The linear optical properties for NaCl phase of calcium mono chalcogenides by density functional theory

M. Dadsetani *, H. Doosti

Physics Department, Faculty of Science, University of Lorestan, Lorestan, Lorestan, Iran

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In this study, a complete theoretical analysis of optical properties of calcium mono chalcogenide compounds CaX (X = O, S, Se and Te) in NaCl crystal structure are calculated using the band structure results obtained through the full potential linearized augmented plane wave (FP-LAPW) method within density functional theory. The exchange correlation potential is treated by the generalized gradient approximation within Perdew et al. scheme. The real and imaginary parts of the dielectric function \( \varepsilon(\omega) \), the optical absorption coefficient \( \alpha(\omega) \), the reflectivity \( R(\omega) \) and the energy loss function are calculated by random phase approximation (RPA). The calculated results show a qualitative agreement with the available experimental results in the sense that we can recognize some peaks qualitatively, those due to single particle transitions, while excitonic peaks are completely missing. Furthermore the interband transitions responsible for the structures in the spectra are specified. It is shown that the chalcogen \( p \) states and Ca 3d states play the major role in optical transitions as initial and final states, respectively. The effect of the spin-orbit coupling on the optical properties is also investigated and found to be quite small, especially in the low energy region. The dielectric constants are calculated and compared with the available theoretical and experimental results for CaO, CaS and CaSe while, for CaTe the dielectric constant is not available.

* Corresponding author. Tel./fax: +98 661 2201335.
E-mail address: dadsetani.m@lu.ac.ir (M. Dadsetani).

1. Introduction

The calcium chalcogenides CaX (X = O, S, Se and Te), together with other alkaline earth chalcogenides form a very important closed shell ionic system with NaCl crystal structure at normal conditions. They are technologically important materials, with applications in the area of luminescent devices, an excellent host material for efficient cathode-ray tube phosphors when activated with rare earths, radiation dosimetry, fast high-resolution optically stimulated luminescence imaging and infrared sensitive devices [1–3]. These compounds form closed shell ionic system crystallizing in the NaCl structure at normal conditions. Under higher pressure prior to metallization, they undergo a first order structural phase transition to CsCl structure [4].

The available experimental results on the reflectivity and absorption of CaX compounds are mostly limited to the excitonic transitions [5–9]. In the optical frequency range, Kaneko et al. [10,11] have measured the reflectivity and imaginary part of the dielectric function for CaS and CaO. But for CaTe and CaSe, to our knowledge, there are not yet any experimental results on these quantities in the optical frequency range. Our calculated results could serve as a reference for future experimental work on this compound.

There are a number of theoretical works on these materials concerning electronic band structure, structural phase stability, elastic properties and the metallization process [12–20]. For the band gap results, there are some discrepancies between different calculations. For example the band gap of CaSe, CaS and CaO is predicted to be direct by Pandey et al. [13,15,16] and indirect by others [6].

Considering the optical properties, to our knowledge there are only two reports, one an ab-initio calculation of only \( \varepsilon(0) \) for crystals with NaCl crystal structure including the CaX compounds, using the time dependent density functional approach [21]; the other one, a calculation of the imaginary part of the dielectric function only for CaO and CaS, using LCAO method (within local density approximation) [22]. Moreover, it seems that there is a lack of both experimental as well as theoretical data on the optical properties of calcium mono chalcogenides.

In this work, we have investigated the full range of the optical properties of calcium chalcogenides including real and imaginary parts of the dielectric function, reflectivity, absorption coefficient and energy loss function using the full potential linearized augmented plane wave (FP-LAPW) method with generalized gradient approximation (GGA) for the exchange correlation potential, within the density functional theory.
The density functional formalism as presented so far has been designed in order to describe the ground state properties of systems of interacting electrons. In many cases, however, we are also interested in excited states properties of systems, for instance, if we consider the electronic band structure or optical properties. The Kohn–Sham energies $e_0$ enter the formalism Lagrange multipliers, due to the requirement that the Kohn–Sham orbitals are orthogonal. Therefore, there is no evident physical interpretation of the energies $e_0$. Nevertheless, it is a common practice to interpret the Kohn–Sham energies, for instance in a crystalline material, as electronic band structure of system. While this work remarkably well in many situations, there are also important limitations of this empirical rule. One of these is the well-known fact that the Kohn–Sham band gap of insulators or semiconductors is roughly 50% smaller than the actual band gap.

A brief description of the calculation method is given in Section 2. In Section 3 we have given the detailed band structure of CaX compounds which is needed for optical studies. The optical properties through the study of the imaginary and real parts of the dielectric function and the absorption and reflectivity spectra are discussed in Section 4. A brief summary and the conclusions are given in Section 5.

