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Electron momentum density and band structure calculations of α- and β-GeTe

Laxman Vadkhiya [a], Gunjan Arora [b], Ashish Rathor [a], B.L. Ahuja [a,*]

[a] Department of Physics, University College of Science, M.L. Sukhadia University, Udaipur 313001, Rajasthan, India
[b] Department of Physics, Techno India NJR Institute of Technology, Udaipur 313002, Rajasthan, India

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ABSTRACT

We have measured isotropic experimental Compton profile of α-GeTe by employing high energy (662 keV) γ-radiation from a ^{137}Cs isotope. To compare our experiment, we have also computed energy bands, density of states, electron momentum densities and Compton profiles of α- and β-phases of GeTe using the linear combination of atomic orbitals method. The electron momentum density is found to play a major role in understanding the topology of bands in the vicinity of the Fermi level. It is seen that the density functional theory (DFT) with generalised gradient approximation is relatively in better agreement with the experiment than the local density approximation and hybrid Hartree–Fock/DFT.

1. Introduction

It is well known that the spectrum of inelastically scattered photons by electrons is related to the electron momentum density (EMD) of the scatterer (see for examples, Cooper et al., 2004; Ahuja, 2010). In bulk materials, the Compton technique is assumed to be valid within the impulse approximation (IA), where the energy transferred in the scattering process is much larger than the binding energy of the electronic states involved.

In Compton spectroscopy, we fix the direction of the incident γ-rays and measure the energy distribution of the scattered photons at a fixed scattering angle θ. The Compton profile (CP), $J(p_z)$, can be deduced from double differential cross-section using the relation

$$\frac{d^2\sigma}{d\Omega\, d\omega_f} = F(\omega_i, \omega_f, \theta, p_z)J(p_z) \tag{1}$$

Here F is a function of incident and scattered photon energies (ω_i and ω_f, respectively), scattering angle (θ) and the electron momentum (p_z) along the scattering vector direction.

Within the IA, the CP is a 2-D integral over the momentum density. Theoretically, CP is determined as

$$J(p_z) = \int_{p_x}\int_{p_y} \rho(\vec{p})dp_x\, dp_y \tag{2}$$

where $\rho(\vec{p})$ is the EMD and is given by

$$\rho(\vec{p}) \propto \left| \int \psi_n(\vec{r})\exp(-i\vec{p}\cdot\vec{r})dr \right|^2 \tag{3}$$

In Eq. (3), $\psi_n(\vec{r})$ is the position space wave function for the electron in the nth state. Therefore, the computed CP provides a way to probe the performance of various electronic structure calculations used to generate solid-state wave functions.

GeTe, which is a IV–VI semiconductor, consists of α-phase (rhombohedral, lower symmetric, ferroelectric, space group R3m) at room temperature and β-phase (cubic, rocksalt-type, highly symmetric, paraelectric, space group Fm$\bar{3}$m) at high-temperature. The α and β structures are related by a ferroelectric type of transition at a critical temperature of 720 K (Chattopadhyay et al., 1987) that can be seen by considering the atomic coordinates. GeTe is an interesting material for industrial applications because when it is alloyed with Sb, its electrical and optical properties change dramatically due to the change in microscopic structure from crystalline to amorphous (Libera and Chen, 1993; Yamada, 1996). Ferroelectric behaviour of GeTe makes it a promising material for various optoelectronic applications. Moreover, GeTe is also suitable for infrared detectors and light emitting devices.

Among theoretical band structure calculations, several authors have used various approaches to describe the ground state properties of α- and β-GeTe. Recently, Shaltaf et al. (2008) have reported the dynamical, dielectric and elastic properties of α phase using plane waves and norm-conserving pseudopotentials (PP) method. By employing fully relativistic projected augmented wave (PAW) method, Ciucivara et al. (2006) have compared the electronic structure of GeTe using local density approximation (LDA) and

* Corresponding author. Fax: +91 294 2411950.
E-mail address: blahuja@yahoo.com (B.L. Ahuja).

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generalised gradient approximation (GGA). Edwards et al. (2006) have employed various methodologies like relativistic plane wave DFT, non-relativistic DFT–LDA and quantum Monte Carlo calculations, to understand the electronic structure of intrinsic defects in α and β states of GeTe. Waghmare et al. (2003) have reported electronic structure using the linear muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA) and plane wave PP schemes.

For the β phase of GeTe, the electronic and optical properties have been computed by Okoye (2002) using full potential linearised augmented plane wave (FP-LAPW) method. The author has used exchange and correlation of Perdew–Wang (PW) and Perdew–Burke–Ernzerhof for LDA and GGA, respectively. Rabe and Joannopoulos (1987) have employed *ab initio* scalar relativistic PP in LDA including spin–orbit coupling to find the structural properties of GeTe. Regarding experimental studies, Onodera et al. (1997) have reported the X-ray diffraction and electrical resistivity of GeTe.

Although a number of theoretical and experimental efforts have been made to describe the structural, electronic and optical properties of GeTe, still studies related to the momentum densities and CPs are lacking. In this paper, we report the first ever CP of α-GeTe measured using our 20 Ci ^{137}Cs Compton spectrometer. Due to non-availability of large size single crystals, we have measured the isotropic CP. To compare our experimental data, we have computed CPs using DFT and hybrid Hartree–Fock (HF)/DFT methods as embodied in the *ab initio* linear combination of atomic orbitals (LCAO) method developed by Torino group (Towler et al., 1996; Saunders et al., 2003). In addition, we report energy bands, density of states (DOS), band gaps and Mulliken's population of both the α and β phases.

