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Electronic structure of some mercury chalcogenides using Compton spectroscopy

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Abstract

We report the first ever isotropic Compton profiles of mercury chalcogenides using our 740 GBq ^{137}Cs Compton spectrometer. To analyze our measurements, theoretical Compton profiles, energy bands, density of states and Mulliken's populations are computed using pseudopotentials within the Hartree–Fock and density functional theories. A comparison of Compton data on equal-valence-electron-density scale shows the decrease of ionicity from HgS to HgTe. It is seen that these semiconductors have narrow band gap and exhibit inverted-type band structure.

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1. Introduction

With the introduction of γ-rays of high energy, the Compton scattering technique is revived as a practical tool for the study of electron states in heavy materials and band-structure models of the ground-state electron momentum density (see for example, Williams, 1977; Cooper, 1985; Cooper et al., 2004). When radiation is Compton-scattered, the emerging beam is Doppler-broadened because of the motion of the target electrons. The broadened line shape, so-called Compton profile $J(p_z)$, is the one-dimensional projection of electron momentum density along the scattering vector direction. It is related to the measured differential scattering cross-section as

$$J(p_z) = \iint \rho(\vec{p})\, \mathrm{d}p_x\, \mathrm{d}p_y \propto \frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\, \mathrm{d}\omega_2}, \tag{1}$$

where $\rho(\vec{p})$ is the electron momentum density of the electrons in the sample and is related to the real-space wave functions. ω_2 is the energy of scattered photon and p_z is the component of the electron momentum along the scattering vector direction (usually chosen as z-axis). A study of anisotropies of $\rho(\vec{p})$ eliminates many systematic errors like multiple scattering, bremsstrahlung background contribution, etc.

It is known that the band gap is an important parameter that affects the electrical, optical and magnetic properties of a semiconductor. Few systems like α-Sn and zinc blende (ZB) Hg-VI are neither real metals, nor semiconductors, nor insulators. An exclusive group with these properties is known as semimetal or zero-gap semiconductors group (Delin and Kluner, 2002). Due to peculiar properties of mercury chalcogenides, many theoretical and experimental investigations have been undertaken which mainly include electronic-structure calculations (Rohlfing and Louie, 1998; Orlowski et al., 2000; Delin and Kluner, 2002; Delin, 2002; Fleszar and Hanke, 2005; Moon and Wei, 2006), photoemission spectroscopy (Gawlik et al., 1997), magneto-optical Fourier transform spectroscopy (von Truchseß et al., 2000), some optical properties (Markowski and Podgorny, 1992), etc.

The electronic structure of ZB mercury chalcogenides differs in a fundamental way from the electronic structure

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of the corresponding isoelectronic Zn and Cd systems (see for example, Wei and Zunger, 1988; Heda et al., 2007; Ahuja and Heda, 2007). Wei and Zunger (1988) have noted that the difference among Hg, Zn and Cd chalcogenides is due to the cation d band. The incomplete screening of the core by the d electrons is thought to be the origin of the very different properties of the IIB–VI compounds relative to IIA–VI compounds.

In this paper, we report the first ever Compton profiles of HgX (where X = S, Se and Te). The decision to measure the isotropic Compton profile was due to (a) non-availability of large-size (diameter 13 mm, thickness 3 mm) single crystals of the chalcogenides and (b) study of the relative nature of bonding of chalcogenides using equal-valence-electron-density (EVED) profiles. To compare our experimental data, we have computed the Compton profiles using Hartree–Fock (HF) and density functional theory (DFT) embodied in *ab initio* CRYSTAL03 code of Torino group (Towler et al., 1996; Saunders et al., 2003). In addition, we have also reported energy bands, density of states (DOS) and band gaps of these chalcogenides.

