Applied Radiation and Isotopes 70 (2012) 942–945

Contents lists available at SciVerse ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

A Compton scattering study of refractory niobium diborides

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ARTICLE INFO

Article history:
Received 12 October 2011
Accepted 28 February 2012
Available online 9 March 2012

Keywords:
Compton scattering
Band structure calculations
Transition metal compounds

ABSTRACT

Isotropic Compton profile of NbB_2 using 20 Ci ^{137}Cs Compton spectrometer is compared with our theoretical profiles obtained from the density functional theory (DFT) within the first and the second order generalized gradient approximation (GGA) and the hybridization of Hartree–Fock and DFT. A good agreement between GGA based profiles and the experiment validates the applicability of second order GGA in momentum densities. Energy bands, density of states and real space analysis of the experimental profile show metallic character of NbB_2.

1. Introduction

The transition metal diborides (TMB_2) show peculiar properties because of their high melting point, high hardness, good wear resistance, small work function, good electrical and thermal conductivity and also high chemical stability. NbB_2, which is the topic of present investigation, crystallizes in a hexagonal structure having the space group P6/mmm, wherein B atoms form graphite-like networks separated by the hexagonal layers of Nb atoms. Regarding earlier studies on the electronic and the thermal properties, Deligoz et al. (2010) have reported the structural, vibrational and thermodynamic properties for TMB_2 (TM=Zr, Nb, Mo) using the first-principles generalized gradient approximation (GGA) as implemented in the SIESTA code. Islam et al. (2006) have investigated the structural parameters, elastic constants and electronic structure of NbB_2 under pressure using gradient-corrected approximation. Electronic structure of AlB_2-type diborides and related compounds has been investigated by Paduani (2003) using the molecular cluster discrete variational method.

The electronic structure, bonding and ground state electronic properties of AlB_2-type TMB_2 have been discussed by Vajeeston et al. (2001). The band structure and the Fermi surface parameter for TMB_2 (TM=Zr, V, Nb, Ta) have been studied by Shein and Ivanovskiĭ (2001) using the self-consistent full potential linear muffin-tin orbital (FP-LMTO) method.

The cohesive properties and chemical stability of TMB_2 (TM=Ti, V, Zr, Nb) have been analyzed by Ivanovsky et al. (1998) using the FP-LMTO calculations. The authors have discussed about the cohesive properties on the basis of TM–B bond strength.

The Compton scattering is a well established tool to check the accuracy of band structure models of the ground state electron momentum density (see, for example, Cooper, 1985; Cooper et al., 2004; Heda and Ahuja, 2010). The Compton profile, $J(p_z)$, is one-dimensional projection (z-axis of the Cartesian co-ordinate system) of the electron momentum density, $\rho(\mathbf{p})$, along the direction of scattering vector. Mathematically, $J(p_z)$ is defined as

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

where p_z is the electron linear momentum along the direction of the experimental scattering vector.

This paper reports on the results of a Compton scattering measurement of NbB_2 using a high-energy (661.65 keV) ^{137}Cs γ-ray source. The first-ever experimental Compton profile of polycrystalline NbB_2 is compared with the theoretical data computed using the first and second order corrected GGA and also the hybridization of the Hartree–Fock (HF) method and the density functional theory (DFT) as embodied in the linear combination of atomic orbitals (LCAO) method. Moreover, by taking the Fourier transform, we have analyzed the experimental Compton profile in real space which enables a critical check of cross-overs of the Fermi level by energy bands and hence helps in exploring the metallic character of the material.

2. Experimental details

The Compton profile measurements were carried out by employing the high energy 20 Ci ^{137}Cs Compton spectrometer (Ahuja et al., 2006) which offers a better resolution than the ^{241}Am based Compton spectrometers. Due to the non-availability of the large size single crystals (thickness 2 mm, diameter 14 mm) of NbB_2, we have measured the isotropic Compton profile.

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doi:10.1016/j.apradiso.2012.02.119

Table 1
Experimental parameters for the Compton profile measurements of NbB_2.

Sample diameter (thickness) (cm)	Bulk density (g/cm^3)	Exposure time (h)	Integrated counts ($\times 10^7$)	Multiple scattering (-10 to $+10$ a.u.) (%)	Normalization of profile (0–$+7$ a.u.) (e^-)
1.26 (0.33)	4.41	126	1.23	11.62	21.88

The pellet made from the sample was placed vertically in scattering chamber and the scattered γ-rays were recorded by a high purity Ge detector (Canberra, GLP210) at a scattering angle of $160 \pm 0.6^{\circ}$. The energy resolution coupled with the divergence of the incident and the scattered radiations led to an overall momentum resolution of 0.38 a.u. (Note: 1 a.u. corresponds to an electron momentum of 1.99×10^{-24} m kg s^{-1}.).

Many energy-dependent corrections like absorption and multiple scattering in the sample, Compton cross-section and detector efficiency were accounted to extract the true Compton profile (see, Timms, 1989; Felsteiner et al., 1974 for data correction). Other important experimental parameters are listed in Table 1. Electronic drift was checked by monitoring the positions of 122.04 and 81.00 keV lines emerging from ^{57}Co and ^{133}Ba calibration sources. No drift greater than one channel (energy bin 0.0615 eV) of 4096-channel analyzer was found. As mentioned in Table 1, the corrected profile was normalized to $21.88e^-$ being the free atom Compton profile area (Biggs et al., 1975) in the momentum range 0–7 a.u.

