

DOI: <https://doi.org/10.24297/jap.v23i.9712>**Energy Band Structures of Group IV Elements Including Fullerene, Graphite, and Diamond Using the Quantum Quantitative Model**

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Abstract

The crystalline accommodation law quantum quantitative model (CALQQM) gives the exact relation between the crystal structure and the electronic energy band structure. In addition, it could explain successfully the superconductivity at room temperature, energy levels, and work functions of materials. This model opens the way to reconsider the energy band structures of all crystalline materials according to it. Therefore, we aim to use CALQQM to determine the electronic band structures of group IV elements including their allotropes such as fullerene, graphite, diamond, and α -Sn. Here, we show a great success in determining the band structures of these elements. CALQQM predicted with high accuracy their electronic properties such as work functions, energy gaps, and spectra in a good agreement with experimental results. A perfect agreement between the calculated value (4.69 eV) and experimental value (4.69 eV) of the work function of fullerene 60 was obtained.

Keywords Tarek's law, Work function, Crystalline Accommodation Law, Quantum Quantitative Model.

1. Introduction

Most of the physical properties (electrical, magnetic, electronic, and optical) of materials can be obtained from their true electronic energy band structures. The electronic properties such as work function, energy gap, emission, and absorption spectra are obtained directly from electronic energy band structure (energy levels). In the literature, [1-6] all the energy states are contained in only one Brillouin zone. In addition, these states vary continuously from point to point and from negative to zero to positive inside the zone. This contradicts the principle of quantum physics and the concept of Brillouin zone. The continuous variation in energy levels means a continuous variation in the energy gaps, which contradicts the constant energy gap for each material. In addition, no one can determine the work functions from such electronic structures. Moreover, the relation between the energy band structure and crystal structure is not known clearly. Brillouin zone is a primitive cell in k-space or energy space, which means that it accommodates only one quantum state. The crystalline accommodation law quantum quantitative model (CALQQM)[7] gives the exact relation between the crystal structure and the electronic energy band structure of materials. CALQQM could explain successfully the superconductivity at room temperature, energy levels, and the work functions of materials. This model opens the way to reconsider the energy band structures of all crystalline materials according to it. This model is based on the crystalline accommodation law (CAL) [8]. Therefore, this model is called crystalline accommodation law quantum quantitative model. CAL succeeded in explaining the crystalline structure of crystalline materials [8-10]. Tarek's law [7] gives the energy band structures of both valence band (VB) and conduction band (CB) as the following;

$$E_N = T (NV_B)^{2/3} \quad (1)$$

where T is Tarek's constant = 1.46622 eV \AA^2 , V_B is the volume of Brillouin zone, $N = 0.5, 1, 1.5, 2, 2.5, \dots, F, \dots, V$

F is label of the Fermi level E_F and V is the label of the internal vacuum level E_V .

Tarek's law can determine accurately the energy levels of the electrons in the solids and can predict successfully the work functions of materials [7].

Group IV elements such as Si, Ge, C, Sn and their allotropes such as graphite, diamond, fullerene and α -Sn have important electronic applications and most of the electronic devices are based on these materials. Therefore, the aim of the present work is to use CALQQM and Tarek's law to determine the band structures and work functions of group IV elements including the allotropes of carbon and the allotropes of tin such as; graphite (C-hex.), diamond (C-dia.), fullerene (C-60), and α -Sn.

2. Computational Methodology

The computations are based on CALQQM using XRD data from ICDD [11] as given in Table 1. The basics of CALQQM are the following; Brillouin zone (BZ) is a primitive cell in the energy space, which can accommodate only one quantum state, and this state has two levels for the two electrons of opposite spins. The higher level of the quantum state is for the electron with spin-up and the lower level is for the electron with spin-down. In addition, the Fermi level (E_F) is the highest occupied level in the VB. The internal vacuum level (E_V) is the highest level in the CB. The band unit (BU) contains both VB and CB as the following;

$$BU = N_U BZ = N_F BZ + N_C BZ \quad (2)$$



where,

$$\mathbf{N}_U = \mathbf{N}_F + \mathbf{N}_C \quad (3)$$

\mathbf{N}_F is the number of filled BZs in the VB, \mathbf{N}_C is the number of BZs in the CB and \mathbf{N}_U is the total number of BZs in the BU. Moreover, the number of BZs per cm^3 is given by \mathbf{N}_B and the number of BUs per cm^3 (\mathbf{N}_{BU}) is given by;

$$\mathbf{N}_{BU} = \mathbf{N}_B / \mathbf{N}_U \quad (4)$$

Table 1 Crystal structure and lattice parameters of group IV elements.

