

# Atomic phase diagram<sup>\*</sup>

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**Abstract** Based on the Thomas-Fermi-Dirac-Cheng model, atomic phase diagram or electron density versus atomic radius diagram describing the interaction properties of atoms of different kinds in equilibrium state is developed. Atomic phase diagram is established based on the two-atoms model. Besides atomic radius, electron density and continuity condition for electron density on interfaces between atoms, the lever law of atomic phase diagram involving other physical parameters is taken into account, such as the binding energy, for the sake of simplicity.

**Keywords:** TFDC model, atom phase diagram, two-atoms model, electron density, atomic radius.

Traditional phase diagram describes the properties of alloy phases in equilibrium state with the typical temperature versus composition diagram. Within the diphasic zone, the relative content of each phase can be obtained according to the so-called lever law. In contrast, atomic phase diagram describes the properties of atoms in equilibrium in the form of electron density versus atomic radius diagram and an equilibrium electron density between two atoms in equilibrium state can be obtained according to a corresponding lever law. Because electron density versus atomic radius diagram is established on the basis of the TFDC model, it is named TFDC diagram.

As far as quantum mechanics is concerned, distribution of electron cloud outside the nucleus decides the shape and size of the atom. When an atom lies in the lattice of other atoms, its electron clouds distribution is affected by the surrounding atoms. For a solid, statistics makes use of electron density and atomic radius to describe the interaction of atoms. The representative theory is Thomas-Fermi-Dirac statistical model which was put forward by Thomas<sup>[1]</sup>, Fermi<sup>[2]</sup> and Dirac<sup>[3]</sup> with emphasis on the isotropy of the interaction of atoms.

TFD model itself has been improved and developed continuously<sup>[4-6]</sup>, but all these efforts aimed at the accuracy of the model. In 1993<sup>[7]</sup>, Chinese physicist Cheng Kaijia studied classical TFD model and advanced continuity condition of electron density

on interfaces when solving solid problems, and continuity condition of work function on interfaces afterwards<sup>[13]</sup>.

The author regards the integrated application of atomic radius, electron density and continuity condition of electron density on interfaces as a key part of TFDC model and has been conducting fundamental researches on the wide application of TFDC model in materials science. For this purpose, the author has seriously considered the Vegard's law for years from the aspect of atomic radius, electron density and continuity condition of electron density on interfaces.

Vegard's law<sup>[8]</sup> deviates from the experimental results in most cases. People have attempted to predict the sign of the departure of Vegard's law from the experiments for eighty years, but the problem has not been solved<sup>[9]</sup>. Based on the concept of TFDC model, the author establishes the atomic model of Vegard's law<sup>[1]</sup> with only atomic radius, electron density, continuity condition and the third physical parameter of the component involved, and the model radically clarifies the physical mechanism of the deviation. The atomic phase diagram just comes from this background knowledge.

## 1 State of atoms

The key concept of TFDC model is the integration of atomic radius, electron density and continuity

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condition on interfaces. Consequently, state of atoms should be clarified when using TFDC model. TFDC model lays emphasis on two states of atoms, i.e. contactless state and contact state. Coincidentally, the Empirical Electron Theory (EET)<sup>[10]</sup> by Yu also stresses two states of atoms, so-called h state and t state. The author has considered TFDC model together with the EET theory in terms of atom interaction volume at the atomic level<sup>[11]</sup>. So, contactless state of atoms in TFDC model is called h state and contact state is called t state.

One main task of TFDC model is to solve the problem of atomic interfaces or phase interfaces, so there should be at least two components involved, i.e. component A and component B. For convenience, assume that the components can form their own crystals, the crystal made of atoms A is called A crystal and that made of atoms B is called B crystal, as shown in Fig. 1. This will not influence the final results of model's application.

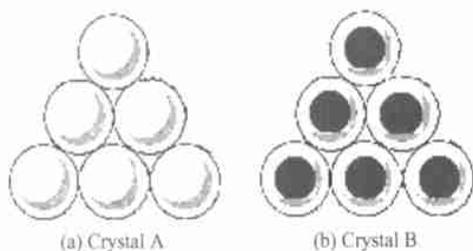


Fig. 1. A atoms and B atoms in crystal state.