3. LCAO model

On the theoretical side, we have used the LCAO scheme (Dovesi et al., 2005, 2009) which includes various approximations like HF, the first/second order GGA, the hybridization of HF and DFT, etc. In case of GGA (Perdew et al., 1996), the gradient of electron density is used to describe the inhomogeneous systems (atoms and molecules).

In the latest LCAO based quantum mechanical model, a more accurate second order GGA so-called the SOGGA (Zhao and Truhlar, 2008) enforces a complete restoration of the gradient expansion for both the exchange and the correlation to second order. In the case of SOGGA, the exchange enhancement factor F_x^{SOGGA} is taken as half-and-half mixing of the PBE (Perdew et al., 1996) and the revised PBE (RPBE) exchange functional (Hammer et al., 1999). Mathematically

$$F_x^{SOGGA} = 1 + \kappa - \frac{\kappa^2}{2(\kappa + \mu s^2)} - \frac{\kappa}{2}\ e^{-\mu s^2/\kappa} \tag{2}$$

Here s is the reduced density gradient. The parameters μ and κ are defined as $\mu = \mu^{GE} = 0.12346$ and $\kappa = 0.552$, determined by enforcing a tighter Lieb and Oxford bound (Zhao and Truhlar, 2008).

We have used the PBE correlation functional in the SOGGA because the PBE correlation functional respects the gradient expansion for the correlation and it performs equally well for the finite and infinite systems. Therefore, unlike other GGAs (Dovesi et al., 2005, 2009), SOGGA functional completely restores the gradient expansion for both the exchange and the correlation through the second order. To retain a similar correlation function as used in SOGGA, we have also used the PBE correlation function (Perdew et al., 1996) in GGA while the exchange potential is based on the prescriptions of Becke (1988).

It is known that HF approximation predicts the correct ground states for strongly correlated insulators due to the lack of self-interaction, while the energy gaps are always overestimated due to an inadequate consideration of the correlation effects. Therefore, to check the role of HF+DFT functionals, we have also used the hybrid functional of HF and DFT namely B3LYP (Becke three-parameter hybrid functional combined with Lee–Yang–Parr correlation functional). In the B3LYP, the exchange-correlation energy E_{xc}^{B3LYP} is expressed as

$$E_{xc}^{B3LYP} = (1-A)\left(E_x^{LDA} + B \times \Delta E_x^{BECKE}\right) + A \times E_x^{HF} + (1-C)E_c^{VWN} + C \times E_c^{LYP}. \tag{3}$$

Here E_x^{LDA} is the exchange contribution from the Dirac–Slater functional (Dovesi et al., 2009) and E_c^{VWN} is the correlation energy deduced from the Vosko–Wilk–Nusair parameterization (Vosko et al., 1980) of the Ceperley–Alder free electron gas correlation results. ΔE_x^{BECKE} stands for Becke's gradient correction to the exchange functional (Becke, 1988) and the E_c^{LYP} represents the Lee–Yang–Parr correlation energy (Lee et al., 1988). In Eq. (3), we have taken the weight parameters as $A=0.2$, $B=0.9$, and $C=0.81$ (standard values).

The all-electron Gaussian type basis sets for Nb and B atoms were taken from http://www.tcm.phy.cam.ac.in.uk/~mdt20/basis-sets. To achieve the ground state of the system, the basis sets were energy optimized using the BILLY software (Dovesi et al., 2009). The lattice constants for the hexagonal NbB_2 were taken to be $a=b=3.116$ and $c=3.264$ Å (Islam et al., 2006). The self-consistent field calculations were performed at 845 ***k***-points in the irreducible Brillouin zone.

4. Results and discussion

In Fig. 1 we have presented the absolute experimental and the convoluted theoretical Compton profiles of NbB_2. The theoretical profiles were convoluted with the resolution function (Gaussian full width at half maximum of 0.38 a.u.) to incorporate the broadening effects in the theoretical data. A small difference is observed in all the theoretical models (HF, B3LYP and first and second order GGA). In the inset of Fig. 1, we have enlarged the theoretical Compton profiles within the momentum region 0–0.3 a.u. to see more clearly the differences among all the theoretical calculations. From the inset, it is observed that the HF theory gives the highest value of $J(p_z)$

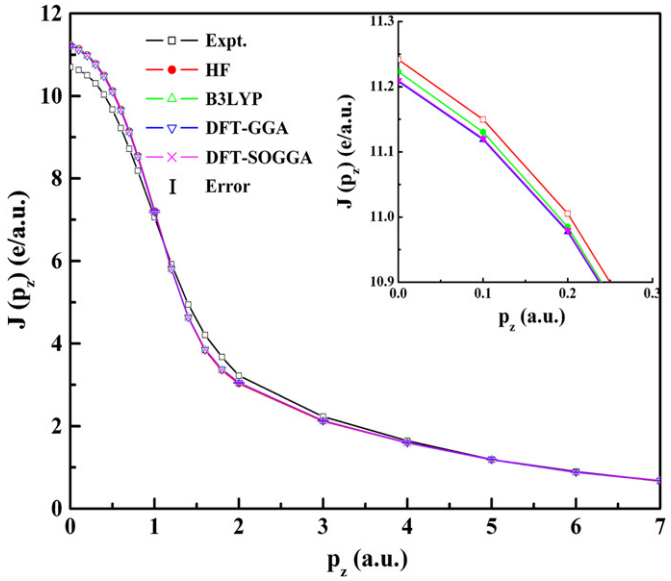

Fig. 1. Absolute experimental and theoretical (convoluted) Compton profiles of NbB_2. In the inset, the profiles are expanded in the region 0–0.3 a.u. The experimental error ($\pm\sigma$) is within the size of symbols used. Solid lines are drawn to guide the eyes.