

## Optical Properties of Oxide Compounds PbO, SnO<sub>2</sub> and TiO<sub>2</sub>

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2004 Phys. Scr. 2004 180

(<http://iopscience.iop.org/1402-4896/2004/T109/023>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 200.130.19.138

This content was downloaded on 02/12/2013 at 11:54

Please note that [terms and conditions apply](#).

# Optical Properties of Oxide Compounds PbO, SnO<sub>2</sub> and TiO<sub>2</sub>

A. Ferreira da Silva<sup>1,\*</sup>, I. Pepe<sup>1</sup>, C. Persson<sup>2,†,\*\*</sup>, J. Souza de Almeida<sup>2</sup>, C. Moysés Araújo<sup>2</sup>, R. Ahuja<sup>2</sup>, B. Johansson<sup>2,†</sup>, C. Y. An<sup>3</sup> and J.-H. Guo<sup>4</sup>

<sup>1</sup>Instituto de Física, Universidade Federal da Bahia, Campus Universitário de Ondina, 40210 340 Salvador, Bahia, Brazil

<sup>2</sup>Condensed Matter Theory Group, Department of Physics, Uppsala University, BOX 530, S-751 21, Uppsala, Sweden

<sup>3</sup>Instituto Nacional de Pesquisas Espaciais, INPE/LAS, 12201 970 São José dos Campos, SP, Brazil

<sup>4</sup>Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Received July 14, 2003; accepted November 3, 2004

PACS Ref: 71.15.Mb, 78.20.Ci

## Abstract

The optical properties of the oxide compounds PbO and SnO<sub>2</sub> have been investigated experimentally by transmission spectroscopy measurements and theoretically by a full-potential linearized augmented plane wave (FPLAPW) method. The dielectric functions of the rutile TiO<sub>2</sub> has also been calculated. The calculated band-gap energies as well as the optical absorption were found to be in a very good qualitatively agreement with the experimental results.

## 1. Introduction

The oxide compounds have been recognized as very promising materials with large technological applicabilities. The compounds PbO and SnO<sub>2</sub>, as sample pellets, were prepared by cold pressing in an uniaxial hardened steel die under 400 MPa and characterized by transmission spectroscopy. These materials have tetragonal structures, and their band-gap energies change from about 2.3 to 4.0 eV. In this work, we have investigated the optical properties of these compounds, both experimentally and theoretically. A transmission spectroscopy technique has been used for the measurements of the optical band-gap energies. The absorption, dielectric functions and optical band gap energies calculations of PbO, SnO<sub>2</sub> and rutile TiO<sub>2</sub> were based on the local density approximation (LDA), employing the full-potential linearized augmented plane wave (FPLAPW) method [1]. We correct the LDA band-gap energy self-consistently with an on-site Coulomb potential  $U$ . This method has been shown to improve the electronic structure and optical properties of sp-hybridized semiconductors [2]. We present calculations of the absorption coefficient and the dielectric function, including this on-site Coulomb correction.

## 2. Experimental details

The experimental transmission spectroscopy apparatus consists of a halogen lamp used as the light source for the measurement. The polychromatic beam is diffracted by plane diffraction gratings attached to a step motor. The wave-length of the beam can be varied from 850 to 300 nm corresponding to photon energies from about 1.5 to 4.0 eV;

a set of lens and collimator produces monochromatic light focused onto the sample. A first order bandpass filter has been used to avoid an eventual second order contamination of the monochromatic light, which in the intrinsic resolution, obtained by the calibration process, is 1.2 nm or 0.2%. The angular spread of the beam at the sample location is 17°. Taking into account the whole equipment and analysis process, the absolute optical error associated with the systematic error gives a final total resolution of 2.8% in the energy gap determination. The light passes through the sample and is detected by a photomultiplier tube (PTM) (EMI 9558), polarized by a negative voltage from –1800 to –2200 V. The light gain sensitivity of this device is enough to measure a very low photon quantity (> 100). For a very opaque sample it is possible to increase the measuring sensibility (X500) connecting a very-low noise homemade amplifier to the PMT output, with no compromise of the signal to noise ratio. Pressed disc samples (diameter of 13 mm and weight around 4 g) of PbO and SnO<sub>2</sub> were compacted by a laboratory hydraulic press at room temperature in an uniaxial hardened steel die under 400 MPa. The die set incorporates a vacuum house attachment (around 1.5 Pa), body with detachable base, single plunger and adsorbed gases. The weight of the samples was fixed by the need to produce thin compacts in order to keep the wall friction to a minimum and avoid significant variations in density along the samples.

