

Structural and Electronic Factors Controlling the Refractive Indices of the Chalcogenides ZnQ and CdQ (Q = O, S, Se, Te)

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On the basis of first-principles electronic band structure theory, we calculated the refractive indices of the zinc blende and wurtzite structures of the chalcogenides ZnQ and CdQ (Q = O, S, Se, Te) and analyzed their trends by calculating the total absorption power per unit formula. The calculated refractive indices are in good agreement with the available experimental data. The total absorption power per formula unit is found to allow one to distinguish the effect of the chromophore from that of the cell volume on the refractive indices of insulating inorganic compounds.

1. Introduction

The refractive index $n(\omega)$ of an insulating material describes its light-scattering property at a given frequency ω of incident light and depends on its chemical composition and structural arrangement.¹ Over the years, simple empirical relations have been developed for a series of closely related compounds to predict and/or rationalize their refractive indices in the visible range. For example, the Moss² relationship shows that the refractive index n increases with decreasing optical band gap E_g , and the Gladstone–Dale³ relationship shows that the refractive index n increases with increasing mass density ρ_m . An accurate description of optical properties requires a quantum mechanical treatment. Both the scattering and absorption properties of an insulating compound are related to the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, which describes the linear response of the electronic structure to the electric field of the incident light of energy $\hbar\omega$.^{4,5} At a given incident light energy $\hbar\omega$, $\epsilon_1(\omega)$

is related to the electronic polarizability of a material, and $\epsilon_2(\omega)$ represents the absorption power of a material per unit volume. The optical properties of a solid as a function of ω can be determined experimentally from electron energy loss spectroscopy (EELS) measurements⁶ and theoretically from electronic band structure calculations⁴ by determining the $\epsilon_2(\omega)$ spectrum.

Recently, we investigated the refractive indices of seven TiO₂ allotropes, TiOF₂, and TiF₄ on the basis of first-principles electronic band structure calculations.^{7,8} These studies showed that the experimentally determined refractive indices n_D (determined by employing the sodium D line, i.e., $\lambda = 589$ nm or $\hbar\omega = 2.1$ eV) of these compounds are explained not by their optical band gaps, but rather by the total absorption power per unit volume $I(\epsilon_2)$, i.e., $n_D \propto I(\epsilon_2)$, where

$$I(\epsilon_2) = \int_0^{+\infty} \epsilon_2(\omega) d\omega \quad (1)$$

The total absorption power per formula unit (FU), i.e., $I(\epsilon_2) \cdot V$, where V is the volume per FU, is found to be nearly constant for the seven TiO₂ phases so that $n_D \propto 1/V \propto \rho_m$.⁷ The latter explains the origin of the Gladstone–Dale relation

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(i.e., $n_D \propto \rho_m$) and implies that as long as the chromophore is the same (i.e., atoms involved in the optical transitions are the same with similar chemical coordination), the refractive index does not depend sensitively on how the electron density is distributed. This observation led us to introduce the concept of “optical channels”,⁸ which are defined as chemical bonds associated with a chromophore. With this local view of light absorption, it is easy to consider two factors affecting optical properties, i.e., the effect of the chromophore and that of the cell volume.

In the present work, we investigate how a chromophore change affects refractive indices by studying the isoelectronic series of chalcogenides ZnQ and CdQ (Q = O, S, Se, Te), for which the refractive indices are believed to depend on the optical band gaps.⁹ Numerous first-principles density functional theory (DFT) calculations have been reported on these phases.¹⁰ However, to our knowledge, there has been no systematic analysis concerning what factors govern their refractive indices and related properties. As the ligand Q changes from O to S to Se to Te in the chalcogenides ZnQ and CdQ (Q = O, S, Se, Te), it is expected that the extent of covalent bonding of the optical channels (i.e., the Zn–Q and Cd–Q bonds) increases gradually, and so does the cell volume V per formula unit (FU). In this work, we probe how these two factors influence the refractive indices of these chalcogenides.