Taking one A atom and one B atom out from the lattice shown in Fig. 1, and setting these two atoms in h state as illustrated in Fig. 2, the independent atoms in h state are quite different from free atoms in that they still maintain the same electron structure as in the original lattice environment in spite of their separation from the surroundings composed of atoms with the same kind. Such atoms in h state do not exist in reality, but this conception is required for the subsequent theory.



Fig. 2. A atoms and B atoms in h state.

When these two atoms in h state contact each other, their electron density should be redistributed to satisfy the equality on the interface. The state in which two contacted atoms have to adjust their re-

spective electron structure to ensure the continuity condition of electron density on interfaces is called t state (Fig. 3).



Fig. 3. A atoms and B atoms in t state.

## 2 The interfaces of different kinds of atoms

Just as the founder of TFDC model Cheng Kaijia says, improved TFD model can be regarded as one probe of theoretical researches in solid physics and provide methods and means for practical materials design<sup>[7]</sup>, while atomic phase diagram establishes one representation form at atomic level for this probe.

When two components form a solid solution or a compound, the atomic radius of each component will change to satisfy the continuity of electron density on the interface so that the atom with larger electron density will expand and the one with smaller electron density will contract. While the expansion and the contraction occur on the different scale, their transformation is related to other physical parameters such as binding energy of each component.

Let the lattice constant of A crystal be  $a_A$ , the corresponding atomic radius be  $r_A$ , the electron density be  $n_A$ , and the binding energy be  $E_A$ ; let the corresponding parameters of B crystal be  $a_B$ ,  $r_B$ ,  $n_B$  and  $E_B$  respectively. In the mean time, assuming that A crystal and B crystal are all cubic structures for simplicity without influencing the generic significance of the results, then

$$N_A \cdot \frac{4}{3}\pi r_A^3 = \alpha_A a_A^3, \quad (1)$$

$$N_B \cdot \frac{4}{3}\pi r_B^3 = \alpha_B a_B^3, \quad (2)$$

where  $N_A$  and  $N_B$  are the numbers of atoms in one cell for A crystal and B crystal respectively,  $\alpha_A$  and  $\alpha_B$  are the efficiencies of space filling for the two crystals respectively. If  $\alpha_A = 1$  and  $\alpha_B = 1$ , the relevant  $r_A$  and  $r_B$  are called Wigner-Seitz atomic radius. Apparently,  $r_A$  and  $r_B$  can be obtained from X-ray diffraction data.

When component A and component B form a solid solution or a compound, the atomic radius of each component will change to satisfy the equality of electron density on the interface. As a result, the atom with a larger electron density will expand to decrease

electron density and the atom with a smaller electron density will contract to increase electron density. Supposing the solid solution or compound is cubic-structured also for simplicity without influence on the generalized application of the results and the lattice constant of the crystal is  $a_s$ , then the relationship between the volume of all atoms in the cell and the lattice constant can be interpreted as

$$N_A \cdot \frac{4}{3}\pi(r'_A)^3 + N_B \cdot \frac{4}{3}\pi(r'_B)^3 = \alpha_s a_s^3, \quad (3)$$

where,  $N'_A$ ,  $N'_B$  are the atom numbers of component A and component B in the cell of the solid solution or compound respectively,  $\alpha_s$  is the efficiency of space filling for component A and component B in the cell,  $r'_A$  and  $r'_B$  are atomic radii of component A and component B in the solid solution or compound. When  $\alpha_s = 1$ , the relevant atomic radius is named Wigner-Seitz atomic radius. Although  $a_s$  can be measured by X-ray diffraction data,  $r'_A$  and  $r'_B$  cannot be got from Eq. (3), the solution of which requires the data of electron density and continuity condition of electron density on the interfaces.

### 3 Electron density data

Thomas<sup>[1]</sup> and Fermi<sup>[2]</sup> established one model describing the distribution of electrons in the atom called TF model with the mathematical expression as follows:

$$n(x) = \frac{Z}{4\pi\mu^3} \left( \frac{\Phi}{x} \right)^{\frac{3}{2}}, \quad (4)$$

where,  $\mu = a_0(9\pi^2/128Z)^{1/3}$ ,  $a_0$  is Bohr radius,  $Z$  the atomic number,  $\Phi$  the TF dimensionless function,  $x$  the dimensionless atomic radius,  $r = \mu x$  the actual atomic radius, and  $n(x)$  the electron density. In 1930, Dirac<sup>[3]</sup> introduced electron exchange action into TF model and established TFD model, which expresses the relationship of electron density and atomic radius as below:

$$n(x) = \frac{Z}{4\pi\mu^3} \left[ \epsilon + \left( \frac{\Psi}{x} \right)^{\frac{1}{2}} \right]^3, \quad (5)$$

where,  $\epsilon$  is the electron exchange item introduced by Dirac  $\epsilon = \left( \frac{3}{32\pi^2} \right)^{1/3} Z^{-2/3}$ ,  $\Psi$  is called the TFD function satisfying famous TFD equation, namely,

$$\frac{d^2\Psi}{dx^2} = x \left[ \epsilon + \left( \frac{\Psi}{x} \right)^{\frac{1}{2}} \right]^3. \quad (6)$$

In fact, the above expression is deduced from Poisson equation, hence the assumption that the distribution of electron cloud is spherical symmetry holds true.

TFD model finds successful applications in the solution of atom scatter coefficient in X-ray diffraction. With only atomic radius combination of Eqs. (5) and (6) can give the solution of electron density at specific atomic radius. Cheng made great efforts in this field early in the 1950s and formally published electron density data of 38 elements in the periodic table in 1996<sup>[13]</sup>.

Electron density data given by Cheng can be regarded as one new parameter of the element. In spite that electron density data in TFDC model can be obtained by classical TFD model, no documents definitely list such data before Cheng, so this is Professor Cheng's contribution to classical TFD model.

It should be emphasized that the boundary condition of Eq. (6) is

$$\Psi(0) = 1, \quad (7)$$

$$x_0 \frac{d\Psi(x_0)}{dx_0} = \Psi(x_0). \quad (8)$$

For one certain atomic radius  $r_0$ , there exists one electron density distribution curve, namely " $n'-r'$ ", corresponding to Eqs. (5) and (6). When the atomic radius changes from  $r_0$  to  $r_0 + \Delta r$ , the relevant electron density distribution curve turns into a completely new one, namely, " $n''-r''$ ", absolutely not the simple extension of " $n'-r'$ " curve, as shown in Fig. 4.

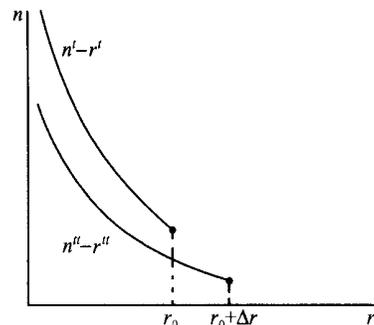


Fig. 4. Effect of atomic radius variation on electron density.

### 4 Electron density condition of TFDC model

Another contribution of Professor Cheng to classical TFD model is the emphasis that wave function on the interface of different kinds of atoms should be continuous. When discussing improved TFD model, Cheng definitely pointed out that "boundary condition between atoms is only the continuity of electron density, which is also the continuity of wave function required by quantum mechanics"<sup>[7]</sup>.

When two components form a solid solution or a compound, surface electron density of each component atom will change to satisfy the continuity of electron density on the interface. Fig. 5 illustrates the continuity of electron density between atoms in TFDC model, where there are four curves of “electron density versus atomic radius”, namely, “ $n-r$ ”, showing the distribution of electron density in the atom obtained from classical TFD model with atomic radius known. It can be seen from the figure that, at h state, electron density of A atom and B atom is  $n_A$  and  $n_B$  respectively; whereas at t state, electron density of both A atom and B atom changes to  $n_{AB}$ . Just as discussed above, t state is the contact state in which electron density on the contact interface should be equal, hence  $n_{AB}$  called the equilibrium electron density of component A and component B occurs. Fig. 5(a) shows component A with a smaller atomic radius and a larger electron density and component B with a larger atomic radius and a smaller electron density; while Fig. 5(b) illustrates component A with a larger atomic radius and a larger electron density and component B with a smaller atomic radius and a