## 3. Computational methods

The calculation of optical properties of the oxides was based on a FPLAPW [1]. We chose the LDA exchange-correlation potential of Perdew and Wang [3]. Since the absorption coefficient and the dielectric function depend strongly on the valence-band to conduction-band transitions, the underestimated LDA band-gap energies need to be corrected. Recently, it was shown [2] that the LDA +  $U$  model (i.e., LDA plus an on-site, angular-momentum dependent Coulomb potential [2,4]) produces accurate band-gap energies, effective masses, and dielectric function of the sp-hybridized semiconductors Si, Ge, GaAs, and ZnSe. We therefore employ this LDA +  $U$  approach for the oxides using  $U_d$  (cation) = 8.0, 10.0, 10.0 eV and  $U_p$  (anion) = 6.0, 8.0, 0.0 eV for PbO, SnO<sub>2</sub> and TiO<sub>2</sub>, respectively. Although the corrections  $U_p$  and  $U_d$  in principal can be computed, we have here chosen  $U_d$  (cation) = 8.0–10.0 eV (which lowers the cation d-state by

\* e-mail: ferreira@fis.ufba.br

\*\* Present Address: National Renewable Energy Laboratory, Golden, Colorado 80401, USA.

† Also at Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, SE-10044 Stockholm, Sweden.

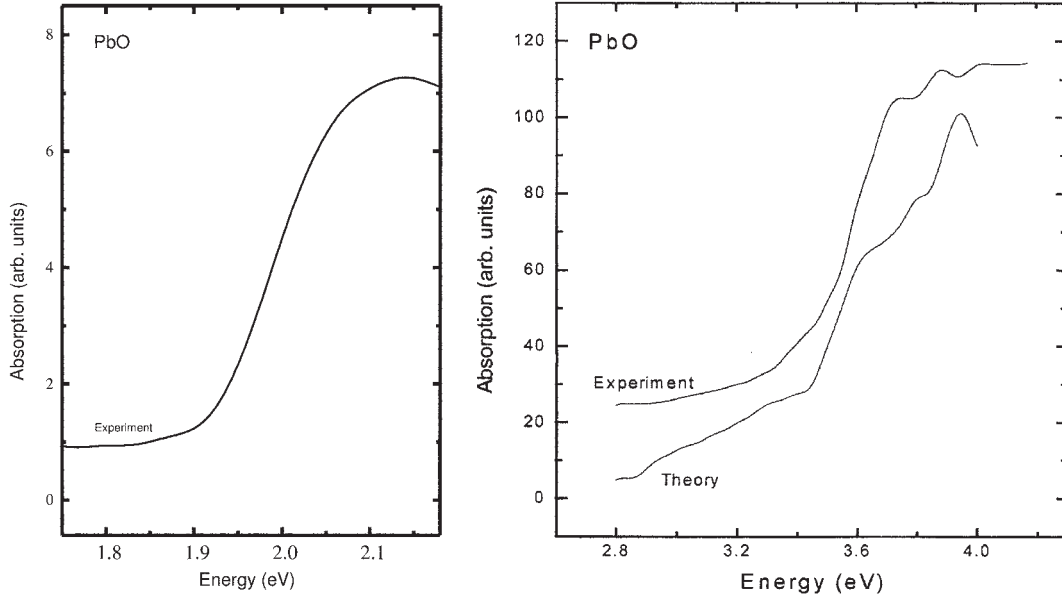


Fig. 1. Absorption spectrum for PbO as a function of photon energy: (a) Experimental result in energy range from 1.75 to 2.2 eV and (b) experimental and theoretical results in energy range from 2.6 to 4.2 eV.

about 2 eV) whereupon  $U_p$  (anion) was chosen in order to give a reasonable correction to the LDA band-gap energy. Small variation of  $U_d$  (cation) (i.e., using  $U_d$  (cation) = 8.0 or 10.0 eV) has only minor effect on the absorption coefficient.

