Topology of Electron Density of Cadmium Telluride Determined from Relief and Contour Plots

(Topologi Ketumpatan Elektron Kadmium Telurida daripada Lakaran Timbul dan Lakaran Kontur)

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ABSTRACT

The topology of the electron density yields a faithful and a reliable mapping of the concepts of atoms, molecular structure, bonds and structure, besides providing the basis for a theory of structural stability. In quantum mechanics and in particular quantum chemistry, the electron density is a measure of the probability of an electron occupying an infinitesimal element of space surrounding any given point. Contour plots of electron density distribution of cadmiun telluride (CdTe) were obtained using the density functional theory (DFT) method and were used as the basis to qualitatively study the bond, structure and stability of the molecule when it is in bulk. We looked at the way the electron density, ρ of CdTe defines the gradient field and hence the bonding type. We identified the bond paths that coincide with the contours of electron sharing. These bond paths indicated that the molecule was slightly covalent. Our topological analysis led us to conclude that CdTe was an n-type semiconductor with covalent bond and slight ionic character.

Keywords: Bonding; DFT; electron density; molecular structure; topology

ABSTRAK

Topologi ketumpatan elektron memberikan maklumat yang sahih dan pemetaan yang baik bagi menerangkan konsep atom, struktur molekul, ikatan dan struktur selain daripada memberikan asas kepada teori kestabilan struktur. Dalam mekanik kuantum, khususnya kimia kuantum, ketumpatan elektron memberikan kiraan keberangkalian sesuatu elektron menghuni satu ruang terhingga, di sekeliling sesuatu titik. Lakaran kontour taburan ketumpatan elektron kadmium telurid telah didapati dengan menggunakan kaedah teori ketumpatan fungsian (DFT) dan telah diguna sebagai asas untuk mengkaji ikatan, struktur dan kestabilan molekul dalam keadaan pukal. Penyelidikan ke atas taburan ketumpatan, ρ CdTe yang membentuk medan kecerunan membolehkan kita menentukan jenis ikatan. Kami mengenal pasti laluan ikatan antara atom Cd dan Te yang memerihalkan perkongsian elektron. Laluan ikatan ini menandakan molekul tersebut memiliki ikatan kovalen yang lemah. Analisis topologi merumuskan CdTe sememangnya semikonduktor jenis-n yang memiliki ikatan kovalen dengan sedikit ikatan ionik.

Kata kunci: DFT; ikatan; ketumpatan elektron; struktur molekul; topologi

INTRODUCTION

The concept of topology has been used to characterize the nature of bonding of a variety of bonds based on *ab initio* valence bond methods. It has been applied to the topology of charge density, especially electrons, for the purpose of analyzing the bonding properties of bulk solids. The properties of a solid can usually be predicted from the valence and bonding preferences of its constituent atoms. Elaborate review on the application of topology on the electron density plots had been done by Bader (1995).

Four main bonding types are commonly found in semiconductor solids: ionic, covalent, metallic and molecular. There are many examples of solids that have a single bonding type, while other solids have a mixture of types, such as covalent and metallic or covalent and ionic.

In quantum mechanics, especially in many-body problems, the manipulation of the anti-symmetric eigen functions has become extremely unmanageable when the number of electrons involved is large. For N electrons, the wave function can be written as $\psi(r_1, r_2, \ldots r_N) = A \Pi_{i=1}^{N} \psi(r_1)$, with A being the normalization constant. The inclusion of spin degree of freedom makes the total anti-symmetric wave function worse and hence electron density approach which is more elegant is particularly more useful. The density functional theory (DFT) is a theory on solving many-body problems using the electron density functional instead of the conventional total wave function approach. When coupled with high performance modern computational tools, DFT is capable to describe the ground state electronic structure, mechanical and optical properties and interatomic forces in systems containing hundreds and sometimes thousands of atoms (Blaha et al. 2001).

