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# Theoretical modification of Hume Rothery condition of phase stability in a good agreement with experimental data

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## ABSTRACT

We presented in this paper a theoretical modification of Hume Rothery condition of phase stability in good agreement with experimental data. This modification 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 ***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.

## Keywords

Fermi shpere; Brillouin zone; Valence electron concentration VEC; Hume Rothery condition.

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## 1. INTRODUCTION

The Hume Rothery condition of phase stability [1] states that the structure of a certain phase will be stable when the Fermi sphere touches the Brillouin zone boundary at a certain plane. In this case the diameter of Brillouin zone ($K_B$) will equal to the diameter of Fermi sphere ($2k_F$), i.e. $K_B = 2k_F$. where $k_F$ is the Fermi wavevector or the radius of Fermi sphere and its magnitude is given by $k_F = \left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}}$ , where $N$ is the number of electrons in the volume $V$. The diameter of Brillouin zone is given by $K_B = 2\pi/d_{(hkl)}$, where $d_{(hkl)}$ is the interplanar distance between ($hkl$) planes. The condition means that the Fermi sphere will touch the Brillouin zone in a certain direction in the reciprocal space. Actually Brillouin zones are not spherical in shape and they are polyhedral in the reciprocal space and depend on the type of crystal structure of the real lattices. For example; the real face centered cubic lattice in reciprocal space becomes body centered and vice versa. We have to compare the volume of the Fermi sphere with the whole volume of Brillouin zone.

Let us assume that there is a relation between the volume of Fermi sphere $V_F$ and the volume of Brillouin zone $V_B$ in the form; $V_F = CV_B$ where $C$ is a dimensionless constant depends on the electron concentration for a particular alloy system. Here also $V_F = \frac{4}{3}\pi k_F^3$ and $V_B = (2\pi)^3/V_P$, where $V_P$ is the volume of primitive cell of the real lattice. At First we will take the body centered tetragonal (BCT) β-Sn. Now let us calculate the volume of the primitive cell of β-Sn. The primitive lattice vectors of BCT is given by [2]; $a_1 = (a/2, a/2, c/2)$ , $a_2 = (a/2, -a/2, c/2)$, and $a_3 = (a/2, a/2, -c/2)$ and since the volume of the primitive cell $V_P$ is given by; $V_P = a_1.a_2xa_3$. After calculation we get $V_P = a^2c/2$, since the volume of conventional cell is $V_C = a^2c$ therefore $V_P = V_C/2$. All the Brillouin zones have the same volume, i.e. the volume of first zone equal to the volume of the second zone and so on. The volume of Brillouin zone is related to the volume of the primitive cell by; $V_B = (2\pi)^3/V_P$ therefore we have $V_B = 16\pi^3/V_C$. Here $V_B$ can be calculated from the XRD data.

Now let us calculate the volume of Fermi sphere $V_F$ from the equation of $k_F$ as the following; $V_F = \frac{4}{3}\pi k_F^3 = \frac{4}{3}\pi(\frac{3\pi^2 N_C}{V_C})$ substituting for $V_F$ and $V_B$ we get; $V_F = \frac{N_C}{4}V_B$ where $N_C$ is the number of electrons in the conventional unit cell. The valence electron concentration ($VEC$) is defined as the number of electrons per atom, i.e. $VEC = N_C/n_a$ where $n_a$ is the number of atoms in the unit cell. Substituting for $N_C$ we get $\frac{V_F}{V_B} = \frac{n_a}{4}VEC$. For Sn unit cell $n_a = 4$, so we get; $\frac{V_F}{V_B} = VEC$ this is the condition of phase stability for pure β-Sn. This condition is derived directly from the quantum conditions on the free electron Fermi gas inside the crystal and it is not an assumption. Therefore the aim of the present work is to check the validity of this condition for some of pure metals with different crystal structure and valencies such as Li, Na, Cu, Ag, Al, Pb, Cd, Zn, and In and for Sn based binary systems. The Sn-based binary systems under investigation in this work are, Sn-Cu, Sn-Cd, Sn-Al, and Sn-Sb. The experimental XRD data are obtained from reference [3] for pure metals and from reference [4] for Sn based binary alloys. Also the data for $k_F$ is taken from reference [5].