The dielectric function was calculated in the momentum representation, which requires matrix elements of the momentum,  $\mathbf{q}$ , between occupied and unoccupied eigenstates. To be specific the imaginary part of the dielectric function,  $\varepsilon_2(\omega) \equiv \text{Im} \varepsilon(\mathbf{q} = 0, \omega)$  was calculated from [5]

$$\varepsilon_2^{ij}(\omega) = \frac{4\pi^2 e^2}{\Omega m^2 \omega^2} \sum_{\mathbf{k}n\sigma} \langle \mathbf{k}n\sigma | p_i | \mathbf{k}n'\sigma \rangle \langle \mathbf{k}n'\sigma | p_j | \mathbf{k}n\sigma \rangle \times f_{\mathbf{k}n}(1 - f_{\mathbf{k}n'}) \delta(e_{\mathbf{k}n'} - e_{\mathbf{k}n} - \hbar\omega). \quad (1)$$

In Eq. (1),  $e$  is the electron charge,  $m$  its mass,  $\Omega$  is the crystal volume and  $f_{\mathbf{k}n}$  is the Fermi distribution. Moreover,  $|\mathbf{k}n\sigma\rangle$  is the crystal wave function corresponding to the  $n$ th eigenvalue with crystal momentum  $\mathbf{k}$  and spin  $\sigma$ . The summation over the Brillouin zone in Eq. (1) is calculated using the tetrahedron interpolation [6] with a  $k$ -mesh consisting of about 450 uniformly distributed  $k$ -points. The matrix elements, eigenvalues and eigenvectors are calculated in the irreducible part of the Brillouin-zone. The total dielectric function is obtained by averaging the calculated dielectric function as will point out later. Finally, the real part of the dielectric function,  $\varepsilon_1(\omega)$ , is obtained from  $\varepsilon_2(\omega)$  using the Kramers–Kronig transformation written below. More details see Ref. [5].

$$\varepsilon_1(\omega) = 1 + \frac{1}{\pi} \int_0^\infty d\omega' \varepsilon_2(\omega') \left( \frac{1}{\omega' - \omega} + \frac{1}{\omega' + \omega} \right). \quad (2)$$

The absorption coefficient,  $\alpha(\omega)$ , is obtained directly from the relation

$$\alpha(\omega) = \frac{\sqrt{2}\omega}{c} \sqrt{-\varepsilon_1(\omega) + \sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2}} \quad (3)$$

where  $c$  is the velocity of light.

#### 4. Results and Discussions

Figure 1(a) shows the measured absorption spectrum in energy range  $1.75 < E < 2.2$  eV and Fig. 1(b) shows the measured and calculated absorption spectrum in energy range  $2.6 < E < 4.2$  eV for PbO as a function of photon energy. PbO is an oxide with indirect fundamental band gap. The room temperature measurements include direct as well as indirect transition, whereas the calculations consider only direct transition. Therefore, from the experimental absorption spectrum we obtain the indirect band gap of 1.9 eV, and from the calculated absorption spectrum (Fig. 1(b)) we find the direct bandgap energy as 2.9 eV. The calculated indirect band gap ( $E_g(\text{indirect}) = 1.7$  eV) is obtained directly from the density-of-states.

Figure 2 shows the absorption spectrum for SnO<sub>2</sub> as a function of photon energy, together with the theoretical

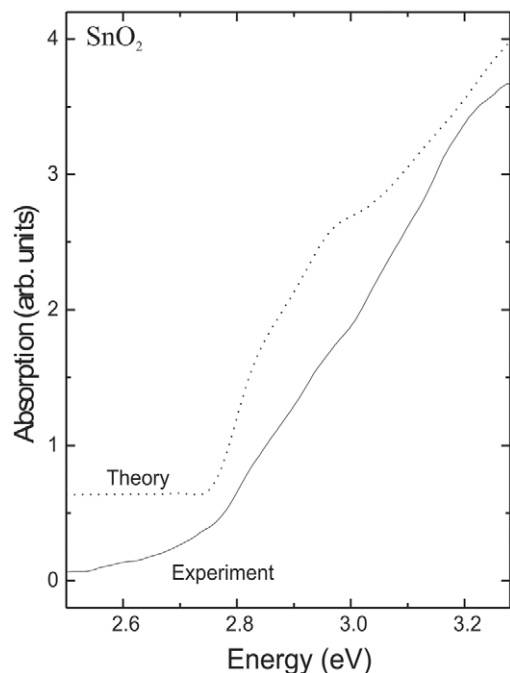


Fig. 2. Absorption spectrum for SnO<sub>2</sub> as a function of photon energy, together with the theoretical results (dotted line).

