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Electronic properties of $PbCl_2$ and $PbBr_2$ using Compton scattering technique

G. Ahmed [a], Y. Sharma [b], B.L. Ahuja [a],*

[a] Department of Physics, University College of Science, M.L. Sukhadia University, Udaipur 313001, Rajasthan, India
[b] Department of Physics, Feroze Gandhi College, Rae Bareli 229001, U. P., India

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ABSTRACT

We present the electron momentum densities of $PbCl_2$ and $PbBr_2$ using 661.65 keV γ-rays from 20 Ci ^{137}Cs source. To supplement our experimental investigations, we also report energy bands, density of states, Mulliken's population and Compton profiles of $PbCl_2$ and $PbBr_2$ using linear combination of atomic orbitals within Hartree–Fock and density functional theories. The energy bands are also computed employing full potential linearized augmented plane wave (FP-LAPW) method. Compton profiles are also analyzed in terms of equal-valence-electron-density scale. It shows that $PbCl_2$ is more covalent than $PbBr_2$, which is in agreement with the Mulliken's population analysis. It is seen that the Hartree–Fock and density functional theory based Compton line shapes show similar type of deviations from the experimental data. The luminescence properties of these halides are explained on the basis of energy band and density of states.

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1. Introduction

The Compton scattering, an inelastic X-ray scattering at large energy and momentum transfer, is a reliable tool for the study of ground-state electronic properties of solids (Cooper, 1985; Cooper et al., 2004). In the Compton scattering experiment one measures the electron momentum density of bulk materials. The Compton profile, $J(p_z)$, is the projection of the one electron momentum density distribution, $n(\mathbf{p})$, along the experimental scattering vector (z-axis of the Cartesian co-ordinate system). The $J(p_z)$ is defined as

$$J(p_z) = \int\int n(\mathbf{p})\, \mathrm{d}p_x\, \mathrm{d}p_y \qquad (1)$$

where p_z is the component of the electron momentum along the z-axis. The target electrons are characterized by the momentum distribution $n(\mathbf{p})$ that is given as

$$n(\mathbf{p}) = \sum_j \left| \int \psi_j(r)\, \mathrm{e}^{(-\mathrm{i}\,\vec{p}.\vec{r})}\, \mathrm{d}^3 r \right|^2 \qquad (2)$$

where $\psi_j(r)$ are the electron wave functions in position space. The summation extends over all the occupied states.

Lead halides have attracted considerable attention because of their interesting features due to electron–lattice interactions. They are known to be insulators with a moderate band gap. They crystallize in the orthorhombic layer structure belonging to the space-symmetry group D_{2h}^{16} (Pnma {62}) with layers perpendicular to the [0 1 0] direction. Most of the earlier work reported by different workers mainly includes luminescence properties (Babin et al., 2002; Iwanaga et al., 2000; Gruijter and Kerssen, 1972), reflectance and electronic studies (Eijkelenkamp and Vos, 2006; Fujita et al., 1991, 2000; Kanbe et al., 1977, 1976; Plekhanov, 2004, 1975, 1973), structural vibrational properties (Nizam et al., 1987), ionic conductivity and activation volumes (Oberschmidt and Lazarus, 1980), etc. The lead halides are characterized by an excitonic fundamental edge, which are formed by electronic states on lead ion. The applications of the lead halides in photography, acoustical-optical devices and radiation detectors can be better understood from the electronic structure of these compounds. To our knowledge, so far, energy band calculations and electron momentum densities have not been reported for $PbCl_2$ and $PbBr_2$.

In this paper, we present the first-ever experimental Compton profiles for $PbCl_2$ and $PbBr_2$. For the present measurements, we have used our 20 Ci ^{137}Cs Compton spectrometer. The Compton profiles have been computed within the framework of pseudopotential (PP) with Hartree–Fock (HF) and density functional (DFT) schemes as embodied in CRYSTAL03 code. In addition to momentum densities, we have also computed for the first time the energy bands and density of states (DOS) using CRYSTAL03 package and full potential linearized augmented plane wave method using Wien2k. The theoretical and experimental momentum densities of both the isoelectronic compounds are also analyzed using equal-valence-electron-density (EVED) scale.

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

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2. Experiment

The Compton profiles of both the halides are measured using a 20 Ci ^{137}Cs Compton spectrometer (Ahuja and Sharma, 2005; Ahuja et al., 2006). The high purity (99.99%) polycrystalline $PbCl_2$ and $PbBr_2$ samples were in form of pellets (diameter 2.5 cm and thickness 0.3 and 0.4 cm). Due to the non-availability of large single crystals (13 mm diameter and 3 mm thickness) we have measured the isotropic momentum densities. The incident beam of 661.65 keV γ-rays was scattered by the sample through a mean angle of $160 \pm 0.6^\circ$. The energy spectrum of the scattered radiation was measured using a high purity Ge detector (Canberra, GL0210P) and the associated electronics like spectroscopy amplifier, analog to digital converter and multi-channel analyzer. The total momentum resolution (Δp_z) of the Compton spectrometer was 0.39 a.u. (1 a.u. of momentum $= 1.9929 \times 10^{-24}\,\mathrm{kg\,m\,s^{-1}}$).

Raw data for the $PbCl_2$ and $PbBr_2$ were accumulated for a total period of 367 and 379 h, respectively. The measurements were made at ambient temperature and normal pressure. During the measurements, the stability of the electronic system was checked from time to time using weak (10–12 μCi) ^{57}Co and ^{133}Ba γ-ray calibrators.

