Physica B 434 (2014) 38–43

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Empirical atom model of Vegard's law

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ARTICLE INFO

Article history:
Received 29 August 2012
Received in revised form
31 October 2013
Accepted 31 October 2013
Available online 7 November 2013

Keywords:
Vegard's law
Electron density
Atom radius
Thomas–Fermi–Dirac
Cohesive energy
Lattice parameter

ABSTRACT

Vegard's law seldom holds true for most binary continuous solid solutions. When two components form a solid solution, the atom radii of component elements will change to satisfy the continuity requirement of electron density at the interface between component atom A and atom B so that the atom with larger electron density will expand and the atom with the smaller one will contract. If the expansion and contraction of the atomic radii of A and B respectively are equal in magnitude, Vegard's law will hold true. However, the expansion and contraction of two component atoms are not equal in most situations. The magnitude of the variation will depend on the cohesive energy of corresponding element crystals. An empirical atom model of Vegard's law has been proposed to account for signs of deviations according to the electron density at Wigner–Seitz cell from Thomas–Fermi–Dirac–Cheng model.

1. Introduction

Vegard [1] established the linear relationship between the lattice parameter of a solid solution and concentrations of two components, known as Vegard's law. However, subsequent experimental investigations show that Vegard's law is seldom accurately valid. In most situations deviations are observed [2,3], having either a negative sign (the lattice parameter of the solid solution is less than the value corresponding to the linear rule) or a positive one. Consequently, Vegard's law is more an approximation rule than a precise law. Nevertheless, it is still widely used in materials science [4,5].

It is well known that three main factors affect the structures of alloy phases:(1) the atomic size factor resting on the difference in atomic radii of alloying elements, (2) charge-transfer factor or the chemical affinity factor which rests on the difference in electronegativities of alloying elements, (3) electron concentration factor. The latter two can be classified as electronic factors. The size factor has been often investigated on the basis of first-order or second-order elasticity theory to account for deviations from Vegard's law. Pines [6] made use of the elastic sphere model for the first time to deduce the functional dependence of deviations on compressibilities of two components. Then Friedel [7] further demonstrated that deviations may result from the difference in the compressibilities of component elements by the similar linear elasticity method. Afterwards, Gschneidner and Vineyard [8] advocated that deviations lie on the square of the difference in lattice parameters of two components by means of a new method based on second-order elasticity theory. Simultaneously, parallel studies based on density functional theory (DFT) have been carried out to explore the effect of size factor on deviations. Barrat, Baus, and Hansen [9] briefly discussed the relationship between DFT and Vegard's law for the first time. Then Denton and Ashcroft [10] further applied DFT of nonuniform fluid mixtures to the simple binary mixtures of hard sphere in fluid-solid transition state and demonstrated the significance of the size factor in ascertaining lattice constants. More recent studies by Murphy et al. [11] established a simple functional dependence of the relative size of the group III (B, Al, Ga, and In) atoms in $M_xN_{1-x}As$ alloys on the predicted magnitude of the deviation from Vegard's law in terms of DFT. All these studies indicated that the simple but very important geometric factor of different atomic sizes, by itself, has a vital role in determining the crystal structure of alloys, although they did not deny the importance of other factors [10].

In the mean time, more and more researchers attached importance to the roles of electronic factors on deviations. Sarkisov [12] suggested that deviations lie on the number of valence electrons of two components on the basis of free electron-gas concept. Similarly, Shao and Tsakiropoulos [13] investigated TM(3d)–Al solid solutions and found that deviations are proportionate to the difference in valence electron densities between Al and the solvent metals. Almost in the mean time, Xie [14] proposed a

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http://dx.doi.org/10.1016/j.physb.2013.10.066

generalized Vegard's law from viewpoints of Characteristic Crystals Theory. In Xie's model, it is the lattice parameters of characteristic crystals rather than those of component crystals that satisfy linear additivity. Afterwards, Lubarda [15] incorporated an apparent size of the solute atom to approximately explain the electronic interactions between the solvent and solute atoms and deviations from Vegard's law, finally obtaining better results. In conclusion, both Sarkisov's model and Xie's model need the introduction of additional parameters that cannot be determined independently, and Shao et al. and Lubarda's investigations aimed at certain alloys. Accordingly, these models still have some limits for predictions of deviations. Furthermore, the embedded atom method (EAM) [16] was also used to explore the effect of energy factor on deviations from Vegard's law. Studies by Hu [17] revealed that there indeed exists a linear relationship between the volume shrinkage and the heat of formation for Mg–Re alloys by means of the analytic modified embedded atom method (MEAM).

In short, deviations closely connected with complex interactions between two components in solid solutions cannot be explicitly explained by a simple size effect or by a single electronic factor. Therefore, it may be a better way to incorporate both size factor and electronic factor together with energy factor into the exploration of deviations from Vegard's law. In our earlier paper [18] we ever explored the interaction among these three factors for solid solution formation. When two components form a solid solution, the atom volumes of component elements will change to satisfy the continuity requirement of electron density at the interface between component atom A and atom B. Here the equilibrium electron density ρ_P at the interface can be obtained by one so-called empirical lever law as follows [18]:

$$(\rho_B-\rho_P)\times E_B=(\rho_P-\rho_A)\times E_A \tag{1}$$

ρ_A and ρ_B are electron density of component atoms A and B, E_A and E_B are cohesive energy of components A and B. The empirical atom model of Vegard's law in this paper is just built on such an idea.