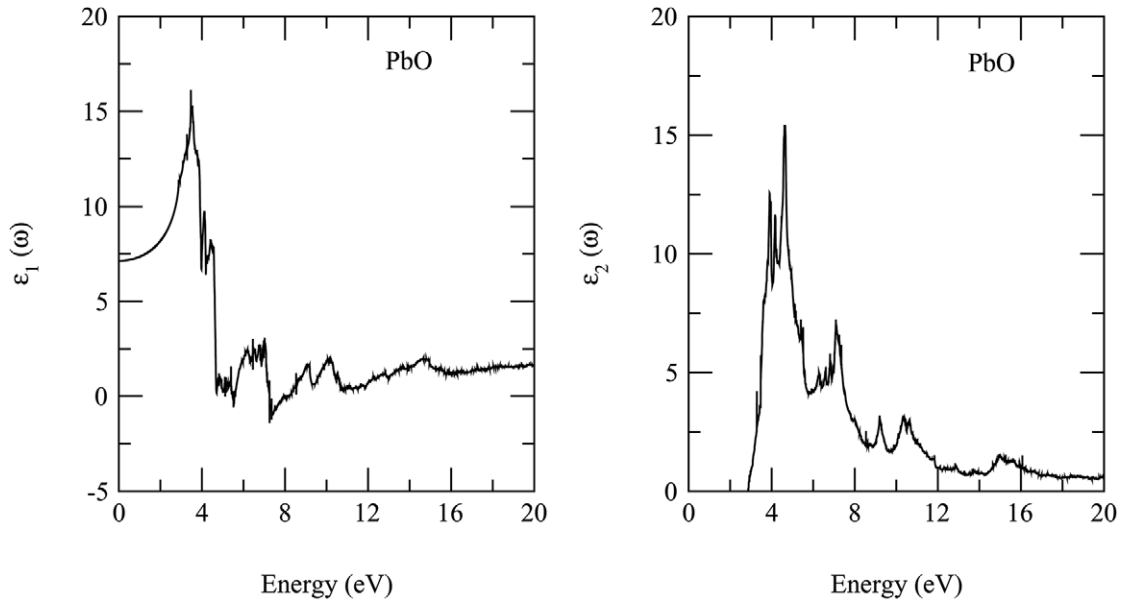


Fig. 3. Calculated dielectric function, for PbO, versus photon energy in the range from 0 to 20 eV (a) real part and (b) imaginary part.

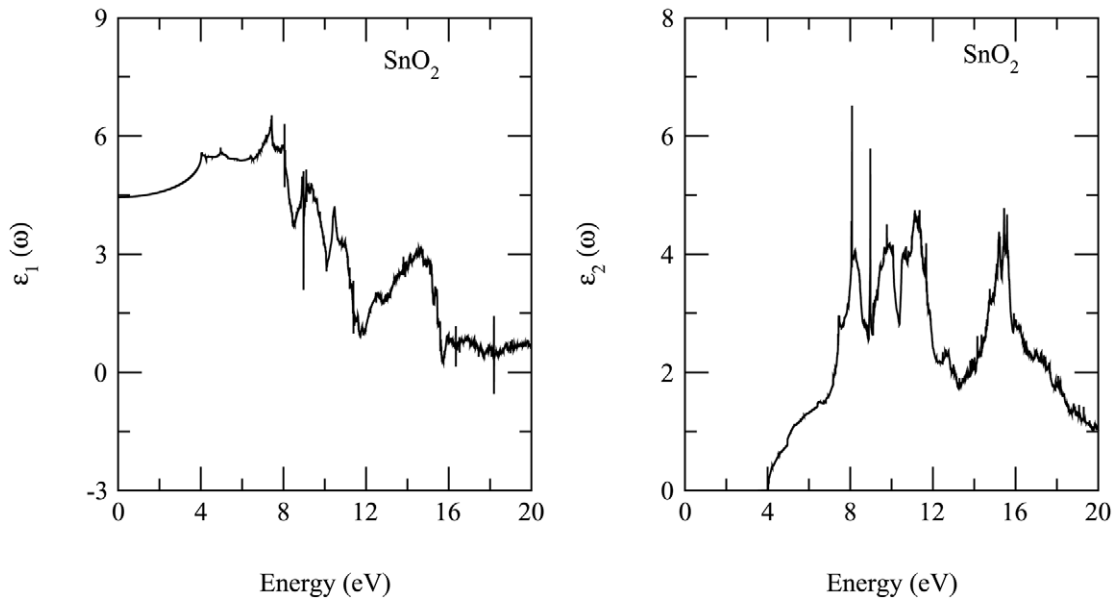


Fig. 4. Calculated dielectric function, for SnO<sub>2</sub>, versus photon energy in the range from 0 to 20 eV (a) real part and (b) imaginary part.

