



## Electronic structure of CaX (X = O, S, Se) compounds using Compton spectroscopy

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### ABSTRACT

The electronic structure of CaO, CaS and CaSe through Compton spectroscopy is reported in this work. Both directional as well as spherically averaged Compton profiles are calculated for all the three compounds employing the CRYSTAL code within the framework of density functional theory (DFT). The anisotropy [100]–[110] for CaO is in agreement with the earlier values. The spherically averaged theoretical values are compared with the first ever measurement made on polycrystalline samples using 59.54 keV gamma-rays from Am<sup>241</sup> source. The calculations are in good agreement with measurements in all cases. Charge transfer in the three compounds has also been estimated following the ionic model. The present study suggests charge transfer from Ca to X (O, S, Se) atom. On the basis of equal-valence-electron-density (EVED) profiles, it is found that CaO is more ionic compared to CaS and CaSe. From the DFT based calculations, we have also determined the cohesive energies, which are compared with other investigations.

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### 1. Introduction

The CaX (X = O, S, Se) compounds form a closed-shell ionic system and crystallize in the NaCl type (B1) structure at ambient conditions [1–3]. A noticeable feature in the electronic band structure of CaX compounds is that there is no *d* electron in the valence band. CaO is present in significant amount in the lower mantle of the earth, therefore despite being a cheap material, it is also of geophysical interest [4]. Alkaline earth chalcogenides namely, CaS and CaSe, are currently under intense investigations driven by their applications in light emitting diodes (LEDs) and laser diodes (LDs). It is expected that these compounds may provide new II–VI candidates for the fabrication of various electrical and optical devices.

In most of the earlier work, both experimental as well as theoretical studies involving electronic, optical and structural properties of CaO, CaS and CaSe are reported. D'Arco et al. [2] employed the periodic Hartree–Fock (HF) method to determine pressure induced phase transition (B1–B2) in CaO and predicted the transition pressure as 68 GPa in good agreement with the available data. The correlation contribution to the cohesive energy and lattice constant of CaO reported by Doll and Dolg [3] using a computational scheme based on the local increments. They observed that lattice constant corrected for correlation effects deviates by less than 1% from experimental values. Bolorizadeh et al. [4] reported the full

energy-momentum resolved electronic structure of the valence band and the Ca 3s and 3p core levels in CaO using electron momentum spectroscopy. They found that experimental results for the dispersion relations in the O valence bands and Ca 3p semi-core level are in good agreement with the LMTO calculations. Medeiros et al. [5] have performed *ab-initio* calculations to determine the structural and optical properties of CaO within the framework of local density approximation (LDA) and generalized gradient approximation (GGA) and compared them with the experimental data. The electronic band structure of CaO has been calculated by Albuquerque and Vasconcelos [6] to obtain its carrier effective masses along  $\Gamma$ –X and  $\Gamma$ – $\Gamma$  lines. Chen et al. [7] have investigated the structural and electronic properties of CaS compound considering all the four B1, B2, B3 (zinc-blende) and B4 (wurtzite) phases, using DACAPO code with the GGA approximation using ultra-soft pseudopotentials [8]. They observed that only B2 phase of CaS has got an indirect band gap, while all the other three phases are direct-band-gap materials. Further, Shaukat et al. [9] also reported the structural, electronic and optical properties of all possible phases of CaS using Wu–Cohen GGA and found that there is an improvement in the structural parameters and band gap values as compared to LDA results. They also found that the *S p* states and Ca *3d* states play major role in optical transitions as initial and final states, respectively. The optical absorption [10] and reflectivity [11] measurements describe CaSe as a direct band gap material ( $E_g = 5$  eV). The HF band-structure calculations of Pandey et al. [12] confirmed the  $\Gamma$  direct band gap character of CaSe and observed that band gap value (11.6 eV) of HF approach lowered to 8.56 eV with correlation corrections. The bulk modulus

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and electronic structure in terms of Mullikan population, band structure and charge density of CaSe have studied by Marinelli et al. [13] using the *ab-initio* periodic linear combination of atomic orbitals (LCAO) method. They observed CaSe as a semi-ionic compound with a slight overlap population between the nearest neighbors. Charifi et al. [14] have used full potential linearized augmented plane wave (FP-LAPW) method to explore the bonding character in terms of the charge density and observed a strong localization of charge around the anion side of CaS, CaSe and CaTe. The effect of covalency, zero-point energy and charge transfer on the phase-transition, elastic and thermo physical properties of Ca-chalcogenides CaS, CaSe and CaTe under pressure have been investigated by Gupta and Singh [15].