The raw Compton data were corrected for several systematic corrections like background, instrumental resolution, sample absorption, detector efficiency, Compton cross-section and multiple scattering in the sample (Williams, 1977; Timms, 1989). The background contribution was determined from an independent measurement with the sample removed. A Monte Carlo simulation of multiple scattering (Felsteiner et al., 1974) was employed to evaluate the correction factor up to triple scattering contribution. It was found that in $PbCl_2$ and $PbBr_2$ the percentage of multiple scattering in the final profile (0–10 a.u.) was 10.6% and 10.8%, respectively. Finally, the Compton profiles of $PbCl_2$ and $PbBr_2$ were normalized to respective free atom profile areas (Biggs et al., 1975), viz, 44.99 and 59.02 electrons, respectively, in the momentum range 0–7.0 a.u.

3. Theory

3.1. Linear combination of atomic orbitals

We have computed the electronic structure (including the momentum densities) of $PbCl_2$ and $PbBr_2$ using the self-consistent (SC) PP scheme within linear combination of atomic orbitals (LCAO) with Kohn–Sham (KS) approximation as embodied in the CRYSTAL03 package of Torino group (Pisani and Dovesi, 1980; Towler et al., 1996; Saunders et al., 2003). The CRYSTAL03 code is a reliable tool for computing the electronic and associated ground state properties of three-dimensional periodic materials. The code facilitates various schemes namely the HF, DFT with local density approximation (LDA) and generalized gradient approximation (GGA).

In case of the HF scheme, the exchange effects are considered while the correlation part is neglected. In the DFT (LDA and GGA) approach the exchange-correlation potential operators are defined as

$$\hat{v}_{xc}(r) = \frac{\partial E_{xc}[\rho]}{\partial \rho(r)} \tag{3}$$

where E_{xc} is the exchange-correlation density functional energy and ρ is the density at a point r. In the LDA, the

$$E_{xc}(\rho) = \int_{\substack{unit\\cell}} \mathrm{d}r\rho(\mathrm{r})\varepsilon_{xc}[\rho(r)] \tag{4}$$

where as in the GGA, the $\varepsilon_{xc}[\rho(r)]$ is replaced by $\varepsilon_{xc}[\rho(r),|\nabla\rho(r)|]$.

Here ε_{xc} is the exchange-correlation energy per particle in uniform electron gas.

The LCAO package also allows the hybridization of the HF and the DFT (so called B3LYP) wherein, the E_{xc} is defined as

$$E_{xc} = 0.80(E_x^{LDA} + 0.90E_x^{BECKE}) + (0.20E_x^{HF} + 0.19E_c^{VWN} + 0.81E_c^{LYP}) \tag{5}$$

E_x^{HF}, E_x^{LDA} and $E_x^{BECKE}$are the exchange energies of the HF, Dirac–Slater and Becke, respectively (Saunders et al., 2003; Becke, 1988), while E_c^{VWN} and E_c^{LVP} are the correlation energies due to Vosko et al. (1980) and Lee et al. (1988), respectively.

Within a frozen core approximation, we have used the effective core pseudopotential (ECP) for Pb to perform the calculations for valence electrons. It is worth mentioning that the PP are convenient for reducing the computational cost of calculations more critically for heavy elements where there is a need to perform a relativistic treatment of the core electrons.

Due to non-availability of all electron basis sets of Pb, only its valence part was considered in the present computations. The ECP's for Pb were taken from Wadt and Hay (1985). The all electron Gaussian basis sets for Cl and Br were taken from the www.tcm.phy.cam.ac.uk/_mdt26/basis_sets. The energy optimization for the basis sets for $PbCl_2$ and $PbBr_2$ was undertaken using BILLY program (Pisani and Dovesi, 1980; Saunders et al., 2003). The SCF calculations have been performed at 343 **k** points in the irreducible Brillouin zone (BZ). For a faster convergence of self-consistent field (SCF) cycles, the BROYDEN scheme was applied after ISTART SCF iteration as facilitated in the CRYSTAL03 code.

The lattice parameters for the orthorhombic structure of $PbCl_2$ ($PbBr_2$) were taken as $a = 7.608(8.068)$, $b = 4.525(4.767)$ and $c = 9.030(9.466)$ Å. All the theoretical directional profiles were normalized to free atom Compton profile area as discussed earlier.

3.2. FP-LAPW calculations

Electronic structure of present PbX_2 compounds is also computed using the SC full potential linearized augmented plane wave (FP-LAPW) method of the DFT (Blaha et al., 1990, 2001). In these calculations, the crystal potential within the muffin tin (MT) spheres are formed by the spherical harmonics, while outside the MT it was represented by plane waves. For this purpose the calculations were undertaken using the Wien2k package. We have used the latest version of GGA using the prescription of Wu and Cohen (2006). The radius of MT sphere (R_{MT}) was chosen as 2.5 a.u. for Pb and 2.25 a.u. for both the Cl and Br. The value of $R_{\mathrm{MT}}K_{\max}$ was taken to be 7 ($K_{\max}$ is the maximum modulus of the reciprocal lattice vectors) and 47 **k** points were considered in the irreducible wedge of BZ. To ensure accuracy in convergence, the total energy of the crystal was converged to 0.01 mRy. The maximum radial expansion ($l_{\max}$) was set to 10. Since Wien2k code does not include the computation of momentum densities, we have not calculated the Compton profiles using FP-LAPW scheme.

4. Discussion of results

4.1. Energy bands and DOS

Our calculated energy bands along with DOS for the PP-DFT-GGA and FP-LAPW schemes are shown in Figs. 1–4. The PP-based energy bands and DOS (Figs. 2 and 4) have been plotted using DL Visualize software (Searle, 2001). The layers in both the crystal are perpendicular to the [0 1 0] direction, which appears as substantial

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