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Research Paper

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Electronic structure of halides

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ABSTRACT

In this paper, we present the Compton profile of CaCl2 and electronic structure of PbCl2 and PbBr2. For the Compton profile measurements we have used 241Am Compton spectrometer while for the theoretical calculations we have used the self-consistent pseudopotential scheme within linear combination of atomic orbitals with Kohn–Sham approximation as embodied in the CRYSTAL03 package of Torino group. To compare and analyze our data, we have computed the energy bands, density of states, etc. using LCAO approach which is embodied in CRYSTAL03 code.

Introduction

Lead chloride is known as an acousto-optical material and a material for the group of heavy-element halogenides. Lead halides are known to be insulators with a moderate band gap. Lead chloride is applicable in solid form and molten form. Lead bromide has high diffraction efficiency and is useful in spectral analysis systems and optical signal processing. The work done on these halides includes luminescence properties, reflectance and electronic studies, structural vibrational properties, etc. [1-6]. In this paper, we report the theoretical results on the electron momentum density of lead halides. The electronic structure of $PbCl_2$ and $PbBr_2$ have been computed using the self-consistent pseudopotential (PP) scheme within linear combination of atomic orbitals (LCAO) with Kohn–Sham approximation as embodied in the CRYSTAL03 package of Torino group [7-9]. The three implemented techniques i.e. Density functional theory, Hartree Fock approximation and Pseudopotential could be successful in the computation of the electronic structures of lead halides.

Compton scattering is a unique probe to study ground-state electron momentum densities [10]. This technique is insensitive to crystal defects. The measured data in such experiments, known as Compton profile, $J(p_z)$. $J(p_z)$ = is one-dimensional projection of the momentum density on the scattering vector. Compton profile is very sensitive to the momentum distribution of loosely bound valence electrons which enables the investigation of behavior of valence electrons, chemical bonding, etc.

EXPERIMENT

The Compton profiles of $CaCl_2$ is measured using a ^{241}Am Compton spectrometer (11). The high purity (99.99%) polycrystalline $CaCl_2$ samples were in form of pellets (diameter 2.5 cm and thickness 0.3 and 0.4 cm). 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 analyser.

The raw Compton data wes corrected for several systematic corrections like background, instrumental resolution, sample absorption, detector efficiency, Compton cross-section and multiple scattering. A Monte Carlo simulation of multiple scattering was employed to evaluate the correction factor up to triple scattering contribution. Finally, the Compton profiles of $CaCl_2$ were normalized to respective free atom profile areas, in the momentum range 0-7.0 a.u.

THEORY

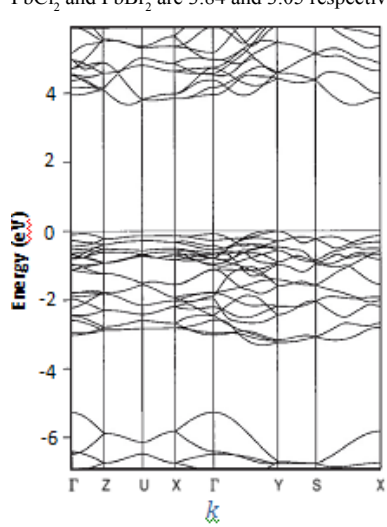
The pseudopotential (PP) is used as an approximation for the general description of complex systems. The PP is a phenomenon to replace the atomic all electron potential such that core states are eliminated and the valence electrons are described by the nodeless pseudo-wavefunctions. In this approach only the chemically active valence electrons are deal with clearly, while the core electrons are frozen being considered together with the nuclei as rigid non polarizable ion cores. We have computed the electronic structure of lead halides using the self-consistent PP scheme within LCAO with Kohn-Sham approximation as embodied in the CRYSTAL03 package of Torino group [8-10]. The code facilitates various schemes namely the HF, DFT with local density approximation (LDA) and generalized gradient approximation (GGA). Within a frozen core approximation, we have used the effective core pseudopotential (ECP) for Pb to perform the calculations for valence electrons.

