Applied Radiation and Isotopes 68 (2010) 286–292

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Compton profiles and electronic structure of $HgBr_2$ and HgI_2

G. Ahmed [a], Alpa Dashora [a], M. Sharma [b], B.L. Ahuja [a,*]

[a] Department of Physics, University College of Science, M.L. Sukhadia University, Udaipur, 313001 Rajasthan, India
[b] Physics Division, State Forensic Science Laboratory, Jaipur, 302016 Rajasthan, India

ARTICLE INFO

Article history:
Received 19 September 2009
Accepted 10 November 2009

PACS:
13.60.Fz
71.15.Ap
71.15.Mb
78.70.−g

Keywords:
Compton scattering
Band structure calculations
Density functional theory

ABSTRACT

In this paper, we present the first-ever experimental Compton line shapes of $HgBr_2$ and HgI_2 using ^{137}Cs Compton spectrometer. To compare our experimental momentum densities, we have computed the Compton profiles using Hartree–Fock and density functional theory within linear combination of atomic orbitals. We have also computed the energy bands and density of states using the linear combination of atomic orbitals and full potential linearized augmented plane wave method. On the basis of equal-valence-electron-density profiles, it is seen that HgI_2 is more covalent than $HgBr_2$ which is in agreement with the valence charge densities. The experimental isotropic profiles are found to be relatively in better agreement with the Hartree–Fock data. We have also discussed the photoluminescence and detection properties of both the halides.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

HgI_2 is a technologically important material because of its use as a room temperature detector for γ- and X-rays. HgI_2 has high bulk electrical resistivity, which ensures a low dark current during detector operation. $HgBr_2$ shows the opto-electronic properties and is also a candidate material for the detection of photons (Fornaro et al., 2006). The HgI_2 is tetragonal with the space group symmetry $P4_2/nmc$ while $HgBr_2$ adopts the orthorhombic structure with the polar space group symmetry $Cmc2_1$ (D_{2h}). Many workers have carried out investigation on the properties of these layered semiconducting materials. The self consistent relativistic electronic structure of tetragonal HgI_2 has been investigated by Turner and Harmon (1989) using the linear augmented plane wave (LAPW) method. Burger and Nason (1992) determined the band gap in HgI_2 by measuring the spectral shifts of excitonic reflection and absorption peaks with change in temperature. Chang and James (1992) have presented empirical nonlocal pseudopotential calculations of HgI_2. The resulting absorption spectra and the polarization dependence are compared with the experiment. Using full potential linear muffin-tin orbital (FP-LMTO) method, Ahuja et al. (1996) have calculated the electronic structure of HgI_2. They derived the anisotropic frequency-dependent dielectric function and the reflectivity spectrum. Ayres et al. (2004) have performed full potential linearized augmented plane wave (FP-LAPW) calculations using the exchange and correlation potential of Perdew et al. (1996). The optical transmission spectra for $HgBr_2$ have been measured by Daviti and Paraskevopoulos (1999). Although the physical and electronic properties of HgI_2 are well documented, to our knowledge the computation of electronic properties of $HgBr_2$ are not available in the literature.

To shed more light on the electronic properties of $HgBr_2$ and HgI_2, we have measured their isotropic Compton profiles (CPs). Due to the non-availability of the single crystals of required size (13 mm diameter and 3 mm thick); we have measured the isotropic CPs of both the halides. It is worth mentioning that the Compton scattering is a well recognized probe to test *ab-initio* electronic structure calculations (Cooper, 1985; Cooper et al., 2004). The CP, also formulated as $J(p_z)$, is the projection of the electron momentum density $n(\vec{p})$ along the z-axis of a Cartesian coordinate system.

To support our experimental data, we have also computed the electron momentum density, energy bands and density of states (DOS) using Hartree–Fock (HF), density functional theory (DFT) with local density approximation (LDA) and generalized gradient approximation (GGA) and the hybridization of HF and DFT. We have also used the latest GGA prescription of Wu and Cohen (2006) within the FP-LAPW scheme (Blaha et al., 2001, 1990) to compute the energy bands and DOS.

