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Electron momentum density distribution in Cd_3P_2

M.S. Dhaka [a,*], G. Sharma [b], M.C. Mishra [c], K.B. Joshi [d], R.K. Kothari [c], B.K. Sharma [c]

[a] Department of Physics, Engineering College Bikaner, Bikaner 334004, India
[b] Department of Physics, Banasthali University, Banasthali 304022, India
[c] Department of Physics, University of Rajasthan, Jaipur 302004, India
[d] Department of Physics, University College of Science, M.L. Sukhadia University, Udaipur 313 002, India

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ABSTRACT

A study of electron momentum density distribution in Cd_3P_2 is reported in this work. The measurement of Compton profile is carried out on a polycrystalline sample using 59.54 keV gamma-rays emanating from an ^{241}Am radioisotope. The theoretical calculations are performed using linear combination of atomic orbitals method following the Hartree–Fock and *a posteriori* density functional theories. The spherically averaged theoretical Compton profiles are in good agreement with the measurement. The best agreement is, however, shown by the Hartree–Fock scheme. Simple ionic model calculations for a number of configurations $(Cd^{+x})_3(P^{-3x/2})_2$ ($0.0 \leqslant x \leqslant 2.0$ in step of 0.2) are also performed utilizing free atom profiles. The ionic model supports transfer of 2.0 electrons per Cd atom from 5*s* state to 3*p* state of P.

1. Introduction

Cadmium phosphide, i.e. Cd_3P_2 is one of the II_3^A–V_2^B group semiconductor compounds which has n-type conductance. It is used in IR detectors as well as in laser sources [1–4]. The method of preparation and its semiconducting properties are described by a number of workers [5–7]. Optical properties and thermomagnetic transport measurements on Cd_3P_2 are studied by Gelten et al. [8]. Radoff and Bishop [9,10] reported the band gap of 0.53 and 0.56 eV at 300 and 90 K, respectively. Blom and Burg [11] and Radautsan et al. [12] suggested the shape of conduction band of Cd_3P_2 from the measurements of thermomagnetic transport properties. Lakhani and Jay-Gerin [13] reported the g-factor of conduction electrons in Cd_3P_2 at low temperature. Phase transition in Cd_3P_2 at high pressure and temperature was reported by Yel'kin et al. [14].

Among theoretical studies, pseudopotential calculations have been employed by Lin-Chung [1] to compute the energy band structures of some II_3^A–V_2^B semiconductors including Cd_3P_2. These calculations overestimated energy gap and found narrow valence bands compared to the experimental data. Lavrentiev et al. [15] performed self-consistent calculations to study electronic density of states (DOS) for Zn_3P_2, Cd_3P_2 and their solid solution considering cubic structure ($P4_232$-space group and lattice constant – 6.06 Å) of Cd_3P_2 compound. A comparison from the X-ray photoelectron spectra showed that the calculated *d* states of Zn and Cd are ~ 1.5 eV higher than the experimentally observed energies. The semi-empirical tight binding electronic energy band structure of Cd_3P_2 was performed by Sieranski et al. [16] considering the zinc-blende crystal structure and found that the Cd_3P_2 is a direct band gap (0.53 eV) semiconductor at room temperature.

The Compton scattering has been recognized as a powerful tool to study ground state properties of materials in momentum space. It probes momentum density distribution of electrons in solids through the Doppler shift of Compton scattered photons by electrons in motion [17,18]. The measured one-dimensional quantity, $J(p_z)$, is a projection of the 3D momentum density $\rho(\boldsymbol{p})$ along the scattering vector parallel to p_z, i.e.

$$J(p_z) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho(\boldsymbol{p})\, dp_x\, dp_y \tag{1}$$

where $\rho(\boldsymbol{p})$ is the momentum density, which can be derived by transforming the real space electron wave function into the momentum space. Thus, $J(p_z)$ is an experimental observable which can be compared directly with the computation. From the survey of the literature, it turned out that no study is reported on any II_3^A–V_2^B compound like Cd_3P_2 using Compton spectroscopy. It was therefore, worthwhile to undertake a Compton profile study of Cd_3P_2. In this paper, the Compton profile study for Cd_3P_2 is presented. The limitation to measure the isotropic Compton profile was due to non-availability of single crystals of the Cd_3P_2. To compare with the measurement, theoretical profiles were also computed using linear combination of atomic orbitals (LCAO) method

* Corresponding author. Tel.: +91 151 2252919, fax: +91 151 2252919.
E-mail addresses: msdhaka75@yahoo.co.in (M.S. Dhaka), gsphysics@gmail.com (G. Sharma).

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embodied in CRYSTAL06 code [19]. An ionic model considering various charge configurations taking free atom profiles has also been attempted.

2. Measurement and data analysis

The ^{241}Am gamma-ray Compton spectrometer developed by Sharma et al. [20] was employed. The sample was in powder form of 99.5% purity. It was kept at room temperature (22 °C) in a rectangular cell with circular mylar on the front as well as the back sides. The thickness of sample was 3.2 mm and density was 2.79 gm/cm^3 (effective). The sample cell was kept vertical by affixing it on the back of a lead covered brass slab having a hole of 18 mm diameter. The chamber was evacuated to about ~ 1.33 Pa of pressure with a rotary oil pump to reduce the contribution of air scattering. The incident gamma-rays of 59.54 keV energy were scattered by the sample through a mean angle $165 \pm 3.0°$. The scattered radiations were detected and analysed using an HPGe detector (Canberra model GL0110P) and associated electronics like spectroscopy amplifier (Canberra, 2020 model), an analog to digital converter (Canberra, 8701 model) and a multi-channel analyzer (Canberra, S-100). To reduce pile-up contribution in the profile, the experiment was performed with 1 μs shaping time. The spectrum was collected in a multi-channel analyzer with 4096 channels having a channel width of 20 eV, which corresponds to about 0.03 a.u. of momentum. The spectrometer had an overall momentum resolution of 0.6 a.u. (Gaussian FWHM), which includes the detector resolution and the geometrical broadening of the incident and the scattered radiations. The Compton scattering spectra were measured for 52 hours to accumulate 3.6×10^6 integrated counts in the Compton profile region. The drift in the electronic system was checked by using a weak ^{241}Am calibration source.