2. Calculations

We carried out full geometry optimizations (atomic positions and cell parameters) of the zinc blende (B) and wurtzite (W) structures of ZnQ and CdQ (Q = O, S, Se, Te) on the basis of DFT calculations using the VASP code¹¹ with projector-augmented wave potentials.¹² The optimized lattice parameters are in good agreement with the available experimental data. Using the optimized structures, we then calculated the optical properties using the WIEN2k code.¹³ In both cases, we employed the Perdew–Burke–Ernzerhof generalized-gradient approximation¹⁴ for the exchange and correlation potential.

The imaginary part $\epsilon_2(\omega)$ of the dielectric function is directly related to the electronic band structure of a solid and can be computed using the one-electron orbitals and energies obtained by solving the Kohn–Sham equations.¹⁵ DFT calculations based on the local density approximation underestimate band gaps. This deficiency is corrected in the more advanced DFT methods such as LDA + DMFT¹⁶ and self-interaction-corrected DFT.¹⁷ In the

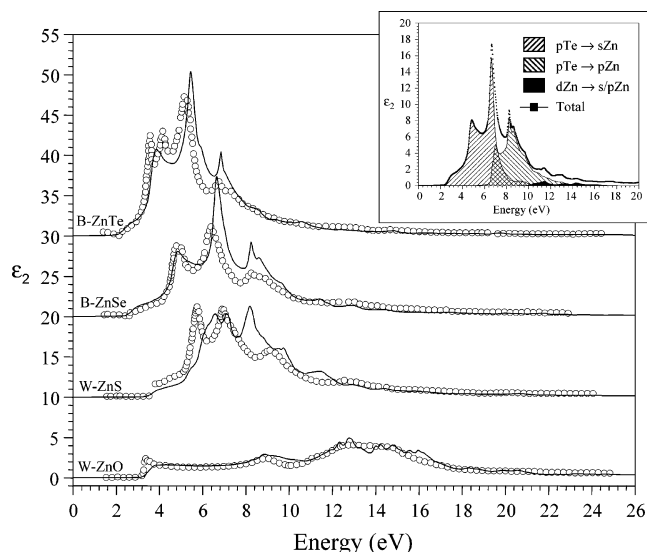


Figure 1. Comparison of the isotropic imaginary part ϵ_2 of the dielectric function for ZnQ (Q = O, S, Se, Te) determined from EELS experiments²⁰ (open circles) and from electronic band structure calculations (solid curves). The inset shows the contributions of several transitions that take place in B-ZnSe.

present work, we correct this deficiency by simply applying a scissors operator, i.e., by shifting the conduction bands rigidly with respect to the top of the valence band until a correct band gap is obtained.^{18,19} Although this approach is too crude to simulate the accurate shape of an optical spectrum, it hardly affects the total absorption power per unit volume, $I(\epsilon_2)$, which has been shown to be the key quantity governing the refractive indices of insulating compounds.^{7,8} Thus, the band gap correction using a scissors operator is sufficient in the present study of the optical properties of ZnQ and CdQ.

3. Results and Discussion

3.1. Energy Dependence of the Absorption Power and Refractive Index. For W-ZnO, W-ZnS, B-ZnSe, and B-ZnTe, Figure 1 compares the experimental $\epsilon_2(\omega)$ spectra obtained from EELS measurements²⁰ with the theoretical $\epsilon_2(\omega)$ spectra determined from our calculations. The agreement is satisfactory, and the main features of the experimental $\epsilon_2(\omega)$ spectra are well reproduced by the calculations. Such an agreement between DFT calculations and EELS measurements was found for B-ZnSe, B-ZnTe, and B-CdTe by Ghahramani et al.²¹ Time-dependent DFT calculations provided similar agreement.²² Numerous GW calculations (in which the self-energy is the product of the single-particle Green function G and the screened interaction W) for these compounds led to a better estimation of the quasiparticle energies^{23–25} and, hence, improved the agreement between theory and experiment.

