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Compton Profiles of CdS, CdSe and CdTe: Theory and Experiment

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In this paper, we report the Compton profiles of zinc-blende CdS, CdSe and CdTe which are measured using 59.54 keV γ-rays from ^{241}Am source. The isotropic experimental Compton profiles are compared with the present hybridised density functional and Hartree-Fock (DF-HF); and pseudopotential calculations using CRYSTAL03 code. To compare the relative bonding in these compounds the equal-valence-electron-density (EVED) profile are also derived. It is seen that the experimental profiles are in better agreement with DF-HF calculations while the ionicity decreases in the order CdSe, CdS and CdTe.

Key Words: Compton scattering, Electronic structure, Band structure calculations, II-VI semiconductors.

INTRODUCTION

The Compton profile, $J(p_z)$, is the one-dimensional projection of the momentum density $\rho(p)$ on the scattering vector (z-axis of the coordinate system). For isotropic distribution, such as polycrystalline samples, the $J(p_z)$ is defined as

$$J(p_z) = 2\pi \int_{p_z}^{\infty} p \langle \rho(p) \rangle \, dp \qquad (1)$$

Due to the normalization of the ground-state electron wave function, the integral over the Compton profile is normalized to the number of electrons in the scattering unit. The Compton profile is a well-established probe to determine the electronic structure of materials[1].

Due to technological importance of II-VI semiconductors[2], there is a great motivation for undertaking Compton profile study of compounds like CdX. In order to gain insight into the electronic structure and the relative nature of bonding of CdX (X = S, Se and Te), the present paper reports the theoretical and the experimental Compton study of these compounds. To undertake Compton measurements, the lowest intensity 100 mCi ^{241}Am Compton spectrometer with momentum resolution of 0.55 atomic units (a.u.) has been used. Theoretical calculations within the hybridized density functional and Hartree-Fock (DF-HF); and pseudopotential (PP) are undertaken using CRYSTAL03 code. It may be noted that in atomic units (a.u.) $m = h/2\pi = 1$, $c = 137.036$ and 1 a.u. of momentum is $1.99289 \cdot 10^{-24}$ kg m s^{-1}.

EXPERIMENTAL

For the present measurements, the planar ^{241}Am Compton spectrometer which employs a 100 mCi disc source is used. Since details of the spectrometer are given elsewhere[3], only salient features of the experiment are given here. For all the compounds, the material was a high purity (99.9 %) powder. It was kept in a circular ampoule with mylar windows on both the front and the back sides. The thickness of the powder samples was 4 mm. The sample cell was held vertical in a sample holder. The incident γ-rays of 59.54 keV energy scattered by the sample through a mean angle of 165° ± 1.5° were detected by a high purity Ge detector (Canberra GL0510P). An integrated Compton intensity of about 16.6, 26.2 and 22.5 million photons were obtained during the measuring time of about 96, 120 and 145 h for CdS, CdSe and CdTe, respectively. During the measurement, the stability of the system was checked several times using a weak ^{241}Am calibration source. First of all, the raw data was corrected for background correction. Thereafter, the profile was corrected for instrumental resolution (stripping off the low energy tail), energy dependent corrections like photon absorption in the sample and Compton scattering cross-section following the approach of Warwick group[1,4]. The data was than converted into momentum scale and normalised to free atom profile area. To remove the effect of multiple scattering events, the Monte-Carlo program of same group[5] was used.

Band structure calculations

For the computation of theoretical Hartree-Fock Compton profiles of these compounds, we have used the CRYSTAL03[6-8] code, which is based on *ab initio* linear combination of atomic orbitals (LCAO). In the LCAO technique, the Bloch functions of crystalline orbitals (CO's) are built from local atom centred Gaussian functions. These are the solutions of the one-electron equations. Here the $\rho(\mathbf{p})$ is derived from the sum of the squared moduli of the occupied CO's as:

$$\rho(\mathbf{p}) = \frac{1}{V_{BZ}} \sum_{m} \int_{BZ} dk \, | \phi_m(\mathbf{k}, \mathbf{p}) |^2 \, \theta(\varepsilon_F - \varepsilon_m(\mathbf{k})) \qquad (2)$$

where ε_F is the Fermi energy, ε_m is the one electron energy corresponding to $\phi_m(\mathbf{k},\mathbf{p})$ and θ is the step function. In DF-HF approach, the exchange of Becke and Lee-Yang-Parr correlations with 20% mixing of Hartree-Fock exchange has been used, while for pseudopotential the effective core pseudopotential and corresponding valence basis sets is taken.