2. Calculation method

The calculations presented in this work were performed using the FP-LAPW method. In this method no shape approximation on the potential or on the electronic charge density is made. The calculations of the electronic and optical properties have been done relativistically with and without the spin-orbit coupling. We use the WIEN2K [23] implementation of the method which allows the inclusion of local orbitals in the basis, improving upon linearization and making possible a consistent treatment of the semicore and valance states in an energy window, hence ensuring proper orthogonality. The exchange correlation potential within the GGA is calculated using the scheme of Perdew et al. [24]. The convergence parameter $R_{\text{max}}$ which controls the size of the basis sets in these calculations, was set to 10. The $G_{\text{max}}$ parameter was taken to be 14.0 Bohr$^{-1}$. Brillouin-zone (BZ) integrations within the self-consistency cycles were performed via a tetrahedron method [25], using 104 K points in the irreducible BZ. But for the calculation of the optical properties (for the imaginary part of the dielectric tensor) a denser sampling of the BZ was needed, where we used 560 K points. The muffin-tin radius was taken as 2.27 a.u. for O and 2.5 a.u. for other elements. All these values have been chosen in a way to ensure the convergence of the results.

Fig. 1. (a) Total density of states with (dotted line) and without (solid line) spin-orbit coupling for all three compounds. (b) Partial density of states without spin-orbit coupling for CaS. (c) Electronic band structure with (dotted line) and without (solid line) spin-orbit coupling for CaS.
3. Electronic structure results

Our calculated total density of states (DOS) for CaTe, CaSe, CaS and CaO are given in part a of Fig. 1. Due to the close similarity between the results obtained for these CaX compounds, in parts b and c the partial DOS and the electronic band structure are given only for CaS. The results are given both with and without the spin-orbit coupling. The major contributions to the occupied part of the DOS come from the Ca 3p and 3d and the chalcogen s and p states.

The first structure in the low lying energy side of the DOS consists of a narrow peak centered on −21.64 eV for CaTe, −20.93 eV for CaSe, −20.28 eV for CaS and −18.75 eV for CaO. This structure originates from Ca 3p and corresponds to the first three lowest lying (overlapping) bands in Fig. 1. These three bands are lower in energy for CaS, CaSe and CaTe than CaO by around 1.53 eV, 2.18 eV and 2.89 eV, respectively. The structure of the spin-orbit splitting and its amount (nearly 0.5 eV) are considerable in this region. Spin-orbit coupling removes the degeneracy between two of the three bands.

The next structure which in the absence of spin-orbit coupling is separated from the first, by a gap of 10.86 eV for CaTe, 8.76 eV for CaSe, 8.6 eV for CaS and 2.64 eV for CaO, is a peak around 9.72 eV for CaTe, 11.16 eV for CaSe, 10.60 eV for CaS and 14.89 eV for CaO, below the Fermi level, and consists predominantly of chalcogen s states. This peak corresponds to the next lowest lying band shown in the band structures in Fig. 1. This band is lower in energy for CaSe, CaS and CaO than CaTe by around 1.44 eV, 0.88 eV and 5.17 eV, respectively. From the band structures we also see that the width of this peak originates from the dispersion in the region near I' and I point in BZ. Spin-orbit coupling has a minor effect on the structure of this peak, shifting it down in energy by a very small amount.

The broader structure that is situated between −3.0 eV and the Fermi level corresponds to the three valence bands in Fig. 1. From the partial DOS, it is seen that just below the Fermi level the bands are dominated by the chalcogen p states. In the absence of spin-orbit coupling there is a triple degeneracy at I' point and a double degeneracy at X point. Spin-orbit coupling removes the degeneracy at these points. The amount of the spin-orbit splitting is 0.86 eV, 0.40 eV, 0.10 eV and 0.05 eV at I' point and 0.42 eV, 0.23 eV, 0.07 eV and 0.03 eV at X point for CaTe, CaSe, CaS and CaO, respectively. These splitting may be used to interpret separations between doublet excitonic excitations which measured by others [11].

The structure above the Fermi level, extending up to around 10 eV, contains a broad peak at around 4.5 eV for CaTe, 5.5 eV for CaSe, 6.5 eV for CaS and 7.37 eV for CaO, and consists mostly of Ca 3d states together with very small contributions from chalcogen p and d states.

In all four compounds we have found an indirect band gap between the top of chalcogen valence p bands occurring at the I' point and the bottom of the Ca 3d bands occurring at the X point, confirming the previously found results by Charifi et al. [12], and in contradiction to the results obtained by others [13,15,16].

The spin-orbit coupling reduces the band gap; similar results have been found for HgI₂ and SnI₂ [26,27]. This reduction is bigger for CaTe than the other three compounds. Comparing with the experimental and other calculated results show that our results are in fair agreement with the previous studies [13,15,16].