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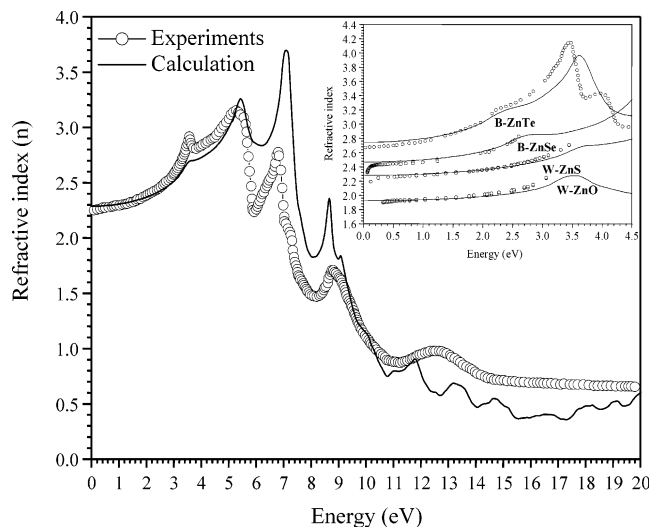


Figure 2. Comparison of the refractive index $n(\omega)$ deduced from EELS experiments²⁶ and DFT calculations for B-ZnS. The inset shows the experimental and calculated $n(\omega)$ for ZnO, ZnS, ZnSe, and ZnTe.²⁸

Table 1. Values of E_g and $n(\omega)$ for ZnQ and CdQ (Q = O, S, Se, and Te)

		E_g (eV) ^a	n			
			0 eV ^b	1 eV ^c	2.1 eV ^c	
ZnO	W	3.4	1.92	1.94 (1.94)	1.99 (2.00)	
	B		1.94	1.95	2.01	
ZnS	W	3.9	2.28	2.30 (2.29)	2.37 (2.38)	
	B	3.7	2.29	2.31 (2.28)	2.38 (2.36)	
ZnSe	W		2.45	2.48	2.60	
	B	2.69	2.47	2.50 (2.46)	2.64 (2.60)	
ZnTe	W		2.71	2.76	3.00	
	B	2.25	2.74	2.80 (2.75)	3.08 (3.09)	
CdS	W	2.5	2.30	2.33 (2.32)	2.50 (2.53)	
	B	2.41	2.31	2.34 (2.33)	2.53 (2.53)	
CdSe	W	1.7	2.49	2.55 (2.52)	2.77 (2.77)	
	B	1.74	2.51	2.57	2.79 (2.85)	
CdTe	W		2.71	2.79	3.01	
	B	1.5	2.73	2.83 (2.77)	3.06 (3.05)	

^a Direct energy gaps determined experimentally at room temperature.²⁸

^b $n^2(0) = \epsilon_1(0)$. ^c Values in parentheses are the experimental results determined at room temperature.²⁸

Figure 2 compares the $n(\omega)$ curve of B-ZnS deduced from EELS experiments²⁶ with that obtained from our DFT calculations. The inset shows the corresponding comparisons for W-ZnO, W-ZnS, B-ZnSe, and B-ZnTe. The energy dependence of the refractive indices is well reproduced by our calculations. In particular, the calculations reproduce the increase in the refractive index in the order ZnO < ZnS < ZnSe < ZnTe. Table 1 lists the available experimental refractive indices of MQ (M = Zn, Cd; Q = O, S, Se, Te) as well as the n values calculated for $\hbar\omega = 0.0, 1.0$ and 2.1 eV. The calculated refractive indices for different $\hbar\omega$ values exhibit similar trends. Thus, as a representative case, we discuss the n values calculated for $\hbar\omega = 1.0$ eV, which lies well within the transparent region for all the ZnQ phases.