2. Theoretical method

In this section, there are three aspects of the problem to be addressed. The first aspect involves the theoretical foundation of TFDC electron density. The second aspect relates to the data processing of lattice parameters of solid solution alloys. The third part deals with the diatomic model to be used in the empirical atom model subsequently.

2.1. TFD statistical model and TFDC electron density

Thomas [19] and Fermi [20] proposed a model describing the electron distribution in the atom. The model is called as TF model with the mathematical expression as below:

$$\rho(x)=\frac{Z}{4\pi\mu^3}\left(\frac{\Phi}{x}\right)^{\frac{3}{2}} \tag{2}$$

where $\mu=a_0(9\pi^2/128Z)^{1/3}$, a_0 is the Bohr radius, Z is the atomic number, Φ is TF function with no dimension, x is the atom radius with no dimension, $r=\mu x$ is the actual atom radius, $\rho(x)$ is the electron density. Dirac [21] introduced the electron exchange action into TF model and established TFD model. TFD model gives the relationship of the electron density and the atom radius as follows:

$$\rho(x)=\frac{Z}{4\pi\mu^3}\left[\varepsilon+\left(\frac{\Psi}{x}\right)^{\frac{1}{2}}\right]^3 \tag{3}$$

where ε is electron exchange item with the expression as $\varepsilon=\left(\frac{3}{32\pi^2}\right)^{1/3}Z^{-2/3}$, Ψ is TFD function satisfying famous TFD equation, namely,

$$\frac{d^2\Psi}{dx^2}=x\left[\varepsilon+\left(\frac{\Psi}{x}\right)^{\frac{1}{2}}\right]^3 \tag{4}$$

TFD model finds successful application in concerned scientific fields [22]. With Wigner–Seitz radius given, the electron density at the corresponding atom radius can be obtained from Eqs. (3) and (4). In turn, with electron density known, the corresponding atomic radius can be solved by these two equations. In other words, Eqs. (3) and (4) can be solved not only directly but also inversely. It should be stated that the electron density involved in this paper refers to the electron density at Wigner–Seitz radius.

Meanwhile, Miedema [23] also concluded one empirical relation to solve electron density at Wigner–Seitz radius according to bulk modulus and molar volume of alkali metals. On above basis, Miedama [24] further put forward one cellular model to describe component changes during the process of alloys' formation. Subsequently, Kaijia Cheng introduced the boundary conditions of Miedema model into TFD model and developed improved TFD model [25], namely, TFDC model. With TFDC model, Cheng [26] reported nearly the same electron density data as Miedema's. In addition, these electron density data can also be obtained by density-functional theory (DFT) [27]. In fact, electron density data deduced from DFT and those from TFDC model make no difference, but the solution with TFDC model seems more simple and needs no commercial softwares.

In this paper, Wigner–Seitz radius and electron density at Wigner–Seitz radius are used to describe atoms. These two parameters and cohesive energy data E_c [28] of concerned elements in crystals are shown in Table 1.

2.2. The data processing method

Lattice parameters of all solid solution alloys are taken from Pearson's book [29]. The involved binary alloy systems add up to 117 kinds, including 35 continuous solid solutions and 82 limited solid solutions. All a–C graphs for solid solution alloys are fitted to quadratic polynomials with the form of $a=\beta_1C^2+\beta_2C+\beta_3$, where a is the lattice parameter of the solid solution alloy, C is the atomic concentration of the solute. If $\beta_1>0$, the lattice parameter of the practical solid solution takes on negative deviation from Vegard's law. On the contrary, if $\beta_1<0$, the lattice parameter of the practical solid solution takes on positive deviation from Vegard's law. Thus, we can obtain statistic results of deviations in solid solution alloys.

Table 1
Atomic parameters of component crystals, including the atomic number Z, Wigner–Seitz radius r_{WS} (10^{-10}m), electron density ρ (10^{29}/m^3), and E_c cohesive energy (kJ/mol).

Z	Element	r_{WS}	ρ	E_c	Z	Element	r_{WS}	ρ	E_c
22	Ti	1.6136	1.3266	468	46	Pd	1.5224	2.6518	376
23	V	1.4901	2.0361	512	47	Ag	1.5982	2.0851	284
24	Cr	1.4202	2.6436	395	51	Sb	1.9393	0.7496	265
26	Fe	1.4119	2.8474	413	73	Ta	1.6288	2.3283	782
27	Co	1.3846	3.1987	424	74	W	1.5573	2.9688	859
28	Ni	1.3780	3.3425	428	77	Ir	1.5015	3.6555	670
29	Cu	1.4119	3.0273	336	78	Pt	1.5336	3.2948	564
40	Zr	1.7746	1.0992	603	79	Au	1.5932	2.7136	368
41	Nb	1.6237	1.7923	730	81	Tl	1.8962	1.0536	182
42	Mo	1.5504	2.3062	658	82	Pb	1.9359	0.9398	196
45	Rh	1.4873	2.9535	554	83	Bi	2.0363	0.7006	210