The SCF calculations have been performed at 343 ***k*** points in the irreducible Brillouin zone. $PbCl_2$ and $PbBr_2$ crystallize in orthorhombic structure having space group 62 (Pnma). The lattice parameters of $PbCl_2$ ($PbBr_2$) were a = 7.608 (8.068), b = 4.525 (4.767) and c = 9.030 (9.466) Å.

RESULTS AND DISCUSSIONS

Our calculated PP-DFT-GGA scheme based energy bands along with DOS are shown in Fig.1. The layers in both the crystal are perpendicular to the [010] direction, which appears as substantial crossing over of bands in the ΓY (Δ) branch. It is also observed that the degenerate states split at Γ point in the ΓX (Σ) and the ΓZ (Λ) branches. In lead halides, the top of the valence band is found to compose of the *6s* orbits of Pb^{2+} and mixing from *np* orbitals of halogen ions and the bands in the conduction band to be composed primarily of the states of 6p orbits of Pb^{2+}. The Fermi energy (E_F) is taken at zero energy level. The band gap is between 0 to 3.5 eV and -4 to -6 eV. There is a maximum overlapping of conduction and valence band electron is from -4 to 0 eV.

The band gap (ΔE_g) derived from PP-DFT-GGA scheme for the $PbCl_2$ and $PbBr_2$ are 3.84 and 3.05 respectively.



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The differences between the convoluted spherically averaged theoretical and the experimental Compton data are plotted in Fig. 2. It is observed that in the high momentum region, all the LCAO calculations show a close agreement with the experiment. It is expected because this region is dominated by the core electrons, which are well defined by the free atom profiles. In the vicinity of the Compton peak, different types of exchange and correlation energies govern the differences.

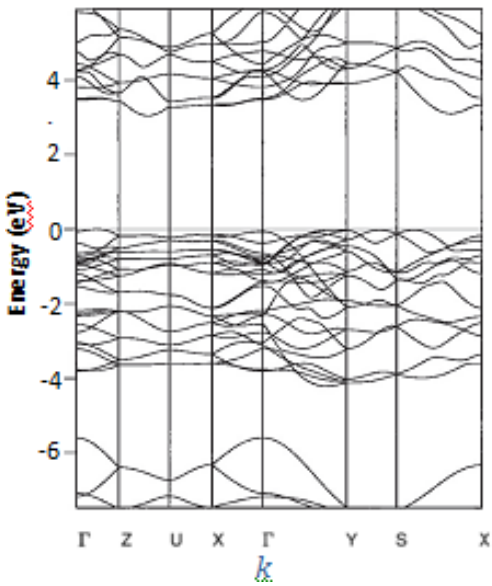

Figure 1:*Band structure and DOS of $PbCl_2$ and $PbBr_2$ along with high symmetry directions of the first BZ using PP-DFT-GGA approach.*

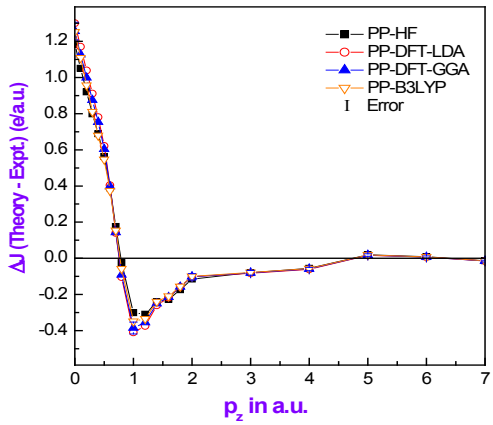

Figure 2: *Differences between the experimental and the theoretical profiles using different schemes of CRYSTAL03 code for $CaCl_2$.*

From Fig. 2 the differences between theoretical and experimental Compton profiles are shown. In the low momentum side, due to the poor quality of the basis sets and the exclusion of the relativistic effects in the LCAO method. A good agreement in high momentum side (p_z >3 a.u.) is due to the dominating contribution of core electrons, which are normally unaffected on the formation of solids.

CONCLUSIONS

In this paper, we have presented the electron momentum densities of$CaCl_2$, $PbCl_2$ and $PbBr_2$. The measured band structure is computed with the PP based HF and the DFT approaches. A good agreement between the theoretical and experimental calculations have been observed.

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