To correct for the background, which is mainly due to scattering from sample holder, mylar and cosmic background, a separate measurement was made with sample holder. Thereafter, the measured background was subtracted from the raw data point by point after scaling it to the actual time. The measured profile was then corrected for the effect of detector response function, energy dependent absorption and scattering cross section using the computer code of the Warwick group [21]. The data reduction for the detector response function was restricted to striping-off the low energy tail of the resolution function. After converting the Compton profile into momentum scale, a Monte Carlo simulation of the multiple scattering was performed [22]. The contribution of the multiple scattering was found to be 3% in the momentum region −10 a.u. to +10 a.u. Thereafter, the profile was normalized in the momentum range from 0 to +5 a.u. to 64.421 electrons corresponding to the free atom Compton profile [23] area. The contribution of 1s electrons of Cd was excluded as they do not contribute in the scattering.

3. Computational method

3.1. The DFT-LCAO theory

To compute the theoretical Compton profiles, the LCAO method embodied in the CRYSTAL06 code [19,24] of Torino group was used which provides a platform to calculate electronic structure of periodic systems considering Gaussian basis sets. In LCAO method, each crystalline orbital $\psi_i(\boldsymbol{r}, \boldsymbol{k})$ is a linear combination of Bloch functions $\varphi_\mu(\boldsymbol{r}, \boldsymbol{k})$ defined in terms of local functions $\varphi_\mu(\boldsymbol{r})$, normally referred as atomic orbitals. The local functions are expressed as linear combination of certain number of individually normalized Gaussian type functions. The standard basis sets for Cd [25] and P [26] were considered for computation. For DFT calculation,

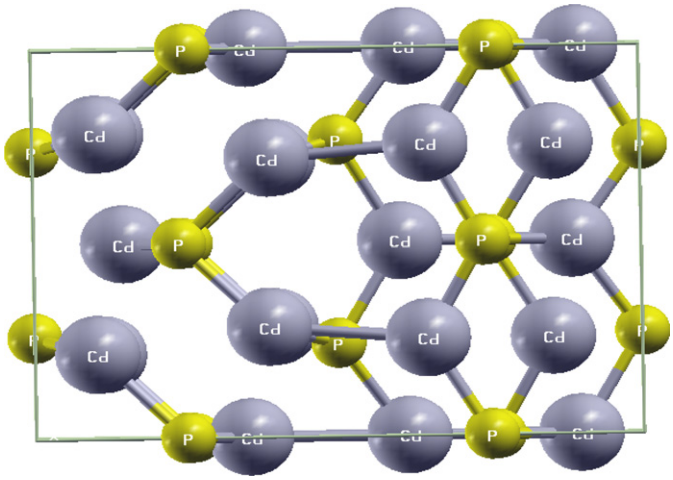

Fig. 1. Tetragonal crystal structure of Cd_3P_2.

the crystal Hamiltonian was generated using the correlation functional proposed by Perdew, Burke and Ernzerhof (PBE) [27] and exchange potential proposed by Becke [28]. The computations were performed taking tetragonal structure (Fig. 1) with lattice constants $a = 8.739$ Å, $c = 12.252$ Å and space group $P4_2nmc$ [2]. This tetragonal crystal structure of Cd_3P_2 contains 40 atoms in the unit cell, i.e. 16 P and 24 Cd atoms. The self-consistent calculations were performed considering $75\vec{k}$ points in the irreducible Brillouin zone with tight tolerances. To achieve self-consistency, 45% mixing of successive cycles was considered and the self-consistency was achieved within 8 cycles.

3.2. Ionic model

The theoretical Compton profiles of Cd_3P_2 for various ionic arrangements were calculated from the free atom profiles [23] of Cd and P. The valence profiles for various $(Cd^{+x})_3(P^{-3x/2})_2$ ($0.0 \leqslant x \leqslant 2.0$ in step of 0.2) configurations were calculated by transferring x number of electrons from 5s shell of Cd to the 3p shell of P and these valence profiles were added to the core contributions to get the total profiles. All the profiles were then normalized and convoluted with a Gaussian function of 0.6 a.u. FWHM to compare with the experimental data.

4. Results and discussion

4.1. Isotropic Compton profiles

The unconvoluted spherically averaged theoretical Compton profiles (HF and DFT) are presented in columns 2–3 of Table 1. The ionic profile for the most favoured ionic arrangement (as discussed later) derived from the free atom model is given in column 4 of the table. The experimental Compton profile is given in column 5 alongwith the experimental errors at selected points. It may be noted that in order to compare the theoretical values with the experiment quantitatively, the theoretical values need to be convoluted with a Gaussian function of 0.6 a.u. FWHM and normalized to free atom area. Accordingly in Fig. 2, the difference curves deduced from the convoluted theoretical profiles (HF and DFT) and the experiment are presented. The figure reveals that the LCAO calculations predict larger momentum density than the measurement in the momentum region ($0.0 \leqslant p_z \leqslant 0.2$ a.u. and $0.7 \leqslant p_z \leqslant 1.7$ a.u.). Further, it is visible that the trend in momentum densities predicted by DFT-LCAO and HF-LCAO schemes are almost similar in the entire range of momentum. It is also visible that these two schemes underestimate the Compton profiles