2. Experiment

We have used our 740 GBq (20 Ci) ^{137}Cs Compton spectrometer details of which have been reported earlier (Ahuja and Sharma, 2005; Ahuja et al., 2006). Table 1 lists the experimental parameters for present Compton profile measurements of HgX (X = S, Se and Te). Incident γ-rays having energy 661.65 keV were scattered by the sample through an angle of $160 \pm 0.6^\circ$. The scattered radiations were energy analyzed by a high-purity germanium detector (Canberra, Model GL0210P) and associated electronics like spectroscopy amplifier (Canberra, Model 2022), analog-to-digital converter (Canberra, Model 8701), 4K channel analyzer (Canberra, Accuspec B), etc. We have measured the background spectrum without any sample for about 87 h. A constant temperature of 21 °C was maintained in the laboratory to minimize the electronic drift in the amplification and analog-to-digital conversion. The overall momentum resolution was 0.38 a.u. (Gaussian full-width at half-maximum), which includes the detector resolution and the geometrical broadening of the incident and the scattered radiations.

The raw experimental data were corrected for several standard corrections like background, detector efficiency, instrumental resolution (limited to stripping off the low-energy tail), Compton cross-section and multiple scattering, etc. using the computer code of Warwick group (Felsteiner et al., 1974; Timms, 1989; Andrejczuk et al., 1993). Finally, the corrected experimental profiles were normalized to have an area equal to that of the free atom profile (Biggs et al., 1975) in the momentum range 0–7 a.u., as listed in Table 1.

3. Computational methods

We have used *ab initio* linear combination of atomic orbitals (LCAO) CRYSTAL03 program (Towler et al., 1996; Saunders et al., 2003) for the computation of theoretical Compton profiles. Moreover, we have also deduced energy bands, DOS and Mulliken's populations (MP). In the CRYSTAL03 package, the Bloch orbitals are generated from LCAO, which are derived from Gaussian-type basis sets. Due to non-availability of the all-electrons basis sets of Hg, we have used effective core pseudopotentials (ECP) to describe the Hg core states and Gaussian basis sets for all electrons of S, Se and Te and also the valence 6sp and 5d electrons of Hg.

The one-electron Hamiltonian operator in pseudopotential (PP)–HF approach is given by the sum of kinetic ($\hat{t}$), Coulomb ($\hat{c}$), exchange ($\hat{x}_{\mathrm{HF}}$) and effective core pseudopotential ($\hat{e}_{\mathrm{pp}}$) operators.

In PP–DFT calculations, the one-electron Hamiltonian operator is

$$\hat{h}_{\mathrm{pp}} = \hat{t} + \hat{c} + \hat{x}_{\mathrm{KS}} + \hat{e}_{\mathrm{pp}}, \tag{2}$$

where $\hat{x}_{\mathrm{KS}}$ is the Kohn–Sham exchange–correlation potential operator. We have also incorporated local density approximation (LDA) and generalized gradient approximation (GGA) to PP–DFT calculations. A hybrid DFT–HF method, so-called B3LYP, was also employed by 20% mixing of the HF matrix with the DFT matrix. Different exchange and correlation functionals used in the present work are mentioned in Table 2.

The present calculations were performed for ZB mercury chalcogenides with space group F$\bar{4}$3m and lattice parameter *a* equal to 5.852, 6.084 and 6.462 Å for HgS, HgSe and HgTe, respectively (Lide, 2001). We have used ECP basis sets for Hg from Hay and Wadt (1985). The valence basis sets of Hg and Gaussian basis sets for all electrons of S, Se and Te were taken from a web site (http://www.tcm.phy.cam.ac.uk/~mdt26/basis_sets). The basis sets were optimized using BILLY software (Saunders et al., 2003). The optimized basis sets are available on

Table 1
Experimental parameters of Compton profile measurements of zinc blende HgS, HgSe and HgTe

Sample	Sample diameter (thickness) (cm)	Bulk density (g/cm^3)	Exposure time (h)	Integrated counts ($\times 10^7$)	Multiple scattering (−10 to +10 a.u.) (%)	Normalization of profile (0 to +7 a.u.) (e$^-$)
HgS	2.5 (0.40)	4.76	299	2.4	12.7	36.18
HgSe	2.5 (0.30)	4.39	238	3.3	10.6	43.26
HgTe	2.5 (0.20)	5.45	245	3.2	9.6	49.21