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# A New Condition of Formation and Stablity of All Crystalline Systems in a Good Agreement with Experimental Data

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## ABSTRACT

In this paper we derived a new condition of formation and stability of all crystalline systems and we checked its validity and it is found to be in a good agreement with experimental data. This condition is derived directly from the quantum conditions on the free electron Fermi gas inside the crystal. The new condition relates both the volume of Fermi sphere $\boldsymbol{V_F}$ and volume of Brillouin zone $\boldsymbol{V_B}$ by the valence electron concentration $\boldsymbol{VEC}$ as ; $\frac{V_F}{V_B} = \boldsymbol{n}\frac{VEC}{2}$ for all crystalline systems (where $\boldsymbol{n}$ is the number of atoms per lattice point).

## Keywords

Fermi shpere; Brillouin zone; Valence electron concentration VEC; Crystal Systems, Primitive Cell.

## Academic Discipline And Sub-Disciplines

Physics; Solid State Physics

## SUBJECT CLASSIFICATION

Fermi surface Brillouin zone interaction

## TYPE (METHOD/APPROACH)

Theoretical and computational

The new condition for crystalline phase formation and stability derived by T. El Ashram [1] for a cubic, hexagonal and tetragonal systems is found to be in a good agreement with experimental data. This condition is derived directly from the quantum conditions on the free electron Fermi gas inside the crystal and it is not an assumption. In this condition the ratio of volume of Fermi sphere $\boldsymbol{V_F}$ to volume of Brillouin zone $\boldsymbol{V_B}$ is related to valence electron concentration **VEC** as; $\frac{V_F}{V_B} = VEC$ for tetragonal and hexagonal systems and as; $\frac{V_F}{V_B} = \frac{VEC}{2}$ for cubic systems.

In the present work we will extend this condition to the other crystalline systems such as orthorhombic, rhombohedral, monoclinic and triclinic. Also we will start by considering Fermi wavevector or the radius of Fermi sphere $\boldsymbol{k_F}$, which is given by $k_F = \left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}}$ , where $\boldsymbol{N}$ is the number of electrons in the volume $\boldsymbol{V}$. In terms of the volume of primitive cell $\boldsymbol{V_P}$ and valence electron concentration **VEC** we can rewrite $\boldsymbol{k_F}$ as $k_F = \left(\frac{3\pi^2 nVEC}{V_P}\right)^{\frac{1}{3}}$ , where $\boldsymbol{n}$ is the number of atoms per lattice point. Since the primitive cell contains only one lattice point, this lattice point may contain 1, or 2,.....or n atoms and every atom has **VEC** of electrons. Now let us calculate the volume of Fermi sphere $\boldsymbol{V_F}$ from the equation of $\boldsymbol{k_F}$ as the following; $V_F = \frac{4}{3}\pi k_F^3 = \frac{4}{3}\pi(\frac{3\pi^2 nVEC}{V_P})$ from which we get; $V_F = (\frac{4\pi^3 nVEC}{V_P})$ and since $V_B = \frac{8\pi^3}{V_p}$ we get; $\frac{V_F}{V_B} = n\frac{VEC}{2}$ . This is a general condition for all crystalline systems, it does not depend on the type of the crystal system. However it depends on $\boldsymbol{n}$, the number of atoms per lattice point or primitive cell. This condition does not contradict the condition derived previously for cubic, hexagonal and tetragonal systems but can be reduced to it if we take $\boldsymbol{n}$ into account. Therefore the aim of the present work is to check the validity of this condition for some of pure elements with different crystal structure and valencies such as O, Li, Na, Cu, Ag, Al, Pb, Cd, Zn, In, Sn, Bi, Ga and P. The experimental XRD data were obtained from reference [2] and the data for $\boldsymbol{k_F}$ were taken from reference [3].

## 2. CALCULATIONS AND RESULTS

### 2.1 Cubic System

### 2.1. I. Simple Cubic (Cub. P)

The primitive cell of simple cubic system is described by the primitive vectors [4]; $\boldsymbol{a_1=(a, 0, 0), a_2=(0, a, 0)}$, ***and*** $\boldsymbol{a_3=(0, 0, a)}$. The volume of the primitive cell $\boldsymbol{V_P}$ is given by; $\boldsymbol{V_P= a_1.a_2xa_3}$, substituting we get; $\boldsymbol{V_P = a^3}$. Let us take the Oxygen (O) element as an example for this structure. From [2] $\boldsymbol{a}$ =6.83 Å this gives for $\boldsymbol{V_P}$= 318.611 Å$^3$ and for $\boldsymbol{V_B}$=0.7785 Å$^{-3}$. For O $\boldsymbol{k_F}$ is calculated to be 1.646 Å$^{-1}$ from which $\boldsymbol{V_F}$=18.680 Å$^{-3}$ therefore $\boldsymbol{V_F/V_B}$=23.99. Now let us calculate ***nVEC/2***; for O, $\boldsymbol{n}$ =8 and **VEC**=6 therefore ***nVEC/2***= 24 which is in a good agreement with the calculated value for $\boldsymbol{V_F/V_B}$.(see Table 1)

