delta}{2} \pm \sqrt{2(t_1 - 2t_2 \cos\phi)^2 + (\Delta/2)^2} \dots, \quad (1)$$

$$E(4^+) = \epsilon(\text{O } 2p) + \frac{\Delta}{2} \pm \sqrt{2(t_1 + 2t_2 \cos\phi)^2 + (\Delta/2)^2} \dots, \quad (2)$$

with $\Delta = \epsilon(\text{Pb } 6s) - \epsilon(\text{O } 2p)$, $t_1 = t(R_1)$ and $t_2 = t(R_2)$, and $\cos\phi = (\frac{1}{2}a\sqrt{2} - R_1)/R_2$. The notation for the symmetries of the states (1^+) and (4^+) is according to Miller and Love.²⁰ For β -PbO₂ $\cos\phi = 0.625$. The small splitting of the (1^+) states at Γ , which is the origin of the semimetallic character, is due to the near cancellation of the hybridization of Pb 6s orbitals with the two oxygens at R_1 and the four oxygens at R_2 , and to the small value $\Delta = 0.6$ eV. For SnO₂ and GeO₂ Δ is much larger, result-

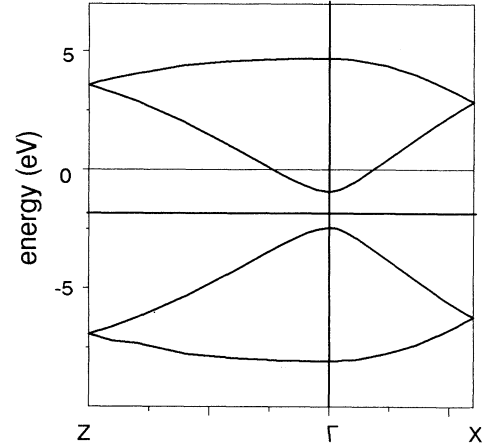


FIG. 4. Electronic structure of β -PbO₂, showing the non-bonding oxygen 2p bands, and the Pb 6s-O 2p broad bands calculated with the tight-binding method, with $t = 2.2$ eV and $\Delta = 0.6$ eV.

ing in a larger splitting of the (1^+) states at Γ , and in semiconductors with a large band gap.⁸

The Pb 5d and O 2s orbitals form bands with sharp peaks in the density of states. The remarkable total width of 5.8 eV of these bands is due to overlap between 2s orbitals of neighboring oxygen atoms and to strong hybridization of Pb 5d orbitals with O 2s orbitals.

β -PbO₂ is a highly conducting material. However, in all reported cases, the electrical properties are measured on samples containing a large number of defects (vacancies, hydrogen), and the data do not provide conclusive evidence about the semiconducting or semimetallic character.

Hall effect measurements of β -PbO₂ show n -type conductivity.⁴⁻⁶ The (apparent) number of charge carriers n^* , deduced from the Hall constant R_H with the relation $n^* = -eR_H$, depends on the equilibrium partial oxygen pressure $p(\text{O}_2)$, and varies from $n^* = 5.7 \times 10^{20} \text{ cm}^{-3}$ [for $p(\text{O}_2) = 10^{21} \text{ atm}$] to $n^* = 10.3 \times 10^{20} \text{ cm}^{-3}$ [for $p(\text{O}_2) = 1 \text{ atm}$].⁶ The change of n^* with $p(\text{O}_2)$ is caused by a change of the concentration of defects in the crystals (oxygen vacancies, hydrogen atoms). If β -PbO₂ is a semimetal, as proposed in this paper, the electrical conduction is by electrons and holes, and the Hall constant is given by the relation

$$R_H = \frac{p\mu_p^2 - n\mu_n^2}{(p\mu_p + n\mu_n)^2}, \quad (3)$$

where n and p are the electron and hole concentrations, with mobilities μ_n and μ_p , respectively.²¹ For an intrinsic semimetal, with $n = p$, the apparent carrier concentration is given by

$$n^* = -eR_H = n \frac{1+b}{1-b}, \quad (4)$$

with $b = \mu_p/\mu_n$. Thus, the apparent carrier concentration n^* , deduced from the Hall effect, is larger than the real charge carrier concentrations in the semimetal. The value $n = p = 1.8 \times 10^{20} \text{ cm}^{-3}$, deduced from the band-

structure calculations, is consistent with Hall-effect data for stoichiometric β -PbO₂ with $n^* = 5.7 \times 10^{20}$ if the ratio of hole and electron mobilities is $b = 0.5$. This is a reasonable value. The mobilities in a highly polar material like β -PbO₂ are determined mainly by polar-mode scattering, in which case the mobility is inversely proportional to the effective mass.²² The effective masses of holes are larger than the effective masses of electrons, so that a value of $b < 1$ is expected indeed.

Optical data^{4,5,7} show a minimum of the absorption of $\alpha \approx 10^4 \text{ cm}^{-1}$ at a photon energy of about 1.5 eV. At lower photon energies the absorption increases, due to free-carrier absorption. The absorption coefficient strongly increases at higher photon energy. These optical data are also consistent with a semimetallic band structure. As a result of the large dispersion of the Pb 6s-O 2p bands, the density of states just above the Fermi energy is small; the DOS begins to increase strongly at about 1.5–2.0 eV. Thus, we expect indeed a strong increase of α at about 1.5 eV, due to strong interband transitions.

We conclude that the experimental data for β -PbO₂ are consistent with the band structure of a semimetal. The

calculations indicate that β -PbO₂ is a semimetal, with charge-carrier holes in an oxygen 2p band, and electrons in a very broad strongly hybridized Pb 6s-O 2p band. However, in view of uncertainties in calculating accurate values for the energy gap, we cannot exclude the possibility that β -PbO₂ is a semiconductor with a small energy gap.

The electronic structures of BaPbO₃ and BaBiO₃ also show very broad Pb,Bi 6s-O 2p bands.^{23–27} According to these band-structure calculations BaPbO₃ is a semimetal. The Pb 6s-O 2p broad band in BaPbO₃ could be described with a tight-binding model with $t = 2.25 \text{ eV}$ and $\Delta = -1.52 \text{ eV}$,²⁵ i.e., with t and Δ values close to the values we used for β -PbO₂. It was pointed out²³ that the very large dispersion of the bands in BaPbO₃ and BaBiO₃ at Γ will lead to a strong electron-phonon interaction, and that this is possibly related to the superconducting character of BaPb_{1-x}Bi_xO₃. In view of the similarities of the electronic structures of β -PbO₂ and BaPbO₃, a further investigation of the properties of β -PbO₂ seems worthwhile.

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