

ELECTRONIC BAND STRUCTURE AND SPECTROSCOPY OF PbWO₄

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ABSTRACT

Within the framework of density functional theory, we have studied the electronic ground-state properties and approximated the optical dielectric constants and reflectivity of PbWO₄. The reflectivity calculated from the single-particle band structure compares with the experimental reflectivity unexpectedly well, including the sharp peak at the absorption threshold. This suggests that the exciton binding energy for PbWO₄ may be small, possibly ~ 0.1 eV, based on data to be discussed.

INTRODUCTION

Lead tungstate (PbWO₄) crystallizes in the scheelite (CaWO₄) structure, is transparent ($E_g \approx 4.2$ eV), and has a broad intrinsic luminescence band at 420 nm. The high atomic numbers, high density, short electron and γ -ray stopping range, radiation hardness, and short lifetime of its intrinsic luminescence at room temperature (~ 10 ns), have resulted in the selection of PbWO₄ as the scintillator for an electromagnetic calorimeter under construction at the Large Hadron Collider. Intensive research and crystal growth development have occurred in the last few years.

ONE-ELECTRON ENERGY SPECTRUM

The electronic band structure of PbWO₄ was calculated for the first time recently along with three other scheelite-structure crystals, CaWO₄, PbMoO₄, and CaMoO₄ (1). The density functional calculations were performed using the Linearized Augmented

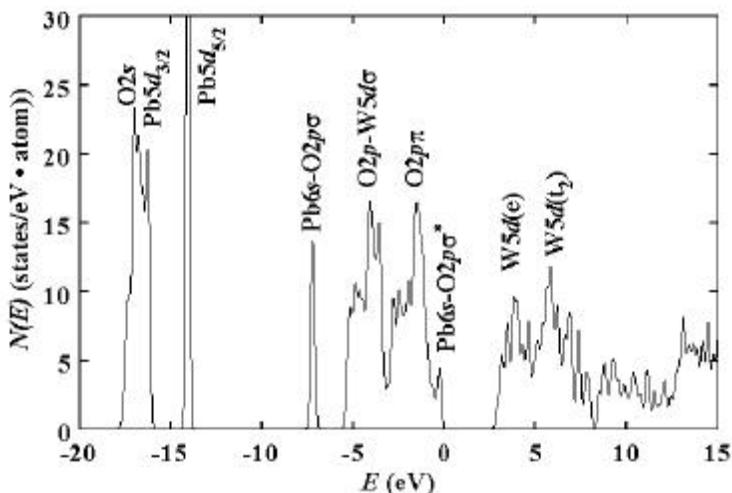


Fig. 1 -- Total density of states for the upper core, valence, and conduction bands of PbWO₄ calculated with a Gaussian smearing function (Ref. (1)). The zero of energy is taken at the top of the last occupied band. The labels indicate the dominant atomic and molecular attributes of each band.

Plane Wave (LAPW) technique using the WIEN97 code (2). The calculational and convergence parameters were detailed in our previous paper(1), although a finer \mathbf{k} -point sampling (35 irreducible \mathbf{k} -points corresponding to 216 points throughout the Brillouin zone) was used to evaluate the optical spectrum (3).

The density of states ($N(E)$) distribution for PbWO_4 from -20 to +15 eV is presented in Fig. 1. The labels appearing above the peaks indicate the dominant atomic and molecular attributes of each band, determined by analyzing the partial densities of states and contour maps of the electron densities for specific energy ranges (1). Much of the structure of $N(E)$ in the vicinity of the band gap is associated with the WO_4 group and is similar to the density of states for CaWO_4 . The main portion of the valence band has two peaks due to a bonding combination of $\text{O}2p\text{-W}5d\delta$ states and a nonbonding group of $\text{O}2p\delta$ states. The lower portion of the conduction band has two peaks due to $\text{W}5d$ states, split into "e" and " t_2 " states by the tetrahedral crystal field of the W-O bonds. In addition, Pb contributes to the band structure by hybridizing with the $\text{O}2p$ states. The bonding hybrid forms a split-off band below the main portion of the valence bands while the antibonding hybrid contributes throughout the valence band and contributes a small peak at the top of the valence band. The basic structure of the calculated $N(E)$ seems to be confirmed experimentally by recent XPS and UPS data from Hofstaetter *et al* (4). In addition, older EPR experiments on Pb-doped CaWO_4 (5) can now be interpreted in terms of an impurity state formed from the antibonding $\text{Pb}6s\text{-O}2p\delta^*$ hybrid. This last point was further studied with calculations for a hypothetical mixed crystal of CaWO_4 and PbWO_4 . The $N(E)$ curve for the $\text{PbCa}(\text{WO}_4)_2$ alloy (3) shows the $\text{Pb}6s\text{-O}2p\delta^*$ states forming an impurity band in what would correspond to the band gap. The hyperfine analysis (5) finds these " Pb^{3+} " hole states in irradiated $\text{CaWO}_4\text{:Pb}$ samples to be comprised of about 50% Pb s character and 50% ligand character, which is consistent with the partial density of states analysis of the impurity band in the alloy calculation.

