



Radiation Sources and Applications

Electronic structure of CaCO₃: A Compton scattering studyS.F. Mohammed^a, F.M. Mohammad^b, Jagrati Sahariya^{c,*}, H.S. Mund^c, K.C. Bhamu^c, B.L. Ahuja^c^a Department of Physics, College of Education, University of Tikrit, Tikrit, Iraq^b Department of Physics, College of Science, University of Tikrit, Tikrit, Iraq^c Department of Physics, ML Sukhadia University, Udaipur-313001, India

H I G H L I G H T S

- ▶ Experimental Compton profile (CP) of CaCO₃ is measured using ²⁴¹Am source.
- ▶ Experimental CP is compared with DFT profiles.
- ▶ Energy bands and density of states are also computed using DFT schemes.
- ▶ Band gap is deduced from the different DFT schemes.

A R T I C L E I N F O

Article history:

Received 17 August 2012

Received in revised form

3 October 2012

Accepted 8 October 2012

Available online 17 October 2012

Keywords:

X-ray scattering

Band structure calculations

Density functional theory

A B S T R A C T

In the present work, we have studied electron momentum density of CaCO₃ using a Compton scattering technique. The experiment has been performed using a 100 mCi ²⁴¹Am (59.54 keV) Compton spectrometer. The experimental data have been interpreted in terms of theoretical Compton profiles. To compute the theoretical momentum densities, energy bands and density of states, we have used linear combination of atomic orbitals method as embodied in CRYSTAL09 code. We have used local density approximation, generalized gradient approximation (GGA) and second order GGA (SOGGA) within the frame work of density functional theory. It is seen that the GGA gives a better agreement with the experimental data than other approximations. We have also discussed the energy bands and density of states of CaCO₃.

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1. Introduction

Calcium carbonate (CaCO₃) is one of the most abundant mineral and continues to attract the interest of the scientific community. It is found in three polymorphs namely calcite, aragonite and vaterite, among which the calcite is the most stable thermodynamic form at room temperature and ambient pressure. It is a wide band gap insulator and is of great interest due to its physical properties and suitability upon wide-range technological and industrial (plastic, rubbers, papers, paints, etc.) applications (see, for example, Dervos et al., 2005). Regarding earlier studies on the electronic structure of CaCO₃, Baer and Blanchard (1993) have studied the cleavage face of single-crystal calcite using reflection electron energy-loss spectroscopy, X-ray photoelectron spectroscopy, and electron-stimulated desorption method. Skinner et al. (1994) have reported the theoretical study on the electronic and structural properties of CaCO₃. Valenzano et al. (2006) have studied the influence of the basis sets and the choice of different Hamiltonians on structural properties and dielectric

function using CRYSTAL03 code. Medeiros et al. (2007) have discussed the electronic and optical properties of CaCO₃ within density functional theory (DFT). Electronic, optical and bonding properties in calcite have been reported by Hossain et al. (2009) using DFT. Dadkhah et al. (2012) have synthesized and characterized the nano-size CaCO₃ using thermal treatment and solid state methods.

Compton spectroscopy is a powerful and sensitive experimental tool to study the electron momentum distribution in materials (Cooper, 1985; Cooper et al., 2004). Using this technique, the chemical properties can be correlated with the electronic structure through the electron momentum density $\rho(\mathbf{p})$. The measured one-dimensional quantity, called Compton profile (CP) $J(p_z)$, is the projection of the three-dimensional momentum density $\rho(\mathbf{p})$ onto the scattering vector (parallel to p_z). Mathematically

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

where the integration is taken over a constant p_z plane and the $\rho(\mathbf{p})$ is given as

$$\rho(\mathbf{p}) = \frac{1}{(2\pi)^3} \sum_{occ} \left| \int \psi(r) \exp(-i\mathbf{p}r) dr \right|^2 \quad (2)$$

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Here $\Psi(r)$ is the electron wave functions and the summation extends overall the occupied state. Eq. (1) is valid within the impulse approximation (IA) (Kaplan et al., 2003). According to IA, an interaction between photon and electron is so fast that the electron does not have any chance to move in the potential well. Thus the bound and moving electron can be respectively approximated as free and at rest.

The main objectives of the present work were to: (i) measure the first-ever isotropic CP of CaCO_3 using 59.54 keV γ -radiations, (ii) compute the theoretical CPs of CaCO_3 using linear combination of atomic orbitals (LCAO), (iii) compute the LCAO based energy bands and density of states (DOS) and (iv) deduce the band gap in CaCO_3 and compare it with the available data.

2. Experiment

For the measurement of CP of CaCO_3 , we have employed a 100 mCi ^{241}Am Compton spectrometer (Ahuja et al., 2007; Ahuja and Heda, 2007). Due to non-availability of large size single crystals (12 mm diameter and 2 mm thickness), we have measured the isotropic CP of CaCO_3 . The γ -rays of energy 59.54 keV were incident on the sample (pellet of thickness 0.31 cm and diameter 2.03 cm). The scattered photons at scattering angle of $165 \pm 1.5^\circ$ were energy analyzed by a high purity Ge detector, which was associated with standard electronics like spectroscopy amplifier, analog to digital converter, multi-channel analyzer. The overall momentum resolution of the spectrometer was found to be 0.55 a.u. (Gaussian full width at half maximum). To extract the true CP, the raw data were corrected for several systematic corrections like background, instrumental resolution (limited to stripping off the low energy tail), sample absorption, Compton cross-section and multiple scattering (Felsteiner et al., 1974; Cooper et al., 2004). For the deduction of the background from the raw data, the background was measured separately after removing the sample from the sample holder. Finally, the experimental profile was normalized to have an area of $23.73 e^-$, which is equal to that of the free atom Compton profile area in the momentum range 0–7 a.u. (Biggs et al., 1975).