### 2.1.II. Volume Centered Cubic (Cub. I)

The primitive cell of volume centered Cubic system is described by the primitive vectors [4]; $\boldsymbol{a_1 = (-a/2, a/2, a/2), a_2 = (a/2, -a/2, a/2)}$, and $\boldsymbol{a_3 = (a/2, a/2, -a/2)}$. Also the volume of the primitive cell $\boldsymbol{V_P}$ is given by; $\boldsymbol{V_P = a_1.a_2xa_3}$, substituting we get; $\boldsymbol{V_P = a^3/2}$. Let us take the Lithium (Li) element as an example for this structure. From [2] $\boldsymbol{a}$ =3.5092 Å this gives for $\boldsymbol{V_P}$ = 21.606 Å$^3$ and for $\boldsymbol{V_B}$=11.480 Å$^{-3}$. For Li $\boldsymbol{k_F}$ is calculated to be 1.11 Å$^{-1}$ from which $\boldsymbol{V_F}$=5.7287Å$^{-3}$ therefore $\boldsymbol{V_F/V_B}$=0.499. Now let us calculate ***nVEC/2***; for Li, $\boldsymbol{n}$ =1 and **VEC**=1 therefore ***nVEC/2***= 0.5 which is in a good agreement with the calculated value for $\boldsymbol{V_F/V_B}$. By the same method of calculations we get the same result for Sodium (Na) element. (see Table 1)

### 2.1.III. Face Centered Cubic (Cub. F)

The primitive cell of Face Centered Cubic system is described by the primitive vectors [4]; $\boldsymbol{a_1=(0, a/2, a/2), a_2=(a/2, 0, a/2)}$, ***and*** $\boldsymbol{a_3=(a/2, a/2, 0)}$. Also the volume of the primitive cell $\boldsymbol{V_P}$ is given by; $\boldsymbol{V_P = a_1.a_2xa_3}$, substituting we get; $\boldsymbol{V_P =a^3/4}$. Let us take the Silver (Ag) element as an example for this structure. From [2] $\boldsymbol{a}$ =4.0855 Å this gives for $\boldsymbol{V_P}$= 17.0480 Å$^3$ and for $\boldsymbol{V_B}$=14.550 Å$^{-3}$. For Ag $\boldsymbol{k_F}$ is calculated to be 1.2 Å$^{-1}$ from which $\boldsymbol{V_F}$ =7.2382Å$^{-3}$ therefore $\boldsymbol{V_F/V_B}$=0.497. Now let us calculate ***nVEC/2***; for Ag, $\boldsymbol{n}$ =1 and **VEC**=1 therefore ***nVEC/2***= 0.5 which is in a good agreement with the calculated value for $\boldsymbol{V_F/V_B}$. By the same method of calculations we get the same result for Copper (Cu), Aluminum (Al) and Lead (Pb) elements. (see Table 1)

### Table 1

| Element | VEC | Crystal System<br>S.G. | n | $V_B$<br>Å$^{-1}$ | $V_F$<br>Å$^{-1}$ | $V_F/V_B$ | nVEC/2 |
|---|---|---|---|---|---|---|---|
| **O** | 6 | Cubic<br>Pm$\bar{3}$n | 8 | 0.7785 | 18.680 | 23.99 | 24.0 |
| **Li** | 1 | Cubic<br>Im$\bar{3}$m | 1 | 11.480 | 5.7287 | 0.499 | 0.5 |
| **Na** | 1 | Cubic<br>Im$\bar{3}$m | 1 | 6.5314 | 3.2617 | 0.499 | 0.5 |
| **Ag** | 1 | Cubic<br>Fm$\bar{3}$m | 1 | 14.550 | 7.2382 | 0.497 | 0.5 |
| **Cu** | 1 | Cubic<br>Fm$\bar{3}$m | 1 | 21.0018 | 10.5367 | 0.501 | 0.5 |
| **Al** | 3 | Cubic<br>Fm$\bar{3}$m | 1 | 14.9401 | 22.4492 | 1.502 | 1.5 |
| **Pb** | 4 | Cubic<br>Fm$\bar{3}$m | 1 | 8.280 | 16.2101 | 1.957 | 2.0 |
| **Cd** | 2 | Hexagonal<br>P$6_3$/mmc | 2 | 5.7436 | 11.4940 | 2.001 | 2.0 |
| **Zn** | 2 | Hexagonal<br>P$6_3$/mmc | 2 | 8.1521 | 16.2101 | 1.988 | 2.0 |
| **In** | 3 | Tetragonal<br>I4/mmm | 1 | 9.4922 | 14.1371 | 1.489 | 1.5 |
| **Sn** | 4 | Tetragonal<br>I$4_1$/amd | 2 | 4.5854 | 17.808 | 3.883 | 4.0 |
| **Ga** | 3 | Orthorhombic<br>Cmcm | 2 | 6.6344 | 18.8165 | 2.836 | 3.0 |
| **Bi** | 5 | Rhombohedral<br>R$\bar{3}$m | 2 | 3.5446 | 17.5151 | 4.941 | 5.0 |
| **P** | 5 | Monoclinic<br>P2/c | 84 | 0.13555 | 17.083 | 126.027 | 126.0 |
| **P** | 5 | Triclinic<br>P$\bar{1}$ | 24 | 0.3904 | 23.425 | 60.003 | 60.0 |