OPTICAL PROPERTIES

Although density functional theory is rigorously a ground-state formalism, there has recently been considerable progress in developing methods to calculate optical properties

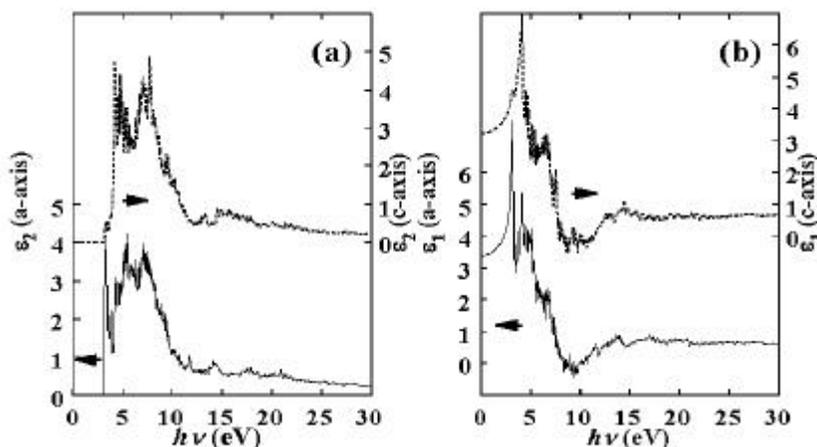


Fig. 2 -- Values of the imaginary (a) and real (b) parts of the dielectric constant of PbWO_4 calculated from the LAPW wavefunctions over a 30 eV range of photon energies $h\nu$ showing results for electric field polarized along an a-axis or along the c-axis as shown.

using density functional results as the starting point (6). As a first step toward investigating the optical properties, we have calculated the imaginary part of the dielectric constant from the self-consistent LAPW wavefunctions $\mathbf{y}_{nk}(\mathbf{r})$ and one-electron eigenvalues E_{nk} , using the code developed by Abt and Ambrosch-Draxl (7). Calculated spectra of ϵ_2 are shown for light polarized along an a-axis and along the c-axis

in Fig. 2(a). The a-axis spectrum is remarkable for the sharp peak leading off the spectrum, which indicates an approximate singularity in the joint density of one-electron states at the band edge. In the c-axis spectrum, this sharp peak is much smaller due to the smaller transition matrix elements. There are of course no excitonic effects included in these calculations.

Taking the Kramers-Kronig transform of ϵ_2 , we obtain the calculated spectrum of ϵ_1 plotted in Fig. 2(b). However, since we have only evaluated ϵ_2 between ~ 4 eV (the band edge) and 30 eV, there is some truncation error involved in ϵ_1 as plotted. The neglected electronic transitions well above 30 eV should contribute a nearly constant positive offset of ϵ_1 at energies below 30 eV. A reasonable choice is $\epsilon_{\text{offset}}=1.64$. This is the difference between a suitable reference dielectric constant, chosen at a photon energy in the visible range measured as $\epsilon_1(1.9 \text{ eV})=5.06$ (8), and the corresponding value from our calculations. The reference dielectric constant was chosen in the visible photon energy range rather than in the low energy photon energy range in order to avoid experimental contributions from phonons which dominate the static dielectric constant but which do not contribute to the ϵ_{offset} correction. The choice of the reference dielectric constant at a photon energy below the band gap also ensured that we could safely assume that $\hat{a}_2(1.9 \text{ eV})=0$. In addition, the one-electron spectrum of density functional theory systematically underestimates the band gap of almost all insulators and semiconductors. (6) The simplest correction to this error is to assume a uniform energy shift of the conduction band relative to the valence band which corresponds to shifting the calculated photon energy $h\nu$ by a constant $h\nu_{\text{shift}}$. The value of $h\nu_{\text{shift}}=1.2$ eV was chosen on an empirical basis in the present work.