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Table 2. Values of V , $I(\epsilon_2)$, and $I(\epsilon_2)V$ for ZnQ and CdQ (Q = O, S, Se, and Te)^a

		V (Å ³) ^a		$I(\epsilon_2)$	$I(\epsilon_2)V$
			(parentheses)		
ZnO	W	24.91	(23.82)	55.19	1374.91
	B	24.79		55.63	1378.94
ZnS	W	40.41	(39.62)	57.29	2315.05
	B	40.43	(39.74)	57.38	2320.05
ZnSe	W	47.33	(45.81)	60.51	2864.25
	B	47.59	(45.67)	60.63	2885.45
ZnTe	W	58.94	(55.26)	65.48	3859.96
	B	59.41	(56.91)	65.67	3901.13
CdS	W	52.15	(49.72)	55.59	2898.84
	B	52.22	(49.55)	55.62	2904.43
CdSe	W	59.53	(56.1)	58.39	3476.10
	B	59.75	(56.11)	58.42	3490.73
CdTe	W	72.30		61.11	4418.79
	B	72.67	(68.11)	61.23	4449.21

^a The volumes reported here correspond to those determined by the present geometry optimization using the VASP code. Value in parentheses are the experimental results taken from X-ray diffraction analyses.

These values increase from 1.94 to 2.30 to 2.50 to 2.80 on going from W-ZnO to W-ZnS to B-ZnSe to B-ZnTe. Similar values are obtained for the zinc blende or wurtzite structure counterparts, because the zinc blende and wurtzite structures of ZnQ have almost identical cell volumes per FU (Table 2). According to the Moss relationship, the increase of n from W-ZnS to B-ZnSe to B-ZnTe can be understood because their optical band gaps decrease from 3.9 to 2.69 to 2.25 eV. However, if we include W-ZnO in the comparison, the Moss relationship fails; W-ZnO has a lower refractive index than does ZnS (1.94 vs 2.30), although it has a smaller optical gap (3.4 vs 3.9 eV).

3.2. Total Absorption Power versus Refractive Index.

The values of $I(\epsilon_2)$ and $I(\epsilon_2)V$ calculated for the zinc blende and wurtzite structures of MQ (M = Zn, Cd; Q = O, S, Se, Te) (Table 2) are plotted as a function of n in Figure 3. Both $I(\epsilon_2)$ and $I(\epsilon_2)V$ increase in the order MO < MS < MSe < MTe and increase with increasing n . This variation of $I(\epsilon_2)$ is expected because the light-scattering properties of an insulator originates from its absorption capability. The $I(\epsilon_2)$ - V value of MQ depends only on the property of its optical channel M-Q bond. The $I(\epsilon_2)V$ values of MQ (M = Zn, Cd) increase almost linearly with increasing n . This trend in the $I(\epsilon_2)V$ values reflects the fact that the extent of covalent bonding of the M-Q bond (i.e., the degree of the overlap between the Q np orbital and the M ns/np orbitals) increases in the order MO < MS < MSe < MTe. In the MQ series, both the cell volume per FU and the extent of covalent bonding of the M-Q bond increase on going from O to S to Se to Te. The cell volume increase should decrease the refractive index. However, the increase in the covalency of the M-Q bond should enhance the refractive index because it increases the probability of electronic excitation from the np -block bands of Q (in which the Q np orbitals have bonding interactions with the M ns/np orbitals) to the ns/np -block bands of M (in which the M ns/np orbitals have antibonding interactions with the Q np orbitals). Figure 3b shows that the relations between $I(\epsilon_2)V$ and n are almost identical for the zinc blende and wurtzite structures, because the zinc blende and wurtzite structures of MQ have nearly the same cell volumes (Table 2).