2. Methodology

2.1. Experiment

The measurements on momentum densities of $HgBr_2$ and HgI_2 were carried out using our 20 Ci ^{137}Cs Compton spectrometer

---

[*] Corresponding author. Tel.: +91 9414317048; fax: +91 0294 2411950.
E-mail address: blahuja@yahoo.com (B.L. Ahuja).

0969-8043/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.apradiso.2009.11.028

(Ahuja and Sharma, 2005; Ahuja et al., 2006). γ-radiations of 661.65 keV were scattered by high purity samples (polycrystalline pellets dia. 20 mm and thickness 3 mm) at a fixed angle of $160 \pm 0.6^{\circ}$. The energy dispersive detection system in the present measurements mainly consisted of a high purity Ge detector (Canberra, model GL0210P) and associated electronics like spectroscopy amplifier, analog to digital converter and 4K-channel analyzer. The overall resolution of the experiment was 0.38 a.u (1 a.u. of momentum = 1.9929 ± 10^{-24} kg m s^{-1}). The data acquisition-times for $HgBr_2$ and HgI_2 were 270.6 and 374.3 h, respectively. The background spectrum, which was measured after removing the samples, was subtracted from the raw Compton data after scaling the measurement time of the raw data and the background. The data were then corrected for several systematic corrections like instrumental resolution, absorption in the sample, detector efficiency, Compton cross section and multiple scattering, etc. using the data correction package of Warwick group (Williams, 1977; Timms, 1989). A Monte Carlo procedure (Felsteiner et al., 1974) was used to calculate the momentum distribution of the multiply scattered γ-rays. The corrected profiles were normalized to the total number of electrons obtained from the free atom HF values (Biggs et al., 1975). These values were 58.52 and 70.32 electrons for $HgBr_2$ and HgI_2, respectively, in the momentum range 0–7 a.u. During the measurements, the stability of the system was checked from time to time using weak (10–12 μCi) ^{57}Co and ^{133}Ba γ-ray calibrators.

2.2. Theory

2.2.1. LCAO calculations

In the linear combination of atomic orbitals (LCAO) method, the crystalline orbitals are expanded as linear combination of a set of Bloch functions

$$\varphi_{ki}(\mathbf{r}) = N\sum_{j=1}^{m} a_{ji}(\mathbf{k})\sum_{g}\chi_{gj}(\mathbf{r})\exp(\mathbf{ik}\cdot\mathbf{g}) \tag{1}$$

The Bloch functions which are built from local atom-centered Gaussian type functions are solutions of the one particle equation given below:

$$H_i\varphi_{ki}(\mathbf{r}) = E_{ki}\varphi_{ki}(\mathbf{r}) \tag{2}$$

In the present LCAO-pseudopotential (PP) calculations, one can employ effective core pseudopotential (ECP) where the core electrons are assumed to have effective averaged potential. The one-electron Hamiltonian includes the kinetic, Coulomb, exchange-correlation and ECP operators. The electronic structure of materials can also be calculated in the framework of PP within the HF, as well as the DFT on various hybrid approximations containing elements of both HF and Kohn Sham (KS) Hamiltonians (Saunders et al., 2003; Pisani and Dovesi, 1980; Perdew and Zunger, 1981). In the HF method, the exact exchange is considered while the correlation effects are neglected. In the DFT, the exchange-correlation potential operator was defined in terms of exchange-correlation energy per particle in uniform electron gas. The DFT-LDA calculations were performed with Dirac–Slater exchange (Saunders et al., 2003) and Perdew–Zunger correlation (Perdew and Zunger, 1981) energy functionals. In the DFT-GGA, the exchange potential proposed by Becke (1988) and the correlation potential of Perdew and Wang (1986, 1992) were used. In the B3LYP, the exchange-correlation energies of Lee et al. (1988) and Vosko et al. (1980) were considered.