Element	Card No.	Cry. St.	a(Å)	c(Å)
C-hex	80-0004	Hex. P6 ₃ mc	2.49	4.144
C-dia	89-3441	Cubic Fd $\bar{3}$ m	3.56658	
C-60	82-0505	Cubic Fm $\bar{3}$	14.26	
α -Sn	86-2266	Cubic Fd $\bar{3}$ m	6.4892	
β -Sn	89-4898	Tetr. I4 ₁ /amd	5.831	3.182
Si	89-5012	Cubic Fm $\bar{3}$ m	5.43086	
Ge	89-2768	Cubic Fm $\bar{3}$ m	5.656	

3. Results and Discussion

3.1. The Calculated Band Structure

Fig. 1 shows the energy band structures of C-hex., C-dia., C-60, α -Sn, β -Sn, Si and Ge. For graphite (C-hex.), VB contains 8 BZs and CB contains 2 BZs and BU contains 10 BZs as the following; BU = 8BZ + 2BZ. In addition it is found that $E_F = 29.26$ eV and $E_V = 33.96$ eV. For diamond (C-dia.) VB contains 4 BZs and CB contains 1 BZ and BU contains 5 BZs; BU = 4BZ + 1BZ, $E_F = 28.89$ eV and $E_V = 33.53$ eV. For fullerene (C-60), VB contains 120 BZs and CB contains 51.5 BZs and BU contains 171.5 BZs; BU = 120BZ + 51.5BZ, $E_F = 17.45$ eV and $E_V = 22.14$ eV. For gray tin (α -Sn) VB contains 4 BZs and CB contains 3.5 BZs and BU contains 7.5 BZs; BU = 4BZ + 3.5BZ, $E_F = 8.72$ eV and $E_V = 13.27$ eV. For white tin (β -Sn,) VB contains 4 BZs and CB contains 3 BZs and the BU contains 7 BZ's; BU = 4BZ + 3BZ, $E_F = 10.19$ eV and $E_V = 14.79$ eV. For silicon (Si), VB contains 4 BZs and CB contains 2.5 BZs and BU contains 6.5 BZs; BU = 4BZ + 6.5BZ, $E_F = 12.46$ eV and $E_V = 17.22$ eV. Finally, for germanium (Ge), VB contains 4 BZs and CB contains 3 BZs and BU contains 7 BZs; BU = 4BZ + 3BZ, $E_F = 11.48$ eV and $E_V = 16.68$ eV.