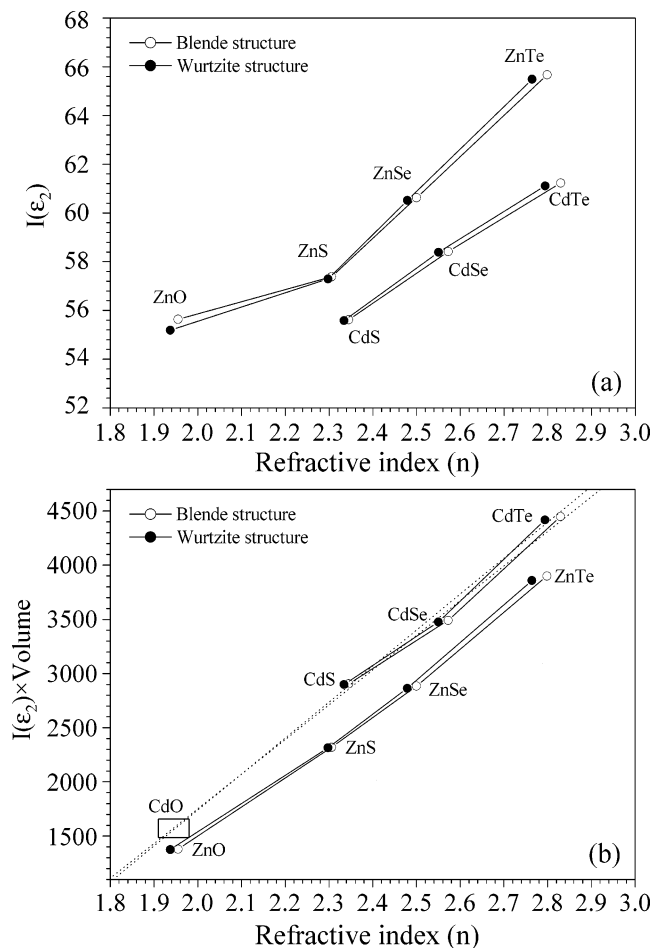


Figure 3. (a) $I(\epsilon_2)$ vs n and (b) $I(\epsilon_2)V$ vs n calculated for the ZnQ and CdQ series (Q = O, S, Se, Te), where the n values were determined at $\hbar\omega = 1$ eV. The values of the refractive index predicted for CdO should lie within the rectangular box.

The $I(\epsilon_2)V$ vs n plots for the ZnQ and CdQ (Q = S, Se, Te) series have nearly the same slope, thereby suggesting that the extent of covalent bonding of the M–Q (M = Zn, Cd) bond varies similarly in the ZnQ and CdQ series. By extrapolating this plot for CdQ (Q = S, Se, Te), the n value of 1.95 (at 1.0 eV) is predicted for the hypothetical zinc blende or wurtzite CdO phase. A zinc blende CdO layer up to the thickness of ~ 2 nm can be grown.²⁷ It would be interesting to measure the refractive index of this zinc blende CdO layer and verify the present prediction.

It is worthwhile to comment on the difference between the ZnQ and CdQ series in their $I(\epsilon_2)V$ vs n plots in Figure 3. The 5s/5p orbitals of Cd are more extended than the 4s/4p orbitals of Zn, so it is expected that the Cd–Q bond has a higher covalent character than does the Zn–Q bond. This