It can be seen that the calculated energy gap values decrease with the increase of the size of the chalcogen atom. Similar behavior was observed in Sr and Ba chalcogenides [28,29].

4. Optical properties

The optical properties of matter can be described by means of the transverse dielectric function $\varepsilon(x)$. There are two contributions to $\varepsilon(x)$, namely, intraband and interband transitions. The contribution from intraband transitions is important only for metals. The interband transitions can further be split into direct and indirect
transitions. Here we neglect the indirect interband transitions which involve scattering of phonons and are expected to give only a small contribution to $\epsilon_2(\omega)$ [30]. To calculate the direct interband contribution to the imaginary part of the dielectric function $\epsilon_2(\omega)$, one must sum up all possible transitions from the occupied to the unoccupied states. Taking the appropriate transition matrix elements into account, the imaginary part of the dielectric function $\epsilon_2(\omega)$ is given by random phase approximation (RPA) neglecting local field effects

$$\epsilon_2(\omega) = \frac{Ve^2}{2\pi \hbar m^* \omega} \int d^3k \sum_{nm} |(kp|kn')|^2 \cdot f(|kn)|$$

where $\hbar$ is the energy of the incident photon, $p$ is the momentum operator $\frac{\hbar}{m^*}$, $|kn|$ is the eigenfunction with eigenvalue $E_k$, and $f(|kn|)$ is the Fermi distribution function. The evaluation of the matrix elements of the momentum operator in Eq. (1) is performed over the muffin-tin and the interstitial regions separately. A full detailed description of the calculation of these matrix elements is given by Ambrosch-Draxl et al. [31].

The real part of the dielectric function $\epsilon_1(\omega)$ follows from the Kramers–Kronig relation [32]. In order to calculate $\epsilon_1(\omega)$, one needs to have a good representation of $\epsilon_2(\omega)$ up to high energies. In the present work, we have calculated $\epsilon_2(\omega)$ up to 65 eV and have used this value as the truncation energy in Kramers Kronig relations. This energy range was chosen so as to produce convergence in the Kramers–Kronig transformation.

Our calculated imaginary parts of the dielectric function for the four compounds in the presence of the spin-orbit coupling, together with the available experimental results (for CaS and CaO by Kaneko et al. [11]) are shown in Fig. 2. The results obtained in the absence of spin-orbit coupling are only given for CaTe and CaSe.

The behavior of $\epsilon_2(\omega)$ is rather similar for all four compounds with some differences in details. The calculated $\epsilon_2(\omega)$ has major peaks, labeled a–e in the figure. We note that all the structures in the imaginary part of dielectric function are shifted toward lower energies as we go from O to Te. This trend may be directly inferred from the band structure results, considering the shift in the location of the first structure above the Fermi level in DOS curves, toward lower energies as we go from O to Te.

It is worthwhile to try to identify the transitions that are responsible for the structures in $\epsilon_2(\omega)$ using our calculated band structures. The locations of the peaks in $\epsilon_2(\omega)$ together with the dominant contributions from interband transitions to each peak are given in Table 1. It is obvious that the chalcogen p states and Ca 3d states play the major role in these optical transitions as initial and final states, respectively. Spin–orbit coupling does not have any significant effect on the result. This is to be expected, since spin-orbit coupling changes the eigenvalues only by around 0.1 eV, which is not significant in the calculation of the optical properties. This has also been found in other FP-LAPW or FP-LMTO calculations for WS$_2$ and HgI$_2$ [26,33].

In order to compensate the GGA underestimation of the band gap, the calculated spectra have been scissors shifted by an amount equal to the difference between the calculated and the experimental band gaps. As can be seen in the figure there is a close match between our calculated results and the experiment in the low energy region. For higher energies considering the overall features of the spectra and the amplitudes, there is a reasonable agreement between the two curves, but the locations of the peaks do not coincide.

The results for the dispersive part of the dielectric function, $\epsilon_1(\omega)$ for the calcium chalcogenides are given in Fig. 3. The main features in these curves are: a peak at around 3 eV; a rather steep decrease between 47 eV and 7 eV, after which $\epsilon_1(\omega)$ becomes negative; a minimum, followed by a slow increase toward zero; another minimum at around 27 eV; and then again a slow increase toward zero at higher energies.