The electronic density, $\rho(r)$ is a measure of the probability of an electron occupying an infinitesimal element of space surrounding any given point, r. From its definition, the electron density is a non-negative function integrating to the total number of electrons. The density is determined, through definition, by the normalized

N-electron wave function which itself depends upon 4N variables (3N spatial and N spin coordinates). Conversely, the density determines the wave function modulo a phase factor, providing the formal foundation of density functional theory (Lieb 1983). The electron density $\rho(r)$ is defined as $\rho(r) = \int_\tau \psi^* \psi d\tau$. The ground state electronic density of an atom is conjectured to be a monotonically decaying function of the distance from the nucleus (Ayers & Parr 2003). In a multi-electron atom or molecule, only the total electron density can be experimentally observed or calculated and it is this total electron density with which we are concerned in this paper.

Contour plots and relief maps of unit cell of the molecules are often obtained computationally so as to reveal the structure and bonding types of the materials. Isodensity contours in a chosen cell plane indicate the congregation of charge around a particular nuclei, whereas the bond paths (lines along the top of the density ridges between nuclei) coincide with bonds as they are normally drawn.

It was the objective of this work to analyze the distribution of $\rho(r)$ topologically, from the relief and contour maps of CdTe and hence identifying the bond, structure and stability of the molecule.

THE LAPLACIAN AND THE ASSOCIATED BOND

Analytical and quantitative topological analysis of the relief and contour plots of the electron density usually employ the application of the Laplacian. The interatomic bonds are classified as closed shell or shared, if the Laplacian of the electron density at the critical point is positive or negative, respectively.

The covalent component of the Laplacian at the bond critical point is found to be largely negative for classical covalent bonds. In contrast, for charge-shift bonds, the covalent part of the Laplacian is small or positive, in agreement with the weakly attractive or repulsive character of the covalent interaction in these bonds. On the other hand, the resonance component of the Laplacian is always negative or nearly zero and it increases in absolute value with the charge-shift character of the bond, in agreement with the decrease of kinetic energy associated with covalent–ionic mixing. A new interpretation of the topology of the total density at the bond critical point is proposed to characterize covalent, ionic and charge-shift bonding from the density point of view. Detailed analysis of chemical bonding of a system based on the topology of the quantum charge density can be found in Bader (1990).

COMPUTATIONAL DETAILS

The DFT computation of the electron density is provided by the linearized augmented plane wave (LAPW) (Madsen at al. 2001) method using WIEN2k code (Blaha et al. 2001). The LAPW is among the more accurate method to investigate the electronic properties via the DFT implementation. The exchange-correlation potential of the many body-problem calculation will be treated by local density approximation (LDA) parameterized by Perdew and Wang (1992) and the latest by Perdew et al. (1996). Many researchers has calculated the exchange-correlation contribution by using LDA, corrected with generalized gradient approximation. However, in this work we concentrate on the LDA as our chosen calculation mode to produce the relief and contour plots of CdTe.

The type of lattice for CdTe we considered is the face centered cubic FCC (space group F-43m) with position of Cd as the center at (0, 0, 0) and Te at (0.5, 0.5, 0.5). The lattice parameter is similar to that of FFC in InAs. We choose experimental value lattice constant $a = 6.424$Å (Gordon et al. 1999). In this computation, we treated the unit cell with regions divided into interstitial region and non-overlapping muffin tin spheres. We used the plane waves in the interstitial field region and linear combination of radial functions multiplied by spherical harmonics in non-overlapping muffin-tin spheres. We have performed convergence studies and determined the optimum value for cut-off parameter $R_{MT}K_{max} = 6.0$, where R_{MT} is the smallest atomic sphere radius in the unit cell and K_{max} is the maximal value of the reciprocal lattice vector.

The k-points for this computation were 1000 (10×10×10) and the separation energy of the core and valence states was equal to -9.0 Ry. This was done to ensure that the charge will leak the atomic sphere (Blaha et al. 2001). We have calculated and produced a contour and relief maps of bulk CdTe. The cadmium and tellurium atoms in their electronic configuration, are [Kr] $4d^{10}$ $5s^2$, [Kr] $4d^{10}$ $5s^2$ $5p^4$, respectively. Other parameters of the computation is found in Table 1.