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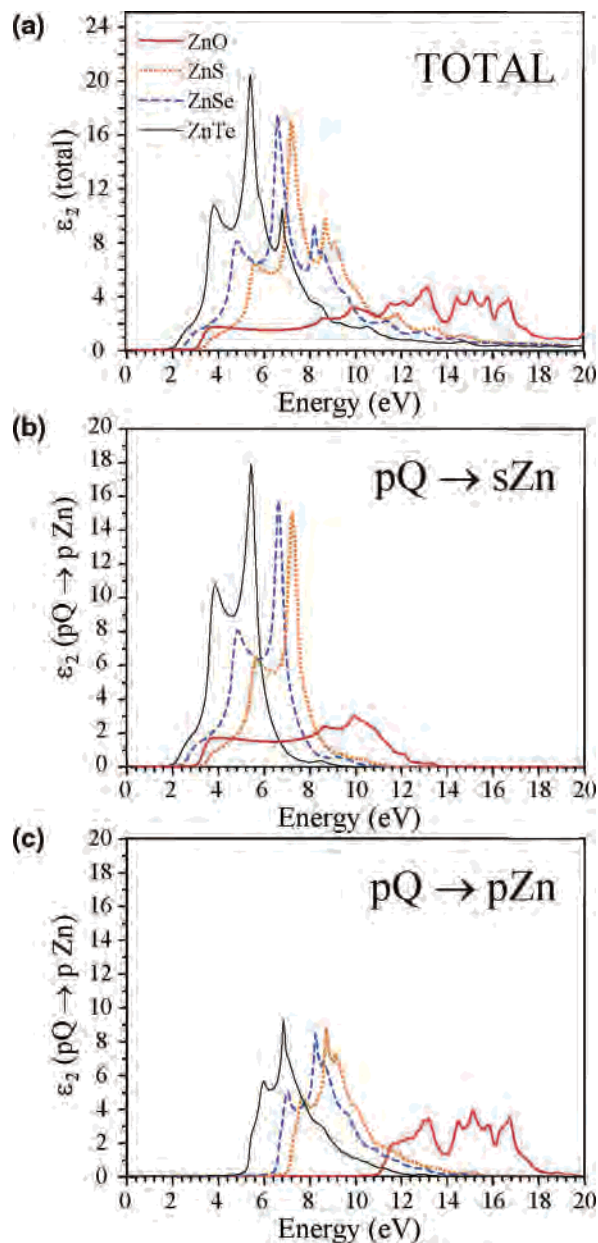


Figure 4. Comparison of the isotropic imaginary part ϵ_2 of the dielectric function for B-ZnO, B-ZnS, B-ZnSe, and B-ZnTe: (a) the total contribution, (b) the contribution of the Q $np \rightarrow$ Zn 4s transition, and (c) that of the Q $np \rightarrow$ Zn 4p transition.

predicts a higher n value for CdQ than for ZnQ. However, the Cd–Q bond is longer than the Zn–Q bond, that is, CdQ has a greater cell volume per FU than does ZnQ (e.g., 40.43 Å³ for ZnS and 52.22 Å³ for CdS), which predicts a lower n value for CdQ than for ZnQ. As a consequence of these opposing effects, the refractive index of CdQ is only slightly higher than that of ZnQ.

3.3. Uniqueness of the Electronic Structure of ZnO. To gain some insight into why ZnO does not follow the Moss relationship, we analyze the shape of the ϵ_2 spectra of the zinc blende ZnQ (Q = O, S, Se, Te) structures deduced from our DFT calculations. This structure type is hypothetical for ZnO, but leads to an optical response similar to that of wurtzite ZnO. Whereas the ϵ_2 spectrum of B-ZnO shows a flat feature in a wide energy region, this is not the case for