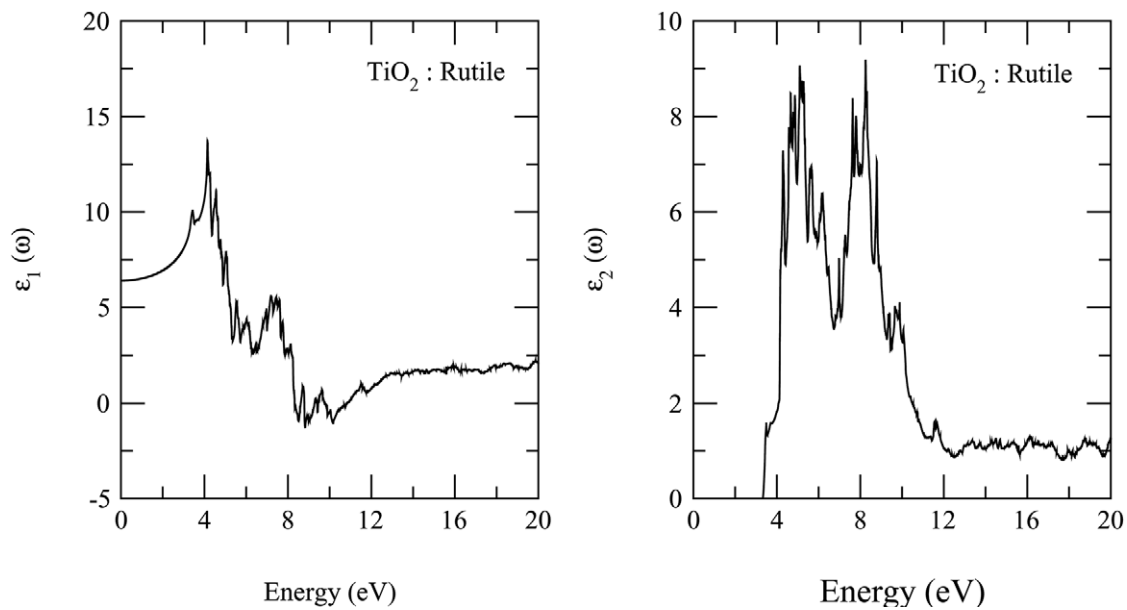


Fig. 5. Calculated dielectric function, for rutile TiO<sub>2</sub>, versus photon energy in the range from 0 to 20 eV (a) real part and (b) imaginary part.

results. Since SnO<sub>2</sub> (and also TiO<sub>2</sub>) is an oxide with direct fundamental band gap, one can directly compare the room temperature measurements and the zero-temperature calculations. The experimental bandgap energy is  $E_g(\text{exp}) = 2.9 \text{ eV}$  and the corresponding theoretical value is  $E_g(\text{theory}) = 3.4 \text{ eV}$ . Normally, the bandgap energy at room temperature is in the order of  $\sim 0.1 \text{ eV}$  lower than the zero-temperature value. Thus, with the on-site Coulomb correction we achieve good agreement between calculated and measure absorption spectra.

Figures 3, 4 and 5 show the calculated total dielectric functions for PbO, SnO<sub>2</sub>, and rutile TiO<sub>2</sub>, respectively, as a function of photon energy. The total dielectric function is obtained from the longitudinal ( $\parallel$ ) and the transverse ( $\perp$ ) components as  $\epsilon(\omega) = (\epsilon_{\parallel}(\omega) + 2\epsilon_{\perp}(\omega))/3$ .

