



High energy Compton scattering study of TiC and TiN

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ABSTRACT

We present the experimental Compton profiles of TiC and TiN using 661.65 keV γ -ray from 20 Ci ^{137}Cs source. To explain our experimental data on momentum densities, we have computed the theoretical profiles, energy bands and density of states using linear combination of atomic orbitals scheme within the framework of density functional theory. In addition the energy bands, density of states and Fermi surfaces using full potential linearised augmented plane wave method have also been computed. Energy bands and density of states obtained from both the theoretical models show metallic character of TiC and TiN. The anisotropies in Compton line shapes and the Fermi surface topology are discussed in term of energy bands.

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1. Introduction

Compton scattering is a well known technique to obtain the momentum density of variety of materials (see, for example, Cooper, 1985; Cooper et al., 2004; Heda and Ahuja, 2010). Compton profile, $J(p_z)$, which is the projection of electron momentum density $\rho(\mathbf{p})$ along the scattering vector (z -axis of a Cartesian coordinate system) is defined as

$$J(p_z) = \int_{p_x} \int_{p_y} \rho(\mathbf{p}) dp_x dp_y \quad (1)$$

An electron with momentum component p_z along the scattering vector shifts the photon energy from ω_1 (incident) to ω_2 (scattered). The p_z can be related to ω_1 , ω_2 and scattering angle θ using the following relation:

$$\frac{p_z}{m_0 c} = \{\omega_2 - \omega_1 + \omega_1 \omega_2 (1 - \cos \theta) / m_0 c^2\} / (\omega_1^2 + \omega_2^2 - 2\omega_1 \omega_2 \cos \theta)^{1/2} \quad (2)$$

Titanium based refractory compounds like TiC and TiN have definite technological importance due to their high melting temperature, wear resistance and extreme hardness (Zhang, 1993). Due to high melting point they are used in crucibles, nuclear reactors, aircraft shielding etc. In addition to being very hard, these refractory compounds may also exhibit metallic conductivity. Among earlier theoretical calculations, several authors (Neckel et al., 1976; Ahuja et al., 1996; Delin et al., 1996; Guemmay et al., 1997; Vines et al., 2005; Upadhyaya et al., 2005) have reported electronic band structure calculations and optical properties of these compounds. Mahapatra and Padhi (1983) have

reported Compton profile of low purity (99%) TiN sample at poor resolution (0.6 a.u.) using 59.54 keV γ -ray. The authors have compared their experiment with a crude calculation, namely, renormalized free atom model.

The purpose of the present paper is many folds

- To measure accurate Compton profiles of TiN and TiC at an intermediate resolution (0.39 a.u.).
- To compute the Compton profiles of both compounds using linear combination of atomic orbitals (LCAO) with density functional theory (DFT) and to compare them with the experimentally measured momentum densities.
- To derive energy bands, density of states (DOS) and Fermi surface topology using LCAO and full potential linearised augmented plane wave (FP-LAPW) calculations.

Accordingly, in the present paper, we report the isotropic Compton profiles of TiC and TiN using our 20 Ci ^{137}Cs γ -ray Compton spectrometer. Due to non-availability of large size single crystals (diameter 15 mm and thickness 2 mm), we could not measure the directional Compton profiles. For the band structure calculations, we have employed the CRYSTAL03 (LCAO) and Wien2k (FP-LAPW) codes. Since Wien2k code does not include the computation of the momentum densities, we have deduced the Compton profiles using DFT approach as embodied in the LCAO method.

2. Methodology

2.1. Experiment

The Compton measurements were performed using indigenous 740 G Bq (20 Ci) ^{137}Cs γ -ray Comptometer (Compton

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spectrometer). The details of experimental set-up are already published by Ahuja et al. (2006) and Heda and Ahuja (2010). The high energy γ -rays of 661.65 keV were scattered at an angle of $160 \pm 0.6^\circ$. High purity (99.99%) polycrystalline samples (pellets of thickness 3.2 mm and diameter 25 mm) of TiC and TiN were used in the present measurements. The scattered γ -rays were energy-analysed using a high purity Ge detector (Canberra, model GL0210P) and associated electronics like spectroscopy amplifier, analogue to digital converter and Accuspec 4K-channel analyser. An overall momentum-resolution of the spectrometer (Gaussian, full width at half maximum), mainly dominated by detector resolution, was found to be 0.39 a.u. The calibration of the spectrometer was checked from time-to-time using weak ^{57}Co and ^{133}Ba γ -ray source. To deduce the true Compton profiles, the raw data were corrected for background, instrumental resolution, sample absorption, detector efficiency, Compton cross-section, etc. (see Cooper, 1985; Cooper et al., 2004; Timms, 1986). The effect of multiple scattering within the sample was eradicated using Monte Carlo simulation (Felsteiner et al., 1974). The corrected profiles of TiC and TiN were normalised to 12.69 and 13.34 e^- (in the p_z range 0–7 a.u.), respectively, following the free atom Compton profiles of Biggs et al. (1975).