2. Experiment

We have measured the isotropic experimental CP of α-GeTe at ambient temperature using our 20 Ci ^{137}Cs Compton spectrometer (Ahuja and Sharma, 2005; Ahuja et al., 2006). The γ-rays of energy 661.65 keV were scattered by polycrystalline GeTe (pellet of thickness 0.2 cm and diameter 2.46 cm) at an angle of $160 \pm 0.6^{\circ}$. The scattered photons were analysed by a high purity Ge detector (Canberra made, operated at bias of -700 V) and associated electronics (spectroscopy amplifier, analog to digital converter, etc.). The channel width of 4096-channel analyser (Canberra; Accuspec B) was about 61 eV. During the exposure time of 276 h about 2.2×10^7 counts were collected in the CP region.

The overall momentum resolution of the present measurement, which includes the detector resolution and the geometrical broadening, was 0.38 a.u. (Gaussian, full width at half maximum). The raw Compton data were processed by the application of a series of corrections like background, detector response function, the variation of detector efficiency with energy, absorption, Compton scattering cross-section, multiple scattering within the sample, etc. (Cooper et al., 2004). The duly corrected profiles were normalised to the respective free atom CP area (Biggs et al., 1975) of 34.28 electrons over the momentum range 0–7 a.u.

3. LCAO calculations

We have computed the electronic structure, including momentum densities, using self-consistent LCAO scheme as embodied in CRYSTAL03 program (Towler et al., 1996; Saunders et al., 2003). The code enables computation of electronic properties using DFT with LDA and GGA, and also *posteriori* Becke's three parameter hybrid functional, i.e. B3LYP.

In DFT–LDA, one electron exchange-correlation potential operator is defined as

$$\hat{v}_{xc}(\vec{r}) = \frac{\partial[E_{xc}(\rho) = \int d\vec{r}\,\rho(\vec{r})\varepsilon_{xc}\{\rho(\vec{r})\}]}{\partial\rho(\vec{r})} \quad (4)$$

where E_{xc} is the exchange-correlation density functional energy and ρ is the electron density at point $\vec{r}$, while in the case of GGA

$$E_{xc}(\rho) = \int d\vec{r}\,\rho(\vec{r})\varepsilon_{xc}\{\rho(\vec{r}), |\nabla\rho(\vec{r})|\} \quad (5)$$

Here the integrals are taken over the unit cell. In the DFT–LDA calculations, we have chosen the Dirac–Slater exchange (Saunders et al., 2003) and Perdew–Zunger correlation potentials (Perdew and Zunger, 1981), while for GGA the exchange and the correlation potential of Perdew–Wang (Perdew and Wang, 1986 and 1992) have been used. In the B3LYP (hybrid HF/DFT), we have used Becke's gradient correction (Becke, 1988) to the exchange and the correlation functionals due to Lee–Yang–Parr (Lee et al., 1988) and Vosko–Wilk–Nusair (Vosko et al., 1980).

In the present calculations, for a better prescription of α and β structures of GeTe, the all electron Gaussian basis sets for Ge and Te were taken from the website http://www.tcm.phy.cam.ac.uk/~mdt26/basis_sets. The basis sets were energy optimised using BILLY software (Saunders et al., 2003). Following the standard truncation criteria for the CRYSTAL03 code, we have performed the SCF calculations with 413 k points in the irreducible Brillouin zone. For β-GeTe the lattice parameter was $a = 5.996$ Å, while in case of α phase the structural parameters were $a = 4.289$ Å, $\alpha = \beta = \gamma = 58.07^{\circ}$.

4. Results and discussion

4.1. Energy bands

4.1.1. β-GeTe

Fig. 1(a,b) shows the energy bands along with the total and partial DOS of β-GeTe calculated using the DFT–GGA scheme of LCAO method. Other schemes as included in the CRYSTAL03 code (viz. DFT–LDA and B3LYP) show almost similar topologies of energy bands and DOS (hence not shown here). We discuss mainly the energy bands in the vicinity of Fermi energy (E_F) which are very important to examine the electronic properties of materials. The non-degenerate valence band maximum (VBM) and the conduction band minimum (CBM; degenerate) located at Z point make it a direct band gap semiconductor. The direct band gap at Z defines the lowest gap M_0 (0.148 eV), as the surfaces of constant energy separation are ellipsoidal in the neighbourhood of Z. The minimum energy separation at L point and Δ(Γ–X) branch define M_1 (0.160 eV) and M_2 (1.459 eV) gaps, respectively. Therefore, in addition to the direct gap at Z, VBM and CBM at L point and along Δ branch are more likely to be saddle points than absolute extrema. Except positions of non-degenerate states, fine structures and band gap values, the present energy bands show a similar topology as reported earlier (Okoye, 2002; Rabe and Joannopoulos, 1987).

4.1.2. α-GeTe

The band structure of α-GeTe along with total and partial DOS obtained by using the DFT–GGA scheme of LCAO method is shown in Fig. 2(a,b). Unlike β-GeTe, α-GeTe has CBM at L point whereas VBM at Z point which gives an indirect band gap of