In Figs. 3(b), 4(b) and 5(b) we present the calculated imaginary part of the total dielectric function  $\epsilon_2$ . Our calculated dielectric functions display basically four main peaks for PbO and SnO<sub>2</sub>, and two peaks for TiO<sub>2</sub>. The peaks are positioned around 4, 7, 9 and 10 eV for PbO, 8, 10, 11 and 16 eV for SnO<sub>2</sub> and around 5 and 8 eV for TiO<sub>2</sub>, respectively. For TiO<sub>2</sub> the peak positions are consistent with the results presented in Ref. [7]. The real part of the total dielectric function  $\epsilon_1$ , presented in Figs. 3(a), 4(a) and 5(a), is obtained from the imaginary part by the Kramers–Kronig relation leading to the features consistent with  $\epsilon_2$ . The complete description of the origin of these peaks will be presented elsewhere with the calculated electronic structures. The low-frequency dielectric constant (not including the optical phonon contribution to the screening) is  $\epsilon_{\infty} = 7.2, 4.4$ , and  $6.7$  for PbO, SnO<sub>2</sub> and TiO<sub>2</sub>, respectively.

## 5. Conclusion

We have investigated the electronic and optical properties of the oxide compounds PbO, SnO<sub>2</sub> and rutile TiO<sub>2</sub> using optical absorption and also theoretically using the FPLAPW method with the on-site Coulomb correction. We show that the LDA +  $U$  [2] can produce accurate band-gap energies for these oxides. Our calculated and experi-

mental values of the band-gap energies present a reasonable agreement between them.

The band-gap energies present the following values. For PbO, according to Landolt-Börnstein, at 300 K,  $E_g(\text{indirect}) = 1.9 \text{ eV}$ ,  $E_g(\text{direct}) = 2.7 - 3.2 \text{ eV}$  [8]. Our results are, at 300 K  $E_g(\text{exp/indirect}) = 1.9 \text{ eV}$ , at zero-temperature  $E_g(\text{theory/direct}) = 2.9 \text{ eV}$  and  $E_g(\text{theory/indirect}) = 1.7 \text{ eV}$ . For SnO<sub>2</sub>, according to LB,  $E_g = 3.5 - 4.0 \text{ eV}$ . Our results, at 300 K,  $E_g(\text{exp}) = 2.9 \text{ eV}$  and the zero-temperature  $E_g(\text{theory}) = 3.4 \text{ eV}$ . For the rutile TiO<sub>2</sub>, our calculated value is  $E_g = 3.2 \text{ eV}$  compared to other calculated value  $E_g = 1.8 \text{ eV}$  and  $E_g(\text{exp}) = 3.0 \text{ eV}$  [9].

The calculated dielectric functions are presented for evaluation of future experiments.

## Acknowledgments

This work was financially supported by the Swedish Research Council (VR), EU TMR EXCITING (HPRN-CT-2002-00317), The Swedish Foundation for International Cooperation in Research and Higher Education (STINT) and Brazilian National Research Council (CNPq).

## References

1. Blaha, P., Schwarz, K., Madsen, G. K. H., Kvasnicka, D. and Luitz, J., WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Techn. University Wien, Austria, 2001), ISBN 3-9501031-1-2.
2. Persson, C. and Mirbt, S., (unpublished).
3. Perdew, J. P. and Wang, Y., Phys. Rev. B **45**, 13244 (1992); Ceperley, D. M. and Alder, B. J., Phys. Rev. Lett. **45**, 566 (1980).
4. Anisimov, V. I., Solovyev, I. V., Korotin, M. A., Czyzyk, M. T. and Sawatzky, G. A., Phys. Rev. B **48**, 16929 (1993); Liechtenstein, A. I., Anisimov, V. I. and Zaanen, J., Phys. Rev. B **52**, R5467 (1995); Novák, P., Boucher, F., Gressier, P., Blaha, P. and Schwarz, K., Phys. Rev. B **63**, 235114 (2001).
5. Ahuja, R. *et al.*, J. Appl. Phys. **93**, 3832 (2003).
6. Blöchl, P. E., Jepsen, O. and Andersen, O. K., Phys. Rev. B **49**, 16223 (1994).
7. Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K. and Taga, Y., Science **293**, 269 (2001).
8. Landolt-Börnstein, "Numerical Data and Functional Relationship in Science and Technology," New Series, Vol. III/17a,b, (Edited by O. Madelung *et al.*), (Springer, Berlin, 1982).
9. Mo, S.-D. and Ching, W. Y., Phys. Rev. B **51**, 13023 (1995).