Figure 3 compares the measured reflectivity from the recent data of Kamenskikh *et al* (9) with the calculated reflectivity adjusted as discussed above. Unfortunately, the crystal and field orientations for the experimental results in Ref. 9 are not known. For the purposes of the present work, we assume a-axis polarization and normal incidence. Fig. 3 also shows the reflectivity calculated with $\epsilon_{\text{offset}}=0$, which shows that while the general peak structure remains the same, the relative peak heights are somewhat sensitive to the choice of ϵ_{offset} . However, the agreement between the measured and calculated reflectivity

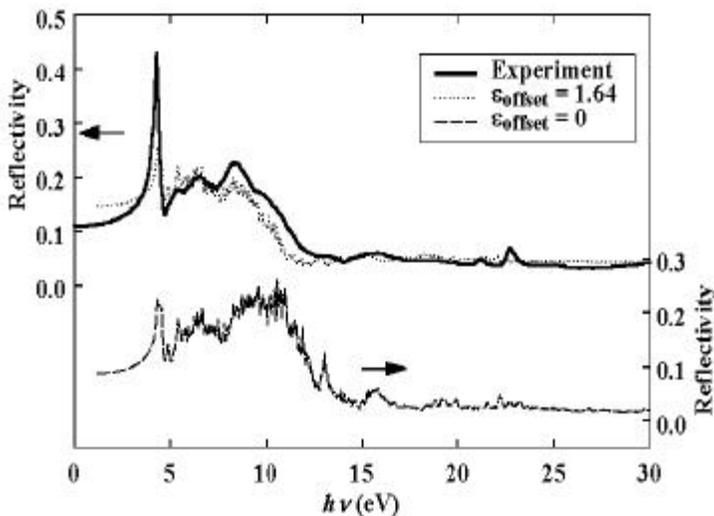


Fig. 3 -- Experimental reflectivity measurements (Ref. 9) compared with the calculated reflectivity spectrum for a-axis polarization for two different choices of ϵ_{offset} . The photon energy scale for the calculated spectra has been shifted by +1.2 eV.

for PbWO_4 is surprisingly good for reasonable values of ϵ_{offset} . For the choice of $\epsilon_{\text{offset}}=1.64$ and $h\nu_{\text{shift}}=1.2$ eV, the sharp initial peak and the three interband peaks at roughly 5.2, 6.5, and 8.5 eV all correspond very well with the experimental curve in both shape

and intensity. Thus, despite many reservations, this comparison may be regarded as empirical evidence that optical transitions calculated within the density functional formalism may be in reasonable correspondence with experiment for this case. This point of view suggests the following speculation about excitons in PbWO₄. Since, as noted above, the sharp peak in the calculated spectrum is due to a near singularity in the joint density of single-particle states, and since no lower-energy discrete features are found in the experimental spectrum, we conclude that whatever exciton discrete states are observable in the absorption spectrum should have a low binding energy compared to the ~0.3 eV width of the experimental reflectivity peak.

The suggestion of a small exciton binding energy in PbWO₄ is supported by additional evidence as follows. In the Wannier model, the exciton binding energy is given by $E_b = E_0 \mu / \epsilon^2$, where E_0 is the hydrogen Rydberg constant, μ is the exciton reduced mass in units of the free electron mass, and ϵ is the appropriate (real) dielectric constant, usually close to the high frequency value. The measured optical and static dielectric constants for PbWO₄ are quite large -- $\epsilon_1(1.9 \text{ eV}) \equiv \epsilon_{\text{opt}} = 5.06$ (8) and $\epsilon_1(0 \text{ eV}) \equiv \epsilon_{\text{static}} = 23.6$ (10), respectively, for a-axis polarization. It is useful to compare exciton binding energies in a sequence of crystals whose dielectric constants bracket the values measured for PbWO₄ and CaWO₄. Approximate data are summarized in Table 1 for a number of semiconductor and insulator crystals, using conduction m^* where μ is not available. The strongest dependence of exciton binding energy is on the square of the dielectric constant, so that even without knowing the reduced effective mass in all cases, trends can be recognized. In particular, we call attention to the comparison of PbWO₄ and TlCl. The heavy metal elements in these two crystals are neighbors in the periodic chart and have the same ionic configuration (Hg-like) in their respective divalent and monovalent salts. The optical dielectric constants are essentially identical at 5.1, and the static dielectric constants are both anomalously large for non-ferroelectrics, with respective values of 23.6 and 37.6. The large optical dielectric constant alone suggests that the exciton binding energy in PbWO₄ may be ≤ 100 meV, interpolating between KBr and CdS.