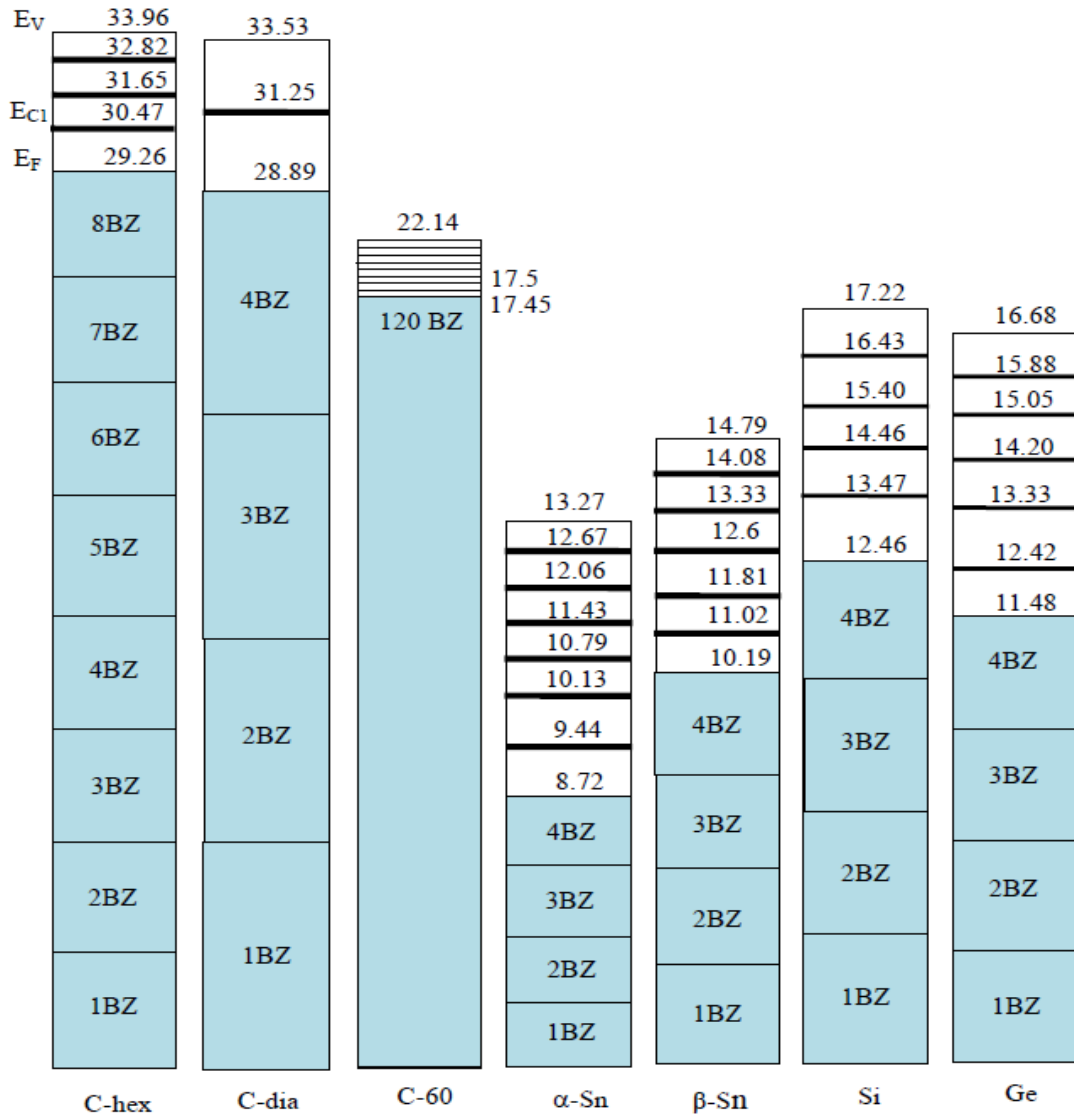


Fig. 1: The band structures of group IV elements including their allotropes.

The details of the band structures are given in Table 2. The largest volume of quantum state V_B was found for diamond, 21.86 \AA^{-3} . In addition, diamond has the largest number of BUs per cm^3 , $N_{BU} = 77.6 \times 10^{20} \text{ cm}^{-3}$. This indicates that diamond can be converted into superconducting state either by compression or by cooling to the critical volume of primitive cell. This predicted behavior of diamond was confirmed experimentally by [12], which observed superconductivity of hole-doped diamond at high pressure and temperature. Fullerene has the smallest volume of quantum state, 0.3421 \AA^{-3} . In addition, fullerene has the smallest number of BUs per cm^3 , $N_{BU} = 0.8 \times 10^{20} \text{ cm}^{-3}$.

Table 2: The detail of the band structures of group IV elements and their allotropes.