## 2. CALCULATION AND RESULTS

### 2.1. PURE METALS

### I. Face Centered Cubic (FCC)

The primitive cell of FCC is described by the primitive vectors [2];

$a_1 = (0, a/2, a/2)$, $a_2 = (a/2, 0, a/2)$, and $a_3 = (a/2, a/2, 0)$. Also the volume of the primitive cell $V_P$ is given by; $V_P = a_1.a_2xa_3$, substituting we get $V_P = a^3/4 = V_C/4$ therefore $V_B = (2\pi)^3/V_P = 32\pi^3/V_C$. Now we have; $V_F = \frac{4}{3}\pi k_F^3 = \frac{4}{3}\pi(\frac{3\pi^2 N_C}{V_C})$ substitute for $V_C$ we get, $V_F = \frac{N_C}{8}V_B$, here $N_C$ is the number of electrons in the conventional unit cell. Since $N_C = n_a VEC$ , therefore we have; $\frac{V_F}{V_B} = \frac{n_a}{8}VEC$. For Cu, Ag, Al, and Pb; $n_a = 4$ and hence we get; $\frac{V_F}{V_B} = \frac{VEC}{2}$ . This theoretical result is in good agreement with the calculated results in Table 1. Therefore we can write; $\frac{V_F}{V_B} = \frac{VEC}{2}$ for FCC.

**Table 1. The structure parameters of FCC metals.**

| Structure parameter | FCC | | | |
|---|---|---|---|---|
| | Cu | Ag | Al | Pb |
| ***Valency*** | 1 | 1 | 3 | 4 |
| $N_C$ | 4 | 4 | 12 | 16 |
| ***VEC*** | 1 | 1 | 3 | 4 |
| ***A*** | 3.61505 | 4.0855 | 4.04963 | 4.93 |
| $N_C/V_C$ (Å)$^{-3}$ | 0.08466 | 0.05865 | 0.18069 | 0.13353 |

| | | | | |
|---|---|---|---|---|
| **$V_C$ $(Å)^3$** | 47.2435 | 68.1923 | 66.4119 | 119.8231 |
| **$V_B$ $(Å)^{-3}$** | 21.0018 | 14.550 | 14.9401 | 8.2805 |
| **$k_F$ $(Å)^{-1}$** | 1.36 | 1.2 | 1.75 | 1.57 |
| **$V_F$ $(Å)^{-3}$** | 10.5367 | 7.2382 | 22.4492 | 16.2101 |
| **$V_F/V_B$** | 0.5017 | 0.4974 | 1.5026 | 1.9576 |

## II. Body Centered Cubic (BCC)

The primitive cell of BCC is described by the primitive vectors [2];

$a_1=(-a/2, a/2, a/2)$, $a_2=(a/2, -a/2, a/2)$, and $a_3=(a/2, a/2, -a/2)$. Also the volume of the primitive cell $V_P$ is given by; $V_P= a_1.a_2xa_3$, substituting we get; $V_P=a^3/2 = V_C/2$ therefore $V_B=(2\pi)^3/V_P=16\pi^3/V_C$. Now we have;$V_F=\frac{4}{3}\pi k_F^3=\frac{4}{3}\pi(\frac{3\pi^2 N_C}{V_C})$ substitute for $V_C$ we get, $V_F=\frac{N_C}{4}V_B$, and since $N_C=n_aVEC$, therefore we have; $\frac{V_F}{V_B}=\frac{n_a}{4}VEC$. For Li and Na, $n_a=2$ and hence we get; $\frac{V_F}{V_B}=\frac{VEC}{2}$ . This theoretical result is in good agreement with the calculated results in Table 2, therefore we can write; $\frac{V_F}{V_B}=\frac{VEC}{2}$ for BCC.

**Table 2. The structure parameters for BCC, HEX and Tetragonal metals.**

| **Structure parameter** | **BCC** | | **Hexagonal** | | **Tetragonal** |
|---|---|---|---|---|---|
| | **Li** | **Na** | **Cd** | **Zn** | **In** |
| ***Valency*** | 1 | 1 | 2 | 2 | 3 |
| **$N_C$** | 2 | 2 | 4 | 4 | 6 |
| ***VEC*** | 1 | 1 | 2 | 2 | 3 |
| ***A*** | 3.51 | 4.29 | 2.9793 | 2.665 | 3.251 |
| ***C*** | 3.51 | 4.29 | 5.6181 | 4.947 | 4.945 |
| **$N_C/V_C$ $(Å)^{-3}$** | 0.04624 | 0.02533 | 0.09262 | 0.1314 | 0.1148 |
| **$V_C$ $(Å)^3$** | 43.2435 | 78.9535 | 43.1865 | 30.4275 | 52.2637 |
| **$V_B$ $(Å)^{-3}$** | 11.4722 | 6.2834 | 5.74369 | 8.1521 | 4.7461 |
| **$k_F$ $(Å)^{-1}$** | 1.11 | 0.92 | 1.4 | 1.57 | 1.5 |
| **$V_F$ $(Å)^{-3}$** | 5.7287 | 3.2617 | 11.49 | 16.2101 | 14.1371 |
| **$V_F/V_B$** | 0.4993 | 0.5190 | 2.0004 | 1.9884 | 2.9786 |