It is well established that Compton profile provides a useful test for determination of electron momentum density distribution in solids [16]. Among Compton profile studies, Redinger et al. [17] measured the Compton profiles of CaO along [100] and [110] directions using 60 keV gamma-rays and compared these with APW and LACO methods. Whereas the two calculations reproduced the general features of anisotropy, the agreement was better with APW results. No similar study has been reported to our knowledge, for CaS and CaSe. Thus, we found it worth to study electronic structure in CaX compounds with the Compton profile perspectives. The Compton profile,  $J(p_z)$ , is related to the ground state electron momentum density  $\rho(\mathbf{p})$  as [16]:

$$J(p_z) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \rho(\mathbf{p}) dp_x dp_y, \quad (1)$$

where integration is performed over a constant- $p_z$  plane,  $p_z$  is the electron momentum along the scattering vector direction (z-axis) and  $\rho(\mathbf{p})$  is given as

$$\rho(\mathbf{p}) \propto \sum_i \left| \int \psi_i(\mathbf{r}) \exp(-i\mathbf{p}\cdot\mathbf{r}) d\mathbf{r} \right|^2, \quad (2)$$

where  $\psi_i(\mathbf{r})$  are the electron wave functions and summation extends over all occupied states. Since in the low momentum region  $J(p_z)$  is mainly due to the valence electrons, the Compton profile is a sensitive tool to investigate the behavior of valence electrons. In this paper the results of a Compton scattering study on the CaX compounds are reported. For the theoretical Compton profiles, first-principles DFT-LCAO calculations are performed using CRYSTAL06 code [18]. The ionic model has been applied to estimate the charge transfer in these compounds. The nature of bonding in isostructural and isovalent CaX compounds is also compared using equal-valence-electron-density (EVED) profiles. To check the feasibility of the Compton data in reproducing the cohesive energies of CaO, CaS and CaSe, we have also derived for the first time the cohesive energy of these compounds through the DFT-LCAO values and compared it with other available theoretical results. The paper is organized as follows: Section 2 gives the experimental details. Key steps and salient features of theoretical calculations are presented in Section 3. In Section 4, the results and discussion are drawn and conclusions are given in Section 5. Unless specified, all quantities are in atomic units (a.u.) where  $e = \hbar = m = 1$  and  $c = 137.036$ ,

giving unit momentum =  $1.9929 \times 10^{-24}$  kg m s<sup>-1</sup>, unit energy = 27.212 eV and unit length =  $5.2918 \times 10^{-11}$  m.

## 2. Experimental details

All measurements are performed on polycrystalline samples using the Am<sup>241</sup> Compton spectrometer. The geometry and details of the spectrometer used in the measurements have been described in Ref. [19]. The salient features of the spectrometer are following: A 5 Ci Am<sup>241</sup> radioisotope emits gamma-rays of 59.54 keV which are scattered by the sample through a mean angle of 166° ( $\pm 3.0^\circ$ ). The samples having purity better than 99.99% were procured from Alfa Aesar, Johnson Matthey Co., USA. The sample holder was a brass sheet with a circular opening of 18 mm diameter, masked with lead. To perform measurements, powder sample was placed behind the sample holder to ensure that the irradiated area of the samples as seen by the detector at the sample position remained same for all materials. The scattered radiation was analyzed by a using an HPGe detector (Canberra model, GL0110S) and associated electronics like spectroscopy amplifier (Canberra, 2010 model), an analog to digital converter (Canberra, 8075 model) and a multi channel analyzer (Canberra, S-100 model). The channel width of the multi channel analyzer was about 20 eV, which corresponds to 0.03 a.u. on electron momentum scale. The spectrometer had an overall momentum resolution of 0.6 a.u. (Gaussian FWHM). The stability of the system was checked twice a day by weak Am<sup>241</sup> calibration source. In processing the raw experimental data, corrections for background, the detector response function, sample absorption, cross section correction and multiple scattering were made in the sample using computer code of the Warwick group [20,21]. To consider the effects of multiple scattering we considered approximately  $10^7$  photons in the Monte-Carlo method for each sample [22]. For final analysis, the experimental Compton profiles of CaO, CaS and CaSe were normalized to the area of 12.994, 16.516, 23.286 electrons respectively. These are the area of free atom Compton profiles taken from the Tables of Biggs et al. [23] within 0 to +7 a.u. range. The 1s electrons of Se were neglected for CaSe since these do not contribute in the present experimental set up. A summary of measurements is given in Table 1.

## 3. Theoretical details

### 3.1. The DFT-LCAO theory

The theoretical calculations are performed using the CRYSTAL code [18]. The code is based on all electron first-principles self-consistent field (SCF) periodic HF-LCAO procedure. In the LCAO technique, each crystalline orbital  $\psi_i(\mathbf{r}, \mathbf{k})$  is a linear combination of Bloch functions  $\varphi_{\mu}(\mathbf{r}, \mathbf{k})$  defined in terms of local functions  $\varphi_{\mu}(\mathbf{r})$ , normally referred as atomic orbitals. The local functions are expressed as linear combination of certain number of individually normalized Gaussian type functions. For Ca, O, S, and Se, the local functions were constructed from the Gaussian type functions [24]. The Kohn-Sham Hamiltonian was constructed by considering the exchange scheme of Becke [25] and the

**Table 1**  
Some details concerning the samples and measurements.

Sample	Sample thickness (mm)	Density (gm/cm <sup>3</sup> ) <sup>a</sup>	Counts at Compton peak ( $\times 10^4$ )	Multiple scattering (-10 to +10 a.u.)%	Exposure time(h)	Normalization (0 to +7 a.u.) e <sup>-</sup>
CaO	0.32	0.9259	4.85	5.6	14.32	12.994
CaS	0.32	0.6355	4.25	4.4	16.95	16.516
CaSe	0.32	1.2141	3.64	12.1	18.36	23.286

<sup>a</sup> Effective density of the sample.

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