Element	V_P \AA^3	V_B \AA^{-3}	N_F	N_C	N_U	E_F eV	E_V eV	N_B $\times 10^{22}$ cm^{-3}	N_{BU} $\times 10^{20}$ cm^{-3}
C-hex.	22.25	11.14	8	2	10	29.26	33.96	4.49	44.9
C-dia.	11.34	21.86	4	1	5	28.89	33.53	8.81	77.6
C-60	724.23	0.3421	120	51.5	171.5	17.45	22.14	0.138	0.8
α-Sn	68.31	3.63	4	3.5	8.5	8.72	13.27	1.46	17.1



β -Sn	54.09	4.58	4	3	7	10.19	14.79	1.84	26
Si	40.04	6.19	4	2.5	6.5	12.46	17.22	2.49	38.3
Ge	45.23	5.48	4	3	7	11.48	16.68	2.21	31.5

3.2. Experimental Verification

Work Function

In literature, the work function (WF) and E_V are considered as surface phenomena and there is no model can predict successfully the work functions of materials. One of the great successes of CALQQM is the accepted physical definition of E_V that considers it belongs to the band structure of materials. E_V is defined as the highest level in the CB. If the electron in this level acquires any energy, it will leave the solid. This definition of E_V led to the precise definition of WF which is the difference between E_V and E_F [7] (see Fig. 1). This definition of WF led to the successful prediction of the work functions of materials, which is conclusive evidence on the validity of CALQQM. The calculated and the experimental results for WF of the elements under consideration are given in Table 3. The data for C-hex is taken from [13], for C-dia. [14], for C-60 [15, 16], for β -Sn, Si and for Ge [17-19]. A perfect agreement between the calculated value (4.69 eV) and experimental value (4.69 eV) [15, 16] of the work function of fullerene C-60 was obtained. In addition, it is clear that a good agreement between the experimental results and the calculated values for WFs for the other elements except for α -Sn because the experimental value of WF for it is not available (see Table 3).

Table 3: Theoretical and experimental values of WF and E_g for group IV elements.

Element	E_F eV	E_{C1} eV	E_V eV	WF (Theo) eV	WF(Exp) eV	E_g (Theo) eV	E_g (Exp) eV
C-hex	29.26	30.47	33.96	4.7	4.62 [13]	1.21	---
C-dia	28.89	31.25	33.53	4.64	4.81 [14]	2.36	5.47 [20]
C-60	17.45	17.5	22.14	4.69	4.69 [15,16]	0.05	1.86 [21]
α -Sn	8.72	9.44	13.27	4.55	---	0.72	0.10 [22, 23]
β -Sn	10.19	11.02	14.79	4.6	4.42 [17-19]	0.83	---
Si	12.46	13.47	17.22	4.76	4.85 [17-19]	1.01	1.12 [20]
Ge	11.48	12.42	16.68	5.2	5 [17-19]	0.94	0.89 [24]

Energy Gap

In literature, all the quantum states are confined in the first BZ and the higher BZs are not included in the band structure for all materials. In addition, metals have zero energy gap and the energy is varying continuously in both CB and VB, which are overlapped. For semiconductors and insulators there are energy gaps between VB and CB. The band gap in semiconductors is small and can be crossed by thermal agitation while, in insulators it is large and cannot be crossed by energy. Therefore, the resistivity decreases by temperature in semiconductors while in insulators this cannot be done because there are no free charge carriers. In addition, literatures consider two types of band gaps; direct gap and indirect gap exist in the same band structure and have different values. In CALQQM the energy is quantized, discontinues, and between the allowed energy levels are energy gaps which are not allowed for electrons and that is true for all crystalline materials. In metals, the electrons are free to move at once when energy is acquired. In semiconductors, the electrons are bound to atoms and to become free they need energy to break the bond. Thermal agitation or any other form of energy can do this. In insulators, thermal agitation cannot release electrons from the bonds. We can define the energy gap (E_g) between CB and VB as the following;

$$E_g = E_{C1} - E_F \quad (5)$$

where E_{C1} is the energy of the first unoccupied level in the CB.