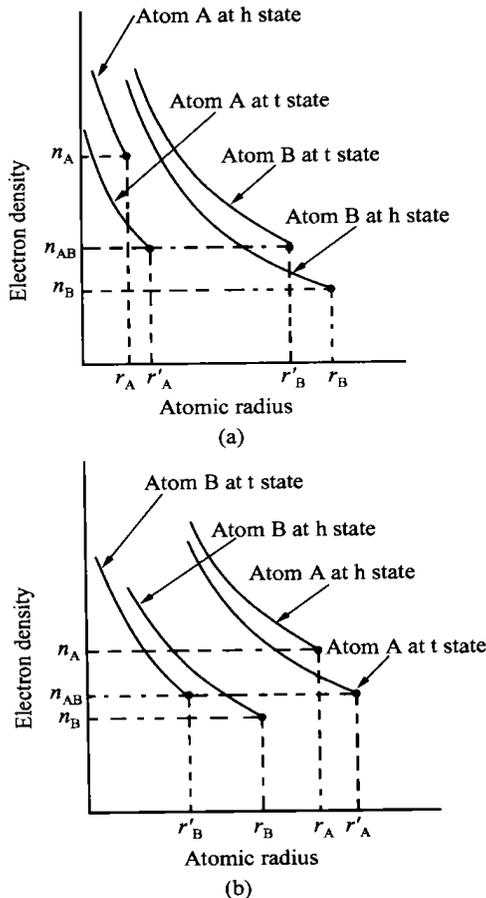


Fig. 5. Continuity condition of electron density on the atom interface. (a)  $r_A < r_B$ ,  $n_A > n_B$ ; (b)  $r_A > r_B$ ,  $n_A > n_B$ .

smaller electron density. Two circumstances correspond to two different kinds of atomic phase diagrams, which will be discussed in detail.

Solution of equilibrium electron density  $n_{AB}$  is the emphasis of this paper. The author has solved  $n_{AB}$  by a simple mathematical mean method with one simple “two-atom model”<sup>[12]</sup>.

## 5 Two-atom model

Supposing A atom and B atom equally tend to one average electron density  $\bar{n}$ , we can get

$$\bar{n} = \frac{n_A + n_B}{2}. \quad (9)$$

Apparently, average electron density  $\bar{n}$  has not taken the atom's physical course from h state to t state into consideration, which is just one rough consideration. According to the concept of atom interaction volume<sup>[11]</sup>, interaction scope of outer valence electron can be obtained, viz.

$$V^{\text{act}} = \frac{4}{3}\pi(r_{\text{ws}}^3 - r_{\text{m}}^3), \quad (10)$$

where,  $r_{\text{ws}}$  and  $r_{\text{m}}$  are respectively Wigner-Seitz radius and closely-packed radius of the atom. It should be pointed out that, for a certain crystal structure, the difference of  $r_{\text{ws}}$  and  $r_{\text{m}}$  only lies in one known constant.  $V^{\text{act}}$  is atom interaction volume, indicating the interaction “depth” of electron cloud between atoms. The electron density of inner electron cloud changes little when the atom changes its radius, so it is approximately believed that change in electron cloud mainly takes place within the scope of atom interaction volume.

With average electron density and atom action volume, the atomic radius of the component A and B ( $r'_A$  and  $r'_B$ ) after contact can be obtained, namely,

$$V_A^{\text{act}} \cdot n_A = V_A^{\text{act}} \cdot \bar{n}, \quad (11)$$

$$V_B^{\text{act}} \cdot n_B = V_B^{\text{act}} \cdot \bar{n}. \quad (12)$$

For a known crystal structure of component A and component B, combination of Eqs. (9) ~ (12) can yield the solution of  $r'_A$  and  $r'_B$ .

In fact, equilibrium electron density  $n_{AB}$  of two atoms does not equal  $\bar{n}$ .  $n_{AB}$  is relevant to other physical parameters of the components. When discussing some properties of near equilibrium, only binding energy taken into consideration is enough. Similarly, the binary system can also be simplified to two atoms.

According to atomic radius and electron density all the solid element pairs in the periodic table can be divided into two categories:

$$r_A < r_B, \quad n_A > n_B, \quad (13)$$

$$r_A > r_B, \quad n_A > n_B. \quad (14)$$

For convenience, the element pair corresponding to Eq. (13) is called a normal match, as illustrated in Fig. 5(a); and the pair corresponding to Eq. (14) is called an abnormal match (Fig. 5(b)). Two kinds of matches lead to two kinds of electron density versus atomic radius diagrams.