The extinction coefficient $k(\omega)$ and energy loss function $L(\omega)$ have been calculated for all four compounds. The results are quite similar, thus we have given these curves only for CaS in Fig. 4. The local maxima of the extinction coefficient $k(\omega)$, correspond to the zeroes of $\epsilon_1(\omega)$. But the energy loss spectra do not show any distinct maxima at these zeroes of $\epsilon_1(\omega)$ with energies smaller than 14 eV. The reason for this is that $\epsilon_2(\omega)$ is still large at these energy

![Fig. 3. Calculated real part of the dielectric function with and without spin-orbit coupling.](image-url)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Peak positions (eV)</th>
<th>The dominant transition(s)</th>
<th>Direct transition location in B.Z.</th>
</tr>
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<tbody>
<tr>
<td>CaTe</td>
<td>CaSe</td>
<td>CaS</td>
<td>CaO</td>
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<tr>
<td>a</td>
<td>3.95</td>
<td>4.00</td>
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<td>b</td>
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<tr>
<td>d</td>
<td>9.78</td>
<td>11.25</td>
<td>11.66</td>
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values. In the range of 15–18 eV and around 29 eV there are some large peaks in the energy loss spectra. At such high energies $\epsilon_2(\omega)$ is small, and thus the amplitude of the energy loss function becomes large.

In Table 2 our calculated dielectric constants $\epsilon(0)$ are compared with the other calculations and the experimental values. Our calculated results are bigger than the experimental value, and scissors shifting improves the results substantially, but the inclusion of spin-orbit coupling increases the dielectric constant by a small amount. On the whole our scissors shifted results in the presence of spin-orbit coupling have an average deviation of about 1% from the experiment.

The calculated reflectivity spectra for the four compounds, together with the available experimental results (for CaO and CaS by Kaneko et al. [11]) are given in Fig. 5, which shows the close resemblance between these compounds. The results obtained in the absence of spin-orbit coupling are only given for CaTe and CaSe.

Our scissors shifted reflectivity starts at around 14% for CaS and 10% for CaO, irrespective of whether the spin-orbit coupling is included or not; and in comparison to the experimental value, it is in good agreement for CaO but is bigger for CaS. The experimental peaks at around 5 eV for CaS and 6 eV for CaO are not present in our results. Kaneko et al. [11] interpreted that the origin of these peaks are excitonic effects, which justifies their absence in our results. Our reflectivity reaches the maximum value of 50% for CaS and CaO at around 9 eV and 12 eV, respectively. This closely coincides with the experimental peak which has a smaller value for both compounds.

There is a dip in the reflectivity spectra at around 11.5 eV for CaS and 15 eV for CaO, which is coincide to experimental value, after which the reflectivity increases and reaches some maximum

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**Table 2**
The calculated and experimental dielectric constants.

| Compound | Present work | Other works | Exp
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<tr>
<td></td>
<td>Without shift</td>
<td>With shift</td>
<td>Without so</td>
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<tr>
<td>CaTe</td>
<td>7.05</td>
<td>7.13</td>
<td></td>
</tr>
<tr>
<td>CaS</td>
<td>5.38</td>
<td>5.99</td>
<td>3.85</td>
</tr>
<tr>
<td>CaSe</td>
<td>3.66</td>
<td>4.02</td>
<td>3.25</td>
</tr>
</tbody>
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$a$ Ref. [21].
$b$ Ref. [22].
$c$ Ref. [34].
structure.

We have shown that the chalcogen p states and Ca 3d states play a major role in these optical transitions as initial and final states, respectively. Regardless of the excitonic transitions, there is a good agreement between our calculated imaginary part of the dielectric function and the reflectivity by RPA with experiment in the low energy part of the spectra, and even better one for CaS, which has a smaller band gap. Therefore we predict that our results for CaTe and CaSe (with a still smaller band gap) will show better agreement with the future experimental works. Our scissors shifted results of the dielectric constants in the presence of spin-orbit coupling have an average deviation of about 1% from the experiment.

The spin-orbit coupling has a very small (almost negligible) effect on the optical properties in the energy range 0–15 eV. At higher energies it has a more pronounced effect on the details of the peak positions and the average values of the calculated reflectivity and absorption coefficient.

The inclusion of the spin–orbit coupling reduces the band gap by about 0.32 eV for CaTe, 0.15 eV for CaSe and 0.07 eV for CaS and 0.01 eV for CaO.

5. Conclusions

We have studied the full range of the electronic and optical properties of the calcium chalcogenides CaTe, CaSe, CaS and CaO using the FP-LAPW method within density functional theory with and without spin-orbit coupling.

We have shown that the chalcogen p states and Ca 3d states play a major role in these optical transitions as initial and final states. Regardless of the excitonic transitions, there is a good agreement between our calculated imaginary part of the dielectric function and the reflectivity by RPA with experiment in the low energy part of the spectra, and even better one for CaS, which has a smaller band gap. Therefore we predict that our results for CaTe and CaSe (with a still smaller band gap) will show better agreement with the future experimental works. Our scissors shifted results of the dielectric constants in the presence of spin-orbit coupling have an average deviation of about 1% from the experiment.

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References