Crystal	μ or m^*	ϵ_{static}	ϵ_{opt}	E_b (meV)
solid Xe	0.3		2.0	950
KF		6.0	1.8	920
KCl	0.5	4.8	2.2	910
KBr	0.43	4.9	2.3	690
KI	0.4	5.0	2.6	460
TlCl	0.25	37.6	5.1	11
TlBr	0.12	35.1	5.41	6
PbWO ₄		23.6	5.1	
CaWO ₄		11.7	3.7	
CdS	0.18	9-10.2	5.3-5.4	28
ZnSe	0.105	9.2	8.4	19
ZnTe	0.12	10.3	9.6	10
CdTe	0.071		9.6	10
GaAs	0.066	13.1	10.9	4.2

Table 1 -- Selected data for Wannier exciton parameters as defined in the text.

Based on the analysis of TlCl exciton and polaron properties by Bachrach and Brown(11), we may expect that the PbWO₄ exciton also achieves a fairly large radius based simply on ϵ_{opt} , so that the lattice may polarize on the time scale of the exciton orbital period. Then the large ϵ_{static} may contribute significantly to screening of the electron-hole interaction, such as accounts for the very low binding energy of 11 meV in TlCl.

The indication of a binding energy small compared to the peak width suggests that exciton effects in the absorption spectrum of PbWO_4 may be mainly the enhancement of absorption strength of the single-particle interband spectrum according to the Elliot theory (12). A discrete exciton peak of small binding energy could be difficult to resolve spectroscopically in a strongly polar crystal such as PbWO_4 due to strong broadening interactions. However, it is worth noting that a doublet structure in the lowest reflectance peak of PbWO_4 was resolved at 4.2 K in the measurements of Kolobanov et al.(13). The separation of the two peaks is 0.1 eV. In Ref. (1), we noted that this is of the order of the energy difference in the two lowest direct band gaps at Δ and Σ . A second possibility now realized is that the lower of the two peaks could be a discrete exciton resonance associated with the single-particle DOS singularity. The latter would be the upper peak of the measured doublet. In this hypothesis, the exciton binding energy would be experimentally assigned as 0.1 eV. Finally, we note that an analysis of thermal ionization of excitons as measured via thermoluminescence in PbWO_4 also yields an estimate of 0.1 eV for the exciton binding energy(14), though this may characterize relaxed excitons, only suggesting what the binding energy of a free exciton may be.

On the other hand, the suggestion of a small exciton binding energy seems at odds with the comparison of the lowest reflectance peak and the onset of free carrier conduction deduced from thermoluminescence excitation spectra in Ref. (14). Nagirnyi et al (15) have recently presented additional data of a similar kind in CdWO_4 , CaWO_4 , and MgWO_4 . Large differences between the onset of interband optical transitions (seen in reflectivity and intrinsic luminescence excitation) and charge separation (thermoluminescence excitation threshold) are found, e.g. 2 eV in CaWO_4 . A hypothesis was advanced that intrinsic emission of tungstate crystals can be efficiently excited in the region of the direct optical creation of "oxyanion molecular excitons", e.g. 5-7 eV in CaWO_4 . The efficiency of charge separation to traps giving thermoluminescence is low in that energy range assigned as the exciton region, with the implied reason being the neutrality of the exciton. In such a model, at least for CaWO_4 and other tungstate crystals with the large difference of thresholds, deep exciton binding seems to be implied.

We suggest an alternative hypothesis which may reconcile the small exciton binding energy suggested in this paper with the fact of a large difference between the onsets of optical transitions and of free carrier charge separation. The hypothesis is grounded in the independent observations that conduction electrons in PbWO_4 are observed to autolocalize (self-trap) on one tungstate group as $(\text{WO}_4)^{3-}$.(16,17) Furthermore, holes in CaWO_4 have also been shown to autolocalize. (18) Therefore, we suggest that it is not the deep Coulombic binding of a small exciton which prohibits charge transport for band edge excitations, but rather the vanishing or low mobility of the carriers due to autolocalization or to heavy polaron masses, respectively. (In the case of electrons in CaWO_4 , the $(\text{WO}_4)^{3-}$ centers have been observed by EPR only in association with stabilizing impurities. This may indicate that in CaWO_4 , the conduction electrons are heavy polarons rather than autolocalized. The effect on inhibiting charge separation is the same as long as the low mobility keeps the electron and hole together long enough for geminate recombination.) The onset of charge transport in CaWO_4 corresponds closely to the onset of transitions into the second highest (Ca3d) conduction bands, in which autolocalization has not been demonstrated, and which are separated by a gap from the lowest (W5d) conduction bands. The time needed to cross the energy gap into the low-mobility bands would be ample for charge transport over the tens of nm needed to account for onset of thermoluminescence excitation.

ACKNOWLEDGMENTS

We acknowledge support by NSF grants # DMR-9403009, DMR-9706575, and DMR-9732023, and by Czech AS CR grant A1010714.

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