## III. Hexagonal System (HEX)

The primitive cell of HEX is described by the primitive vectors [2];

$a_1=(a/2, -a\sqrt{3}/2, 0)$, $a_2=(a/2, a\sqrt{3}/2, 0)$, and $a_3=(0, 0, c)$. Also the volume of the primitive cell $V_P$ is given by; $V_P= a_1.a_2xa_3$, substituting we get $V_P=a^2c\sqrt{3}/2 = V_C$ therefore $V_B=(2\pi)^3/V_P=8\pi^3/V_C$. Now we have; $V_F=\frac{4}{3}\pi k_F^3=\frac{4}{3}\pi(\frac{3\pi^2 N_C}{V_C})$ substitute for $V_C$ we get, $V_F=\frac{N_C}{2}V_B$, Substitute for $N_C=n_aVEC$, we have; $\frac{V_F}{V_B}=\frac{n_a}{2}VEC$. For Cd and Zn $n_a=2$ and hence we get; $\frac{V_F}{V_B}=VEC$. This theoretical result is in good agreement with the calculated results in Table 2, Therefore we can write; $\frac{V_F}{V_B}=VEC$ for hexagonal structure.

## IV. Tetragonal System (TET)

In the introduction we have discussed the body centered tetragonal, here we will discuss primitive tetragonal cell decribed by[2];

***$a_1$=(a,0, 0), $a_2$=(0, a, 0),*** and ***$a_3$=(0, 0, c)*** by substituting we get for ***$V_P=a^2c=V_C$*** therefore ***$V_B=(2\pi)^3/V_P=8\pi^3/V_C$***. Now we have; $\boldsymbol{V_F=\frac{4}{3}\pi k_F^3=\frac{4}{3}\pi(\frac{3\pi^2N_C}{V_C})}$ substitute for ***$V_C$*** we get, $\boldsymbol{V_F=\frac{N_C}{2}V_B}$. Substitute for ***$N_C=n_aVEC$***, we have; $\boldsymbol{\frac{V_F}{V_B}=\frac{n_a}{2}VEC}$. For In ***$n_a$ = 2*** and hence we get; $\boldsymbol{\frac{V_F}{V_B}=VEC}$**.** This theoretical result is in good agreement with the calculated results in Table 2, Therefore we can write; $\boldsymbol{\frac{V_F}{V_B}=VEC}$ for primitive tetragonal.

## 2.2. SN BASED BINARY ALLOYS

In this work the study is restricted on the primary substitutional solid solutions of a solute atom in Sn. Also we assume one solute atom substitutes one Sn atom in each unit cell.

### I- Sn-Cu system

For Sn-Cu system the unit cell will contain 3 Sn atoms and one Cu atom of valency +1, therefore ***$N_C$=3x4+1x1=13*** electron and ***VEC=13/4=3.25*** electron per atom (e/a). The crystal structure of this solution is BCT and the condition of phase stability we have derived for this structure is $\boldsymbol{\frac{V_F}{V_B}=VEC}$. We calculate ***$V_F/V_B$*** to be 3.25. Now let us calculate ***$V_B$*** and ***$V_F$*** and check the result we have obtained. The volume of the conventional unit cell ***$V_C$= 105.90 Ǻ$^3$*** (see Table 3) and hence ***$V_B$= 16$\pi^3$/$V_C$ = 4.6846 Ǻ$^{-3}$***. Now we will calculate ***$k_F$*** using $\boldsymbol{k_F=\left(\frac{3\pi^2N_C}{V_C}\right)^{\frac{1}{3}}}$ And then we can calculate ***$V_F$*** from $\boldsymbol{V_F=\frac{4}{3}\pi k_F^3}$. By calculation we get; ***$V_F$=15.2249 Ǻ$^{-3}$***. Finally we get; ***$V_F/V_B$ = 3.25*** which equal the ***VEC*** for this alloy as predicted by the modified condition of phase stability. By the same method we can proceed for the other systems.