## 2.2. Hexagonal System (Hex. P)

The primitive cell of Hexagonal system is described by the primitive vectors [4]; $a_1=(a/2, -a\sqrt{3}/2, 0)$, $a_2=(a/2, a\sqrt{3}/2, 0)$, and $a_3=(0, 0, c)$. Also the volume of the primitive cell $V_P$ is given by; $V_P= a_1.a_2 x a_3$, substituting we get $V_P=a^2c\sqrt{3}/2$. Let us take the Cadmium (Cd) element as an example for this structure. From [2] $a$ =2.9793 Å and $c$ =5.6181 Å this gives for $V_P$ = 43.1865 Å$^3$ and for $V_B$=5.7436 Å$^{-3}$. For Cd $k_F$ is calculated to be 1.4 Å$^{-1}$ from which $V_F$ =11.4940 Å$^{-3}$ therefore $V_F/V_B$ =2.001 Now let us calculate **nVEC/2**; for Cd, $n$ =2 and **VEC**=2 therefore **nVEC/2**= 2.0 which is in a good agreement with the calculated value for $V_F/V_B$. By the same method of calculations we get the same result for Zinc (Zn) element. (see Table 1)

## 2.3. Volume Centered Tetragonal System (Tet. I)

The primitive cell of the volume centered Tetragonal system is described by the primitive vectors [4]; **$a_1$=(-a/2, a/2, c/2), $a_2$=(a/2, -a/2, c/2)**, and **$a_3$=(a/2, a/2, - c/2).** Also the volume of the primitive cell **$V_P$** is given by; **$V_P$= $a_1$.$a_2$x$a_3$**,by substituting we get for **$V_P$ =$a^2$c/2.** Let us take the Tin (white Sn) element as an example for this structure. From [2] **a** =5.831Å and **c** =3.182 Å this gives for **$V_P$** = 54.094 $Å^3$ and for **$V_B$**=4.5854$Å^{-3}$. For Sn **$k_F$** is calculated to be 1.62 $Å^{-1}$ from which **$V_F$** =17.808 $Å^{-3}$ therefore **$V_F/V_B$** =3.883 Now let us calculate **nVEC/2**; for Sn, **n** =2 and **VEC**=4 therefore **nVEC/2**= 4.0 which is in a good agreement with the calculated value for **$V_F/V_B$**. By the same method of calculations we get the same result for Indium (In) element. (see Table 1)

## 2.4. Base Centered Orthorhombic System (Orth. C)

The primitive cell of base centered Orthorhombic system is described by the primitive vectors [4]; **$a_1$=(a/2, -b/2, 0), $a_2$=(a/2, b/2, 0),** and **$a_3$=(0, 0, c)** Also the volume of the primitive cell **$V_P$** is given by; **$V_P$= $a_1$.$a_2$x$a_3$**, by substituting we get for **$V_P$=abc/2.** Let us take the Gallium (Ga) element as an example for this structure. From [2] **a** =2.9 Å, **b** =8.134 Å and **c** =3.17 Å this gives for **$V_P$** = 37.3879 $Å^3$ and for **$V_B$** =6.6344$Å^{-3}$. For Ga **$k_F$** is calculated to be 1.65 $Å^{-1}$ from which **$V_F$** =18.8165 $Å^{-3}$ therefore **$V_F/V_B$** =2.8362 Now let us calculate **nVEC/2**; for Ga, **n** =2 and **VEC**=3 therefore **nVEC/2**= 3.0 which is in a good agreement with the calculated value for **$V_F/V_B$**. (see Table 1)