3. Theory

On the theoretical side, we have used the CRYSTAL09 code (LCAO method) of Torino group (Dovesi et al., 2005, 2009) to deduce the theoretical CPs of CaCO_3 . In the LCAO approach, the crystalline orbitals are expanded in terms of the basis sets of the atomic orbitals. This code facilitates the DFT calculations within the local density approximation (LDA), generalized gradient approximation (GGA) and second order corrected GGA (so called SOGGA). In the DFT approach, the exchange-correlation potential operator (V_{XC}) is derived from the exchange-correlation energy per particle in a uniform electron gas. Mathematically

$$V_{XC}(\mathbf{r}) = \frac{\partial E_{XC}[\rho]}{\partial \rho(\mathbf{r})} \quad (3)$$

where E_{XC} is the exchange-correlation density functional energy and ρ is the electron density at position \mathbf{r} . In the LDA and GGA, the E_{XC} is defined as

$$E_{XC}^{LDA}[\rho] = \int \rho e_{XC}^{LDA}[\rho] d^3r \quad (4)$$

and

$$E_{XC}^{GGA}[\rho] = \int \rho e_{XC}^{GGA}[\rho] F_X(s) d^3r \quad (5)$$

where s is the reduced density gradient, e_{XC}^{LDA} is the exchange energy density per particle for a homogeneous electron gas and

the $F_X(s)$ is known as the exchange enhancement factor. In case of PBE (Perdew et al., 1996), the $F_X(s)$ for exchange is given by

$$F_X(s) = 1 + \kappa - \frac{\kappa^2}{\kappa + \mu s^2} \quad (6)$$

where the constants $\mu = 0.2195$ and $\kappa = 0.804$.

Further, the correlation energy takes the following form:

$$E_c^{GGA}[\rho] = \int \rho \{ \epsilon_c^{LDA}(\rho) + \beta_c t^2 \} d^3r \quad (7)$$

Here ϵ_c^{LDA} , β_c and t correspond to the correlation energy density for a uniform electron gas, the coefficient for gradient expansion of the correlation energy and the reduced density gradient, respectively.

To check the effect of the second order exchange and correlation and the tighter Lieb–Oxford bound, we have also considered the recently suggested second order GGA (so called SOGGA) functional (Zhao and Truhlar, 2008). In the SOGGA, the $F_X(s)$ for exchange is given as

$$F_X^{SOGGA}(s) = 1 + \kappa + \frac{1}{2} \left(\frac{\kappa^2}{\kappa + \mu s^2} \right) - \frac{\kappa}{2} \left(e^{-(\mu/\kappa)s^2} \right) \quad (8)$$

In Eq. (8), the $F_X^{SOGGA}(s)$ can be explained as a equal (50% each) mixing of the PBE (Perdew et al., 1996) and the RPBE (revised PBE functional, Hammer et al., 1999). In the SOGGA, the value of κ was taken as 0.552 (Zhao and Truhlar, 2008) which is very low in comparison to other GGA exchange functionals and results to tightening in the Lieb–Oxford bound. The value of μ was set to 0.21591. The use of PBE correlation functional in the SOGGA respects the gradient expansion for the correlation. In the present computations, we have taken the exchange of Dirac–Slater for the LDA scheme (Towler et al., 1996) and that of Wu and Cohen (2006) for the GGA scheme. The PBE correlation function (Perdew et al., 1996) has been used in all the schemes namely LDA, GGA and SOGGA.

In the present computation, the all-electron basis sets for Ca, C and O were taken from http://www.tcm.phy.cam.ac.uk/~mdt26/basis_sets. Following the default tolerances in the CRYSTAL09 code, the SCF calculations have been performed for 189 k points in the irreducible Brillouin zone. For the valence electrons, the momentum density function was calculated from the sum of squared moduli of all electron wave-functions in momentum-space.

Table 1

Experimental and convoluted theoretical Compton profiles of CaCO_3 . Experimental errors ($\pm \sigma$) at some points are also shown.

p_z (a.u.)	$J(p_z)$ (e/a.u.)			
	DFT–SOGGA	DFT–GGA	DFT–LDA	Experiment
0.00	15.801	15.743	15.884	13.812 \pm 0.026
0.10	15.411	15.319	15.491	13.779
0.20	14.940	14.820	15.015	13.617
0.30	14.482	14.336	14.551	13.369
0.40	13.995	13.825	14.057	13.011
0.50	13.453	13.261	13.506	12.517
0.60	12.851	12.647	12.893	11.956
0.70	12.183	11.981	12.213	11.405
0.80	11.441	11.261	11.460	10.831
1.00	9.747	9.669	9.743	9.392 \pm 0.022
1.20	7.913	7.975	7.895	7.954
1.40	6.193	6.361	6.171	6.532
1.60	4.779	4.980	4.760	5.351
1.80	3.722	3.895	3.710	4.308
2.00	2.966	3.088	2.960	3.581 \pm 0.013
3.00	1.385	1.403	1.391	1.653 \pm 0.008
4.00	0.891	0.897	0.893	1.001 \pm 0.007
5.00	0.611	0.613	0.612	0.622 \pm 0.006
6.00	0.425	0.426	0.426	0.423 \pm 0.005
7.00	0.309	0.310	0.309	0.318 \pm 0.004

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