### II- Sn-Cd System

In this system the unit cell will contain 3 Sn atoms and one Cd atom of valency +2 therefore ***$N_C$=3x4+1x2=14*** electron and ***VEC=14/4=3.5 e/a***. (see Table 3) By calculation we get ***$V_F/V_B$ =3.5*** and comparing with ***VEC*** we find a good agreement with the modified condition of phase stability $\boldsymbol{\frac{V_F}{V_B}=VEC}$

**Table 3. The structure parameters of BCT Sn based binary alloys.**

| **Structure parameter** | **BCT** | | | | |
|---|---|---|---|---|---|
| | **Sn-Cu** | **Sn-Cd** | **Sn-Al** | **Sn pure** | **Sn-Sb** |
| ***Solute Valency*** | 1 | 2 | 3 | 4 | 5 |
| ***$N_C$*** | 13 | 14 | 15 | 16 | 17 |
| ***VEC*** | 3.25 | 3.50 | 3.75 | 4.00 | 4.25 |
| ***$N_C/V_C$ (Ǻ)$^{-3}$*** | 0.1227 | 0.1322 | 0.1402 | 0.1479 | 0.1610 |
| ***$V_C$ (Ǻ)$^3$*** | 105.90 | 105.88 | 106.98 | 108.18 | 105.56 |
| ***c/a*** | 0.5476 | 0.5464 | 0.5455 | 0.5457 | 0.5418 |
| ***$V_B$ (Ǻ)$^{-3}$*** | 4.6846 | 4.6854 | 4.6373 | 4.5858 | 4.6997 |
| ***$k_F$ (Ǻ)$^{-1}$*** | 1.5375 | 1.5760 | 1.6072 | 1.6360 | 1.6831 |
| ***$E_F$ (eV)*** | 9.0068 | 9.4641 | 9.8415 | 10.1981 | 10.7937 |
| ***$V_F$ (Ǻ)$^{-3}$*** | 15.2249 | 16.3992 | 17.3899 | 18.3435 | 19.9737 |
| ***$V_F/V_B$*** | 3.25 | 3.50 | 3.75 | 4.00 | 4.25 |

### III- Sn-Al System

In this system the unit cell will contain 3 Sn atoms and one Al atom of valency +3 therefore ***$N_C$=3x4+1x3=15*** electron and ***VEC=15/4=3.75 e/a***. (see Table 3) By calculation we get ***$V_F/V_B$ =3.75*** and comparing with **VEC** we find a good agreement with the modified condition of phase stability $\frac{V_F}{V_B} = \boldsymbol{VEC}$.

### IV- Sn-Sb System

In this system the unit cell will contain 3 Sn atoms and one Sb atom of valency +5, therefore ***$N_C$=3x4+1x5=17*** electron and ***VEC=17/4=4.25 e/a***. (see Table 3). By calculation we get ***$V_F/V_B$ =4.25*** and comparing with **VEC** we find a good agreement with the modified condition of phase stability $\frac{V_F}{V_B} = \boldsymbol{VEC}$.

## 3. Discussion

The derivation of the modified condition of phase stability is based on the equation of the wavevector ***$k_F$*** given above and this equation originated from the quantum conditions on the free electron Fermi gas inside the crystal. Now let us see what will happen to the crystal structure of the primary solid solution based on Sn when the electron concentration changes.