RESULTS AND ANALYSIS

The relief map of the electron density of CdTe in the 110 plane, is shown in Figure 1 and the macro topology of the relief map almost conforms to the zinc-blende lattice structure with face-centered cubic sublattice. We have performed both the relativistic and non- relativistic computation as described by Cottenier (2009) to produce

TABLE 1. Values of parameters used in the computation

Characteristic	Data
Latice type	*Face centered cubic, FCC*
With	$a=b=c = 6.48$ Å
Ltice angle α, β and γ ($\alpha=\beta=\gamma$)	90°
Atomic Cd	position (0,0,0), NPT = 781, RMT = 2.35, R0 = 0.00001
Atomic Te	Position (0.25,0.25,0.25), NPT = 781, RMT = 2.55, R0 = 0.00001

the relief and contour plots. We have done similar computational approach using the same computational parameters to compute the density of states and energy band of the same compound and we were satisfied with the results (Othman et al. 2012).

In the relief plots, the two computational approaches gave no obvious visual difference. However the contour plots of relativistic and non-relativistic computation do show differences as shown in Figure 3.

In order to investigate the bonding properties of CdTe, the total valence charge distribution is shown in Figures 3(a) and 3(b). The figures show that the electrons have a higher density at the cations Te as compared with the anion Cd. The high gradient field in almost spherical region around each Te atom arises from the tightly held core electrons. Topological analysis (Figure 3) of the contour plots confirmed this, with the critical points of charge distribution in the neigbourhood of energetically stable Te nuclei are of rank about 3.

When we associate the dominant forms exhibited by the electron density $\rho(r)$ and its classification in terms of its critical points, at the positions of the nuclei as in the relief and contour plots of Figures 1, 2 and 3, the associated gradient vector field of the electron density leads to the theory of structure and structural stability (Bader & Beddall 1972). The structural stability is associated with the nuclear configuration.

In the contour plot of the CdTe, the gradient of the vector field of the electron density with the relativistic effect calculation in Figure 3(a) from the critical point was steeper than the gradient vector field of the one without the relativistic effect. With the critical points being at the cations Te, this indicated that the ionic bonding nature of the CdTe, with Te being more electronegative.

Walter and Cohen (1971) suggested that the similarity of chemical bonding in zinc selenide (ZnSe) with that of CdTe, (ionic Zn and Se having 2+ and 6+ charges, respectively) with the Te atom has a larger number of positive charge. Thus more electrons tend to congregate at the critical points of ionic Te as demonstrated by the topology of the contour plot of Figure 3 and relief maps of Figures 1 and 2. Accordingly, the unequal sharing of charge between the Cd atom and Te atom, with slightly more to the anion Te makes the bonding to be ionic. Besides being ionic, Figures 3(a) and 3(b) also
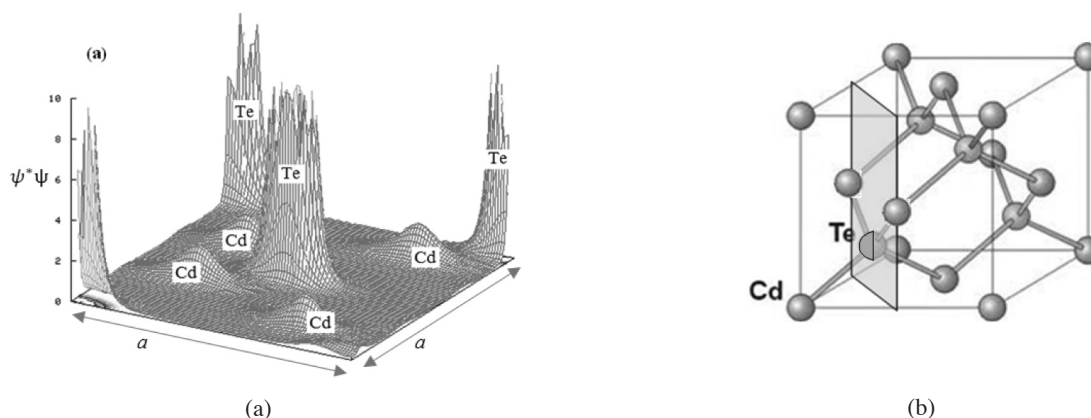