## 2.5. Rhombohedral System (Rho. R)

The primitive cell of Rhombohedral system is described by the primitive vectors [4]; **$a_1$ = (a cos($\alpha$/2), -a sin ($\alpha$/2), 0), $a_2$ = (a cos($\alpha$/2) ,a sin($\alpha$/2), 0),** and **$a_3$=(a cos $\alpha$/cos ($\alpha$/2), 0, a $\sqrt{1-\cos^2\alpha/\cos^2(\frac{\alpha}{2})}$).** Also the volume of the primitive cell **$V_P$** is given by; **$V_P$= $a_1$.$a_2$x$a_3$**, by substituting we get for **$V_P$=$a^3\sqrt{1-3\cos^2\alpha+2\cos^3\alpha}$.** Let us take the Bismuth (Bi) element as an example for this structure. From [2] **a** =4.7236 Å, $\alpha$ =57.35° Å. This gives for **$V_P$** = 69.979 $Å^3$ and for **$V_B$** =3.5446 $Å^{-3}$. For Bi **$k_F$** is calculated to be 1.611 $Å^{-1}$ from which **$V_F$** =17.5151 $Å^{-3}$ therefore **$V_F/V_B$** = 4.941 Now let us calculate **nVEC/2**; for Bi, **n** =2 and **VEC** =5 therefore **nVEC/2**= 5.0 which is in a good agreement with the calculated value for **$V_F/V_B$**. (see Table 1)

## 2.6. Simple Monoclinic System (Mon. P)

The primitive cell of simple Monoclinic system is described by the primitive vectors [4]; **$a_1$ = (a, 0, 0), $a_2$ = (0, b, 0),** and **$a_3$=(0, c cos $\alpha$, c sin $\alpha$).** Also the volume of the primitive cell **$V_P$** is given by; **$V_P$= $a_1$.$a_2$x$a_3$**,by substituting we get for **$V_P$=abc sin $\beta$.** Let us take the Phosphorus (violet P) element as an example for this structure. From [2] **a** =9.21 Å, **b**=9.15 Å, **c** =22.6 Å, and $\beta$ =106.1°. This gives for **$V_P$** = 1829.83 $Å^3$ and for **$V_B$** =0.13555 $Å^{-3}$. For P **$k_F$** is calculated to be 1.894 $Å^{-1}$ from which **$V_F$** =28.47 $Å^{-3}$ therefore **$V_F/V_B$** = 210.04 Now let us calculate **nVEC/2**; for P, **n** =84 and **VEC** =5 therefore **nVEC/2**= 210.0 which is in a good agreement with the calculated value for **$V_F/V_B$**. (see Table 1)

## 2.7. Triclinic System (Tri. P)

The primitive cell of Triclinic system is described by the primitive vectors [4]; **$a_1$ = (a, 0, 0), $a_2$ = (b cos $\gamma$, b sin $\gamma$, 0),** and **$a_3$=(c cos $\beta$, c/sin$\gamma$ [ cos $\alpha$-cos$\beta$ cos$\gamma$, c/sin $\gamma$ [$\sqrt{\sin^2\gamma-\cos^2\alpha-\cos^2\beta+2\cos\alpha\cos\beta\cos\gamma}$).** Also the volume of the primitive cell **$V_P$** is given by; **$V_P$=$a_1$.$a_2$x$a_3$**, by substituting we get for **$V_P$=abc$\sqrt{1-\cos^2\alpha-\cos^2\alpha-\cos^2\beta+2\cos\alpha\cos\beta\cos\gamma}$.** Let us take the Phosphorus (white P) element as an example for this structure. From [2] **a** =11.45 Å, **b**=5.503 Å, **c** =11.261 Å, $\alpha$ =71.84°, $\beta$ =90.37°, and $\gamma$ =71.58°. This gives for **$V_P$** = 635.237 $Å^3$ and for **$V_B$** =0.3904 $Å^{-3}$. For P **$k_F$** is calculated to be 1.775 $Å^{-1}$ from which **$V_F$** =23.425 $Å^{-3}$ therefore **$V_F/V_B$** = 60.003 Now let us calculate **nVEC/2**; for P, **n** =24 and **VEC** =5 therefore **nVEC/2**= 60.0 which is in a good agreement with the calculated value for **$V_F/V_B$**. (see Table 1)

## 3. CONCLUSION

It is found that the theoretically derived condition is in a very good agreement with the experimental data which confirm the validity of this condition for crystalline phase formation and stability. Therefore we can conclude that the alloy adapts its crystal structure in such a way, the ratio of volume of Fermi sphere **$V_F$** to volume of Brillouin zone **$V_B$** is related to valence electron concentration **VEC** as; $\frac{V_F}{V_B}=n\frac{VEC}{2}$ for all crystal systems (where **n** is the number of atoms per lattice point or primitive cell).

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