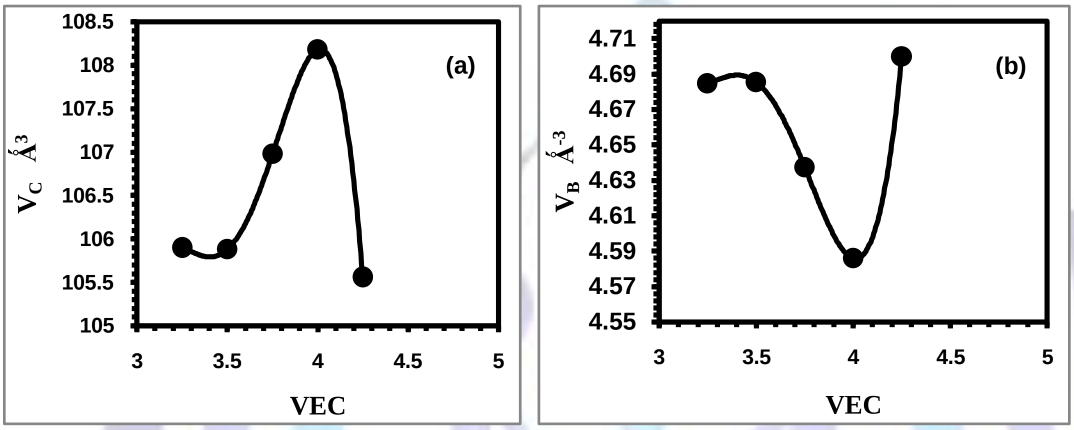

**Figure 1 (a) Variation of $V_C$ with VEC (b) Variation of $V_B$ with VEC.**

Figure 1(a) shows the variation of the volume of the unit cell ***$V_C$*** with ***VEC***. ***$V_C$*** increases up to maximum value at ***VEC=4*** and then decreases with increasing ***VEC***. Figure 1(b) shows the variation of volume of Brillouin zone with ***VEC***. Here ***$V_B$*** decreases with increasing ***VEC*** up to minimum value at ***VEC=4*** and then increases. Both ***$V_C$*** and ***$V_B$*** are inversely related since for BCT; ***$V_B$= 16$\pi^3$/$V_C$***. When the electron concentration changes the atoms arrange themselves, due to the quantum interaction with these electrons, to have a certain positions and hence a certain shape and volume of the unit cell ***$V_C$***. Accordingly ***$V_B$*** changes in such a way to obey the condition of stability $\frac{V_F}{V_B} = \boldsymbol{VEC}$. The inversion point in both curves for ***$V_C$*** and ***$V_B$*** is at ***VEC=4*** which is ***VEC*** of pure base metal Sn and this means that the cell accommodated for ***VEC = 4*** and when the ***VEC*** exceeds this value a change has to be occur to account for the extra electrons.

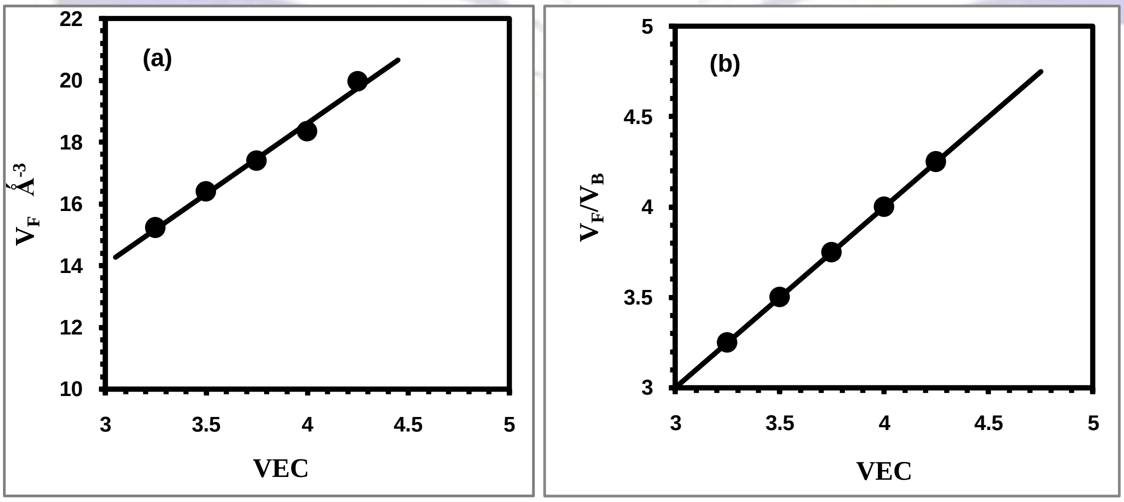

**Figure 2 (a) Variation of $V_F$ with VEC (b) The ratio $V_F/V_B$ with VEC.**

Figure 2 (a) shows the variation of volume of Fermi sphere $\boldsymbol{V_F}$ with **VEC**. $\boldsymbol{V_F}$ increases linearly as indicated from $\boldsymbol{V_F} = \frac{4\pi^3 n_a VEC}{V_C}$ where $\boldsymbol{n_a}$ is the number of atoms in the unit cell. Figure 2 (b) shows the verification of the condition of phase stability experimentally which shows exact agreement with the theoretically derived condition $\frac{V_F}{V_B} = \boldsymbol{VEC}$.

## 4. CONCLUSION

The theoretically derived condition is in a very good agreement with the experimental data which confirm the validity of this modified condition of phase stability. Therefore we can conclude that the alloy adapts its crystal structure in such a way , 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; $\frac{V_F}{V_B} = \boldsymbol{VEC}$ for tetragonal and hexagonal systems and as; $\frac{V_F}{V_B} = \frac{VEC}{2}$ for cubic systems.

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