The lattice parameters of orthorhombic $HgBr_2$ were taken to be a=4.628, b=6.802 and c=12.476 Å (Daviti and Paraskevopoulos, 1999), while for tetragonal phase of HgI_2 the parameters were a=b=4.361 and c=12.450 Å (Ahuja et al., 1996). Due to the non-availability of Gaussian basis sets of Hg, we have taken the PP basis sets (Hay and Wadt, 1985) so that the chemically inactive atomic core electrons are eliminated from the quantum mechanical calculations. In case of halide ions, we have taken the Gaussian basis sets from http://www.tcm.phy.cam.ac.uk/~mdt26/basis_sets. The energy optimization of the basis sets was undertaken using the BILLY software. The self-consistent field (SCF) calculations have been performed at 328 k points in the irreducible Brillouin zone (BZ). All the theoretical directional CPs were normalized to the corresponding free atom CP area.

2.2.2. FP-LAPW calculations

We have also carried out band structure computations using FP-LAPW method (Blaha et al., 2001, 1990). We have used for the

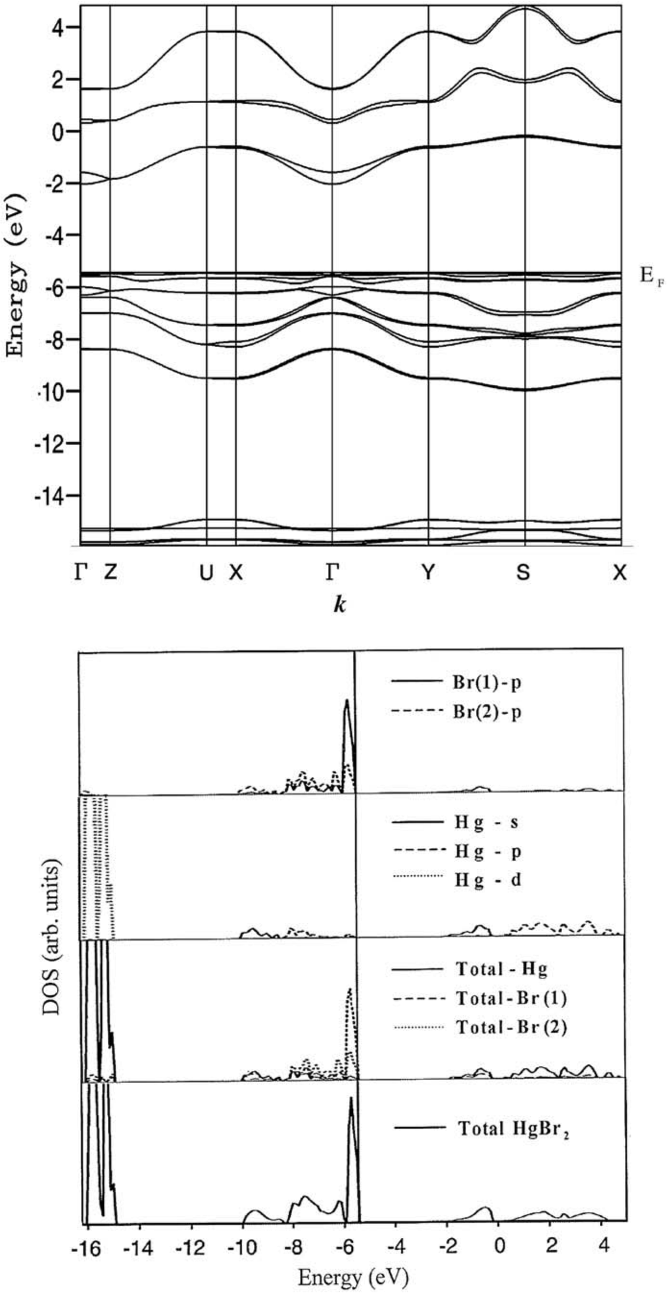

Fig. 1. Band structure and DOS of $HgBr_2$ along with high symmetry directions of the first Brillouin zone using LCAO-DFT-GGA. The horizontal solid line corresponds to the Fermi energy (E_F). The positions of Γ, Z, U, X, Y and S correspond to (0,0,0), (0,0,1), (0,1,1), (1,0,0), (0,1,0) and (1,1,0), respectively.

Download English Version:

https://daneshyari.com/en/article/1879368

Download Persian Version:

https://daneshyari.com/article/1879368

Daneshyari.com