2.2. Theory

2.2.1. LCAO

To derive theoretical Compton profiles, energy bands and DOS, the LCAO with DFT method (Saunders et al., 2003; Towler et al., 1996) and also the hybridisation of DFT with Hartree–Fock (HF) have been used. According to the DFT formalism, the electronic energy E is regarded as a functional of the electron density ρ . The present LCAO package so called CRYSTAL03 facilitates the exchange and correlation effects and treats them approximately within the local density and generalised gradient approximation (LDA and GGA, respectively). The LDA functionals depend only on $\rho(\mathbf{r})$, while the GGA functionals depend on both $\rho(\mathbf{r})$ and its gradient $\nabla\rho(\mathbf{r})$.

In case of DFT-LDA the exchange potential of Dirac–Slater (Towler et al., 1996) and the correlation potential of Perdew and Zunger (1981) have been adopted, while in the DFT-GGA, the exchange and correlation potentials as prescribed by Becke (1988) and Perdew and Wang (1986), respectively, have been used.

In the hybrid (HF+DFT) Hamiltonian so called B3LYP (Becke three-parameter hybrid functionals), E_{XC} can be calculated as follows:

$$E_{XC} = E_X^{LDA} + 0.72 \Delta E_X^{BECKE} + 0.20(E_X^{HF} - E_X^{LDA}) + 0.19 E_C^{VWN} + 0.81 E_C^{LYP} \quad (3)$$

Here E_X^{HF} , E_X^{LDA} and E_X^{BECKE} are the exchange energies of HF, Dirac–Slater (Saunders et al., 2003) and Becke (Becke, 1988), respectively. E_C^{LYP} and E_C^{VWN} represent the correlation energies of Lee–Yang–Parr (Lee et al., 1988) and Vosko–Wilc–Nusair (Vosko et al., 1980), respectively. Therefore, the B3LYP functional involves exact exchange (through HF) with local and gradient-corrected exchange and correlation terms (through DFT).

Using the LCAO approach, $\rho(\mathbf{r})$ can be calculated as follows:

$$\rho(\mathbf{P}) = \sum_{n,occ} \sum_k^{BZ} \sum_G \delta_{p,k+G} [\chi_n(k, p)]^2 / N \quad (4)$$

$\chi_n(\mathbf{k}, p)$ is the Fourier transform of wave function derived from the *ab initio* calculations, n is the band index, \mathbf{k} is the wave vector, and N is the normalisation constant.

Since the Compton profile has a directional property, the difference between each pair of directional Compton profiles gives anisotropy in the momentum density.

The self-consistent field calculations were performed at 413 (24, 24, 24) \mathbf{k} points in the irreducible Brillouin zone (BZ) for both compounds. The all electron Gaussian basis sets used for the present computations consist of five s, four p and one d-type shells for Ti (86411/6411/3 set) and three s and two p-type shells for N (731/31 set). Three s, two p-type and one d shells (731/31/1 set) were used for C. All the basis sets for TiC and TiN have been energy optimised up to standard tolerance values using BILLY software (Saunders et al., 2003).

2.2.2. FP-LAPW

To calculate the energy bands, DOS and Fermi surfaces we have also employed FP-LAPW scheme (Blaha et al., 2001). This scheme combines the choice of the LAPW basis sets with the treatment of full potential and charge density without any shape approximation in the interstitial and the muffin-tins (MT) regions. The latest version of gradient-corrected exchange and correlation approach as suggested by Wu and Cohen (2006) has been considered. The value of $R_{MT}K_{Max}$ (multiplication of MT radius and largest amplitude of reciprocal lattice vector) was kept equal to 7 for both compounds. In case of TiC, the MT radius for Ti was kept equal to 2.15 Å while for C this was 1.91 Å. In case of TiN, the values of MT radii were 2.11 and 1.87 Å for Ti and N, respectively. The \mathbf{k} points in the present calculations were about 364 for both TiC and TiN. The convergence criterion for total energy was set to 10^{-5} Ry and maximum radial expansion l_{max} was kept equal to 10.

In both computational techniques, the lattice parameters for TiC and TiN (rock salt structure) were taken to be $a=4.328$ and 4.242 Å, respectively (Neckel et al., 1976).

3. Results and discussion

3.1. Isotropic compton profiles

In the inset of Fig. 1(a), we have shown the absolute experimental Compton profiles of TiC and TiN, normalised to the respective free atom Compton profile areas 12.69 and 13.34 e^- in the momentum range 0–7 a.u. It is seen that near $p_z=0$, the Compton profile of TiN is higher than that of TiC. To check the role of 2p electrons in electronic properties of TiC and TiN, in Fig. 1(a), we have compared the equally normalised (EN) isotropic experimental Compton profiles of TiC and TiN. It is seen that both the EN (to 13.34 e^-) profiles almost overlap, particularly in the low momentum ($p_z < 0.5$ a.u.) region. A similarity in both EN profiles in low momentum side shows a similar type of behaviour of 2p electrons of C and N. This is in contradiction to other hard materials like TaC and TaN (Fig. 1b), where N-2p electrons in TaN are more localised in momentum space leading to sharper Compton profiles (Dashora, 2010).

The difference between the convoluted spherically averaged theoretical and the experimental Compton data along with statistical accuracy ($\pm \sigma$) of the experiment are plotted in Fig. 2(a) and (b) for TiC and TiN, respectively. It is observed that in the high momentum region ($p_z \geq 4$ a.u.), all LCAO calculations show a close agreement with the experiment. It is expected because this region mainly consists of contribution from 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 show almost similar differences. In the low momentum region, the differences between theoretical and experimental Compton profiles may be due to (a) non-relativistic

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