### 6 Atomic phase diagram

Fig. 6(a) is the curve of electron density versus atomic radius for a normally-matched pair, showing the atom state before and after the components forming the solid solution or compound. Point A represents component A and point B denotes component B,  $\bar{r}$  is mean atomic radius of two atoms and  $\bar{n}$  is mean electron density of these two atoms,  $n_P$  corresponding to  $r_P$  is equilibrium electron density of two atoms. V point and P point in the figure are respectively called mean point and equilibrium point of atomic phase diagram, having different physical significance on the solid solution and compound, which will be discussed in another paper combined with concrete problem.

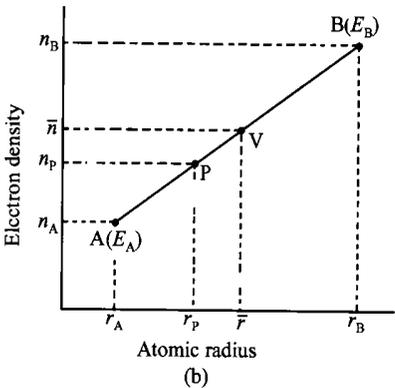
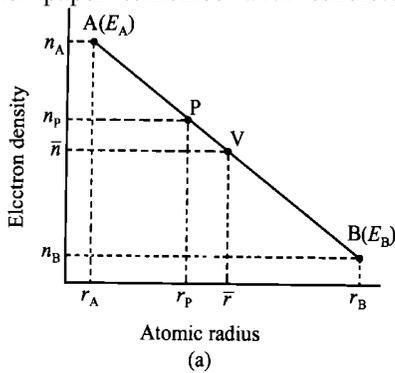


Fig. 6. Atomic phase diagrams. (a)  $r_A < r_B, n_A > n_B$   
 (b)  $r_A < r_B, n_A < n_B$ .

Fig. 6(b) illustrates the atomic phase diagram for abnormally-matched pair.

Under the constraint of electron density continuity on the interface, surface electron density of component A and component B in the solid solution or compound equals the same value as  $n_P$  in atomic phase diagram called electron density of solid solution or compound. Solution of  $n_P$  involves one empirical formula called the empirical lever law.

### 7 Empirical lever law of atomic phase diagram

Traditional alloy diagram gives a relative percentage of equilibrium phase with the lever law, while lever law of atomic phase diagram contributes to solution of atom equilibrium electron density in equilibrium state. As shown in Fig. 7, when the atoms of component A and component B reach equilibrium of interface electron density, the pivot of equilibrium lever is  $n_P$ , namely, the electron density of the solid solution or compound; end points of the lever are  $n_A$  and  $n_B$  respectively; in the mean time, ends of the lever respectively “hang” binding energy of component A and component B.

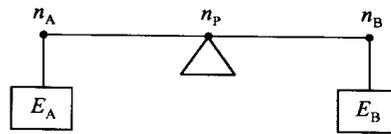


Fig. 7. Empirical lever law of atomic phase diagram.

When the lever reaches equilibrium, we have

$$(n_A - n_P) \cdot E_A = (n_P - n_B) \cdot E_B. \quad (15)$$

After simple transformation, we will get

$$n_P = \frac{n_A E_A + n_B E_B}{E_A + E_B}. \quad (16)$$

Eq. (16) is just the empirical lever law of atomic phase diagram. It also indicates that it is difficult for the component with larger binding energy to change its atomic radius so that the atomic radius of two components with different binding energy change in different scale in order to satisfy the continuity of electron density. Only when  $E_A = E_B$ , does  $n_P = \frac{n_A + n_B}{2} = \bar{n}$  hold true, which is the mean electron density approximation mentioned above.

### 8 Applications of atomic phase diagram

According to the atomic phase diagram and the

empirical lever law, with electron density and binding energy in document<sup>[13]</sup>, electron density of AB type compound and (50at% A + 50at% B) type solid solution can be obtained, as shown in Tables 1 and 2.

Table 1. Electron density of typical AB compounds ( $10^{29} \cdot \text{m}^{-3}$ )

Compound	TiN	TiC	NbN	NbC	VN	VC	ZrN	ZrC
<i>n</i>	0.793	2.48	1.19	2.52	1.18	2.75	0.73	2.27

Table 2. Electron density of typical (50at% A + 50at% B) solid solutions ( $10^{29} \cdot \text{m}^{-3}$ )

Solid solution	Ag+Pd	Au+Ag	Au+Pt	Cu+Ni	Cu+Pd	Ni+Pt	Au+Pd
<i>n</i>	2.41	2.44	3.06	3.20	2.83	3.31	2.67

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