Theoretical and experimental values of E_g are given in Table 3. It is clear that from Table 3 there is a discrepancy between both values. This discrepancy can be eliminated if we consider that the transition to the conduction band occurs in two steps; first, part of the absorbed energy is used to release the electron from the bonded atoms, secondly the other part of the absorbed energy is used for the transition from VB to CB. For example let us take diamond, $E_g(\text{theo}) = 2.36$ eV and $E_g(\text{Exp}) = 5.47$ eV [20]. The difference between both values equal to 3.11 eV, this energy was consumed in releasing process of the electron. This energy can be considered as the binding

energy of the electron in the solid state. For fullerene $E_g(\text{theo}) = 0.05$ eV and $E_g(\text{Exp}) = 1.86$ eV [21]. Thus, the binding energy of the electron in fullerene is 1.81 eV. Therefore, the electrons in diamond are more tightly bound than in fullerene. For Si, $E_g(\text{theo}) = 1.01$ eV and $E_g(\text{Exp}) = 1.12$ eV [20] this gives 0.11 eV for the binding energy of the electron in solid Si. The experimental value of E_g for α -Sn is 0.1 eV [22, 23], which is much smaller than the theoretical value 0.72 eV. For Ge $E_g(\text{theo}) = 0.94$ eV and $E_g(\text{Exp}) = 0.89$ eV [24], the two value are close to each other. We must differentiate between the energy gap and the binding energy of the electron. In metals, the binding energy of the electron is zero. In semiconductors, this energy is small, for example for Si it is 0.11 eV. For insulators, the binding energy of the electron is large, for example for diamond it is 3.11 eV.

Possible Electronic Transitions

When a material takes an amount of energy, the electrons in E_f are the only electrons, which can make transitions to the higher levels. Therefore, the electronic transitions will be from E_f to the higher levels according to the band structure of each material. As long as this amount of energy is less than WF, the electrons stay in the solid. If the energy is more than WF, the electrons will leave the solid. The energy given to the electrons must match the energy difference between the two levels in order to make transitions. Table 4 shows the possible electronic transitions for the elements under consideration. For graphite (C-hex) there are 4 transitions, 2 in UV, one green (G) and one IR. For diamond (C-dia) there are 2 transitions only, one UV and one G. For fullerene (C-60) there are 103 transitions ranges from UV to Far IR. For α -Sn there are 7 transitions, 3 UV, one blue (B), one orange (O) and 2 IR. For β -Sn there are 6 transitions, 2 UV, one violet (V), one G, and 2 IR. For Si there are 5 transitions, 2 UV, one V, one O, and one IR. For Ge there are 6 transitions, 3 UV, one B, one red (R), and one IR.

Table 4: Possible electronic transitions for the group IV elements.

Element	WF (Theo) eV	WF wavelength nm	Possible Transitions nm	No. of transitions
C-hex	4.7	263.79	263.76, 348.27, 518.76, 1024.66	4
C-dia	4.64	267.20	267.20, 525.35	2
C-60	4.69	264.35	264.35, 267.2, 269.5, 271.9, 274.9, 277.3, 279.8, 283, 285.6, 288.3, 291.73757, 4275.31, 5166, 6525.48, 8856, 13776, 24796.85	103
α -Sn	4.55	272.49	272.49, 313.88, 371.21, 457.50, 598.95, 879.32, 1722.00	7
β -Sn	4.6	269.53	269.53, 318.72, 394.85, 514.45, 765.33, 1493.78	6
Si	4.76	260.47	260.47, 312.30, 421.71, 619.92, 1227.56	5
Ge	5.2	238.43	238.43, 281.78, 347.29, 455.82, 670.18, 1318.98	6

4. Conclusions

A perfect agreement between the calculated value (4.69 eV) and the experimental value (4.69 eV) of the work function of fullerene (C-60). In addition, a good agreement between the experimental and the calculated values for WFs of the other elements was obtained. The calculated WF, energy gap and the binding energy for diamond was found to be 4.64 eV, 2.36 eV, and 3.11 eV respectively. For Si these values are 4.76 eV, 1.01 eV, and 0.11 eV respectively. These values confirm the insulating nature of diamond and the semiconducting nature of silicon. However, the diamond has the largest volume of quantum state (21.86 \AA^{-3}) which indicates on the capability of diamond to be superconducting by compression at room temperature. CALQQM was succeeded in determining the electronic band structures of group IV elements and their allotropes. Moreover, it predicted with high accuracy their electronic properties such as work functions, energy gaps, and spectra.

Conflicts of Interest

There are no conflicts of Interest

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