RESULTS AND DISCUSSION

The difference profiles (convoluted theory–experiment) for zinc-blende CdS, CdSe and CdTe are plotted in Figs. 1 (a-c). Fig. 1 shows that the curves for all three samples follow similar trend. On the basis of χ^2 fitting, it is seen that the density functional with Hartree-Fock gives better agreement with experiment for all the cadmium chalcogenides.

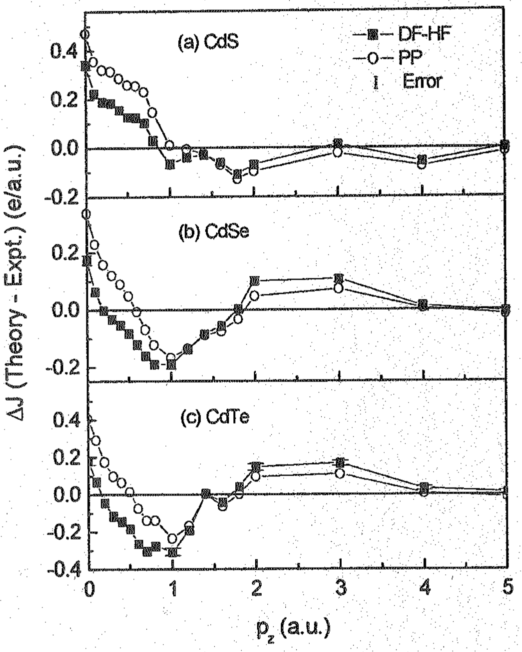

Fig. 1. Difference profiles between the isotropic experimental and the convoluted theoretical profiles corresponding to (a) CdS (b) CdSe and (c) CdTe.

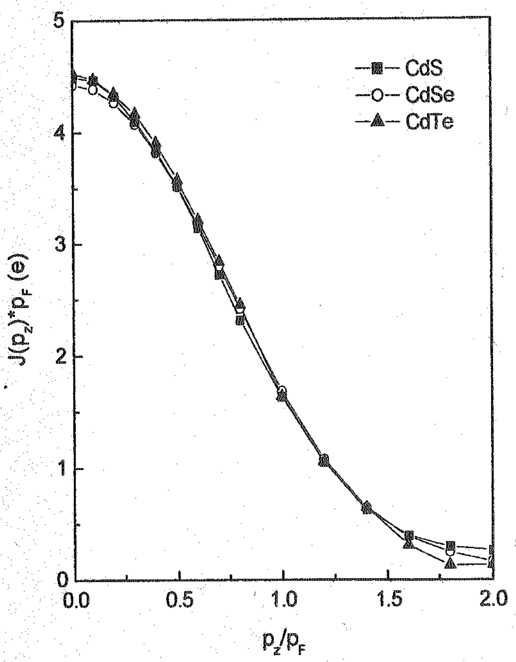

Fig. 2. Equal-valence-electron-density (EVED) experimental profiles of CdS, CdSe and CdTe. The experimental error is within the size of symbols used.

Now, the relative bonding character of both the isovalent semiconductors CdS, CdSe and CdTe is compared. For this purpose, the scaled experimental valence profiles known as equal-valence-electron-density (EVED) Compton profiles has been deduced. This methodology is very useful in predicting the nature of bonding in isovalent compounds[9,10]. Fig. 2 depicts the EVED experimental profiles of three compounds. The Fermi momentum for CdS, CdSe and CdTe were taken to be 0.893, 0.859 and 0.802 a.u., respectively. All the EVED profiles were normalized to four electrons. It is seen from Fig. 2 that near $p_z = 0$ a.u., the sharpness of Compton profiles decreases in the order CdTe, CdS and CdSe; which suggests more localization of charge in CdTe in the bonding direction. It is worth mentioning here that the covalent bonding is a result of sharing of electrons and hence it increases localization of charge in the direction of bonding which results in a sharper Compton line shape. Therefore, we conclude that the ionicity decreases in order to CdSe, CdS and CdTe, which is in agreement with the results of Christensen *et al.*[11] in which they have computed the ionicities of various semiconductor compounds.

Conclusion

In this work, it is found that the density functional theory with HF Hamiltonian gives good ground state properties in CdS, CdSe and CdTe. The equal valence electron density profiles of all the three compounds confirm that covalent character of these compounds increases in the order CdSe, CdS and CdTe.

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