FIGURE 1. a) relief map of the Laplacian of the electron density for CdTe, in the plane containing Te atoms and b) Zincblende CdTe with (110) plane
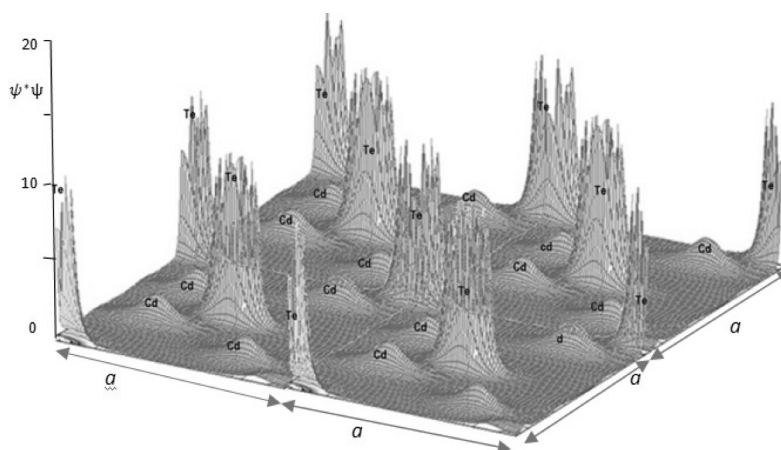

FIGURE 2. A relief map of the Laplacian of the electron density for CdTe, in the plane containing Te atoms taken at two unit cells
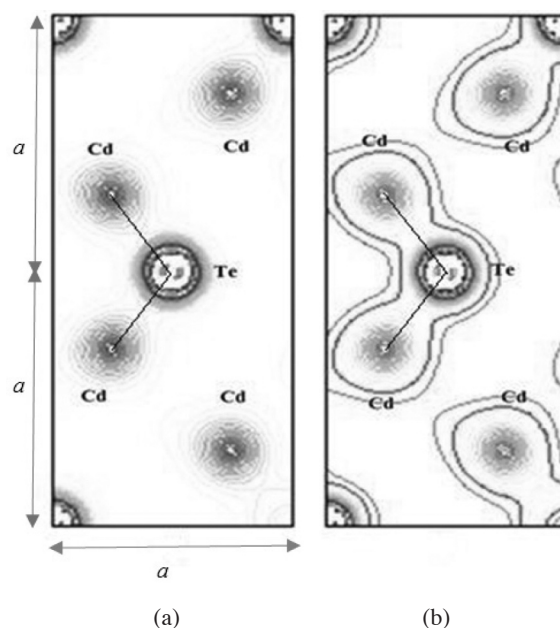
(a)   (b)

FIGURE 3. A contour plot of electron density for CdTe in the (110) plane containing the Te atom. (a) with the relativistic effect and (b) without the relativistic effect. The lines connecting the Cd and Te nuclei are the bonding paths

show the bond paths (the lines along the top of density ridges between the Te and Cd nuclei) that coincide with the contours of electron sharing. These bond paths indicate the molecule is slightly covalent.

On another case where the field gradient of the charge density with relativistic effect is steeper than the non-relativistic (Figures 3(a) and 3(b)) and hence the electron density, attributed to the dependence of the charge density to the effective Bohr radius, a_o. With the relativistic effect taken into account, the effective Bohr radius, a_o is shortened.

CONCLUSION

We have employed the gradient fields of the electron density plots to analytically study the bonding type and structural nature of the compound. The density plots were both presented in relief and contour forms using the DFT approach. The topological study thus confirms the ionic and covalent bonding of the compound.

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