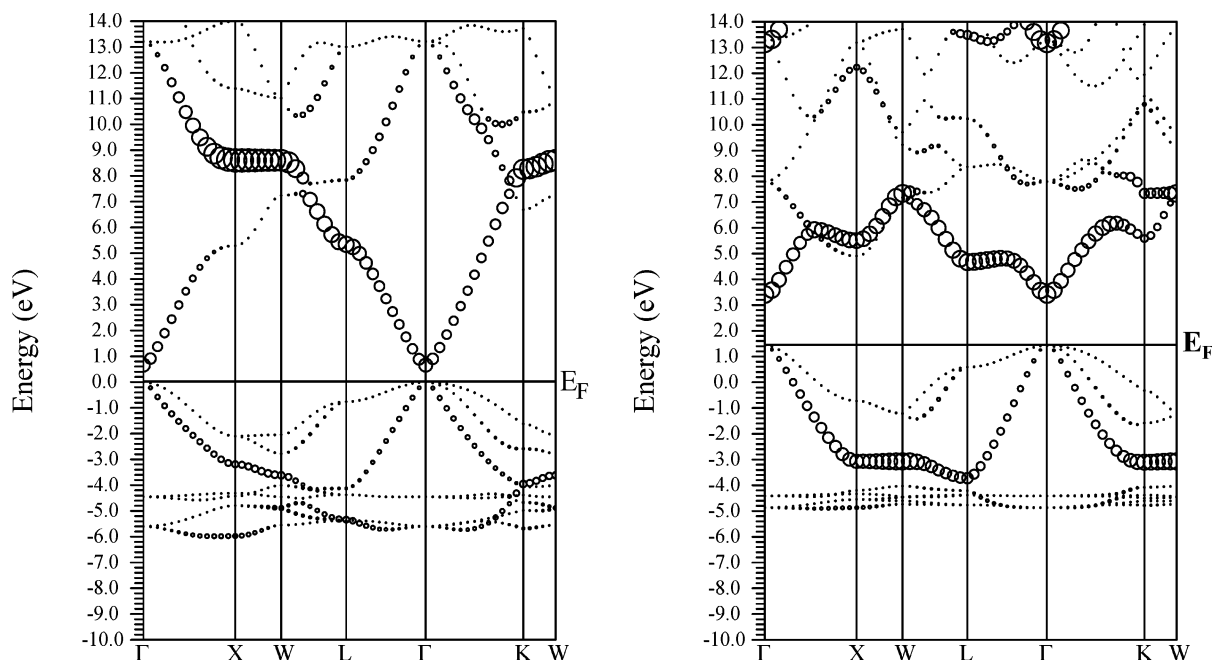


Figure 5. Dispersion relations of the electronic band structures of B-ZnO (left) and B-ZnS (right). The extent of the Zn 4s orbital contribution is represented by the size of the circle (the higher the extent, the larger the circle).

B-ZnS, B-ZnSe and B-ZnTe (Figure 4a). The contributions of the $Q np \rightarrow Zn 4s$ transitions to ϵ_2 are shown in Figure 4b, and those of the $Q np \rightarrow Zn 4p$ transitions to ϵ_2 in Figure 4c. Clearly, these contributions occur in a much wider energy region for ZnO than for ZnS, ZnSe, and ZnTe. As highlighted for the electronic band structures of B-ZnO and B-ZnS in Figure 5, where the contribution of Zn 4s orbitals is emphasized by means of the “fat band” representation, the Zn 4s- and 4p-block bands are much wider in ZnO than in ZnS, ZnSe, and ZnTe. The latter reflects the fact that the Zn–Q bond and thus the cell parameter of ZnQ are much shorter for $Q = O$ than for $Q = S, Se, Te$. As a consequence, the nearest-neighbor Zn–Zn distance is considerably shorter in ZnO than in other ZnQ chalcogenides ($Q = S, Se, Te$) (e.g., Zn–Zn = 3.209 Å for ZnO and 3.830 Å for ZnS). As a result, the Zn 4s-block band, which covers the bottom part of the conduction bands, is considerably wider in ZnO than in other ZnQ species ($Q = S, Se, Te$). This is the primary reason that ZnO has a smaller band gap than does ZnS.

4. Concluding Remarks

The optical scattering properties of an insulating material depend on the nature of its optical channels (i.e., the extent of covalent bonding) and the distribution of the optical channels in space (i.e., the cell volume). For a given compound the total absorption power per FU, i.e., $I(\epsilon_2)V$,

depends on the nature of its chromophore, but not on its cell volume. Thus, this quantity is important in understanding the optical properties of a material. The refractive indices of MQ ($M = Zn, Cd$) increase steadily in the order $MO < MS < MSe < MTe$, even though the cell volumes per FU increase in the same order. This is due to the fact that, on going from O to S to Se to Te, the extent of covalent bonding of the Zn–Q and Cd–Q bonds increases, as does the efficiency of the optical excitation in ZnQ and CdQ. In other words, the efficiency of the optical channels increases in the order $M-O < M-S < M-Se < M-Te$ ($M = Zn, Cd$), and this effect outweighs the opposing volume effect. Calculations of $I(\epsilon_2)V$ do not require an accurate value of optical band gap. Thus, although known to underestimate optical gaps, DFT electronic structure calculations can provide useful information about optical properties of materials in terms of $I(\epsilon_2)V$ values.

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