# Electronic structure and physical property of TiAl[①]

Gao Yingjun[1](高英俊), Chen Zhenhua[2](陈振华),

Huang Peiyun[2](黄培云) and Zhong Xiaping[1](钟夏平)

1. *Physical Department, Guangxi University, Nanning 530004, P. R. China*

2. *Institute of Nonequilibrium Materials Research,*

*Central South University of Technology, Changsha 410083, P. R. China*

**Abstract:** Using a new developed valence bond theory of intermetallic compound, the electronic structure and properties of TiAl were analysed systematically. It was determined that the valence electronic structure of Ti and Al atom in TiAl to be $[(4s_f)^{0.42}(4s_c)^{1.36}(3d_c)^{2.22}]_{Ti}$ and $[(3s_f)^{0.39}(3s_c)^{0.59}(3d_c)^{2.02}]_{Al}$ respectively. According to these electronic structure, lattice constant, cohesive energy, potential curve, bulk modulus and temperature dependence of linear thermal expansion coefficient have been calculated, most of the theoretical values of these properties are in good agreement with experiment ones.

**Key words:** TiAl; electronic structure; physical properties      **Document code: A**

## 1 INTRODUCTION

In recent years, the Pauling's valence bond (VB) theory has made a great progress in China. First, Yü developed the Pauling's valence bond theory and established the EET theory[1], and then based on the energy-bond theory and EET theory, Xie produced the one-atom-state theory[2](OA theory ) of pure metals with the unity of "shape" and "energy" and then developed the central atoms model in the statistic thermodynamics and built the characteristic crystal theory(CC theory )[3]. Now the OA theory has made a new progress and can be applied to intermetallic compound system[4]. The purpose of the present work is to made comprehensively systematical analysis of TiAl with these new progresses.

## 2 BASIC CELL STATE OF TiAl

As far as intermetallic compounds, which are composed of different kinds of atoms are concerned, the unit that reflects the characteristics of intermetallic compounds is not the atoms, but the primary cell or crystal cell, so electronic structure for intermetallic compound can be illustrated by one-cell-state[4]. Each one-cell-state $\Psi_k$ consists of some basic cell states(BCS)[4]:

$$\Psi_k = \sum c_k \psi_k^{Cell} \qquad (1)$$

where the BCS $\psi_k^{Cell}$ is a composite state[4] composed of some basic-atom states (BAS) of all atoms which belong to the same cell. The electron-occupation numbers of each BCS $\psi_k^{Cell}$ are described by QEO[2] numbers and can be explained by the Pauli exclusion principle. In non-ferromagnetic intermetallic compound, there are covalent electron $n_c$, free-electron $n_f$ and non-valence electron $n_n$ in its atoms. If $s_k^c$, $p_k^c$ and $d_k^c$ denote respectively the number of covalent electrons of s, p and d shells in $k$ BCS, $d_k^n$ and $s_k^f$ denote respectively the number of non-valence electrons and free electrons, considering the TiAl having the $L1_0$ type crystal structure, and a crystal cell containing four atoms, two of them belonging to Ti atom, others belonging to Al atom, according to the BCS construction principle[4], the BCS of TiAl can be written as

$$\psi_k^{cell} = [(s_f, s_c, d_c)^2_{Ti} \cdot (s_f, s_c, p_c)^2_{Al}] \qquad (2)$$

The state parameters of cell can be obtained

by the following expressions:

$$s_c^{Cell} = 2\sum_k C_k s_{k,c}^{Cell}$$

$$= 2\sum_k C_k (s_{k,c}^{Ti} + s_{k,c}^{Al}),$$

$$p_c^{Cell} = 2\sum_k C_k p_{k,c}^{Al},$$

$$d_c^{Cell} = 2\sum_k C_k d_{k,c}^{Ti}$$

$$N_f^{Cell} = \sum_k C_k (2s_{k,f}^{Ti} + 2s_{k,f}^{Al}),$$

$$N_c^{Cell} = s_c^{Cell} + p_c^{Cell} + d_c^{Cell},$$

$$N_T^v = N_f^{Cell} + N_c^{Cell}$$

$$R^{Ti} = \sum_k C_k R_k^{Ti},$$

$$R^{Al} = \sum_k C_k R_k^{Al},$$

$$R_k^{Ti} = 1.377 - 0.090\delta_k^{Ti}$$

$$R_k^{Al} = 1.308 - 0.25\delta_k^{Al} \tag{3}$$

where $R_k^{Ti}$ and $R_k^{Al}$ are the single bond radius which can be obtained by modifying Pauling's equation.

For a certain cell state, the characteristic properties( lattice constant and cohesive energy ) of the corresponding pseudo-crystal can be calculated by a series of equations presented in the following sections. Because the covalence bonds in TiAl have a great advantage over ionic bond, so the charge transfer can be neglected. Table 1 gives some natural BCS and the characteristic properties of pseudo-crystal of TiAl.

## 3 MAIN EQUATIONS

### 3.1 Lattice constant

Supposing that Pauling's bond length equation[1] is suitable to the various bonds in the pseudo-crystal. Then we have

$$r_1^A = 2R_k^A - \beta \lg n_1^A,$$

$$r_1^B = 2R_k^B - \beta \lg n_1^B,$$

$$r_1^{AB} = R_k^A + R_k^B - \beta \lg n_1^{AB}$$

$$r_2^A = 2R_k^A - \beta \lg n_2^A,$$

$$r_2^B = 2R_k^B - \beta \lg n_2^B,$$

$$r_2^{AB} = R_k^A + R_k^B - \beta \lg n_2^{AB}$$

$$\cdots\cdots\cdots$$

$$r_{s_1}^A = 2R_k^A - \beta \lg n_{s_1}^A,$$

$$r_{s_2}^B = 2R_k^B - \beta \lg n_{s_2}^B,$$

$$r_{s_3}^{AB} = R_k^A + R_k^B - \beta \lg n_{s_3}^{AB} \tag{4}$$

where A, B denote Ti and Al atoms respectively; $r_{s_1}^A$, $r_{s_2}^B$ and $r_{s_3}^{AB}$ denote the bond length; $n_{s_1}^A$, $n_{s_2}^B$ and $n_{s_3}^{AB}$ denote the number of pair of covalent electrons on the related bond , and $\beta$ is taken as 0.600 for $\gamma$-TiAl. From Eqns. (3) and (4), the following equations can be derived:

$$n_c = \sum_{s_1} I_{s_1}^A n_{s_1}^A + \sum_{s_2} I_{s_2}^B n_{s_2}^B + \sum_{s_3} I_{s_3}^{AB} n_{s_3}^{AB}$$

$$= 2\sum_k C_k (s_{k,c}^{Ti} + s_{k,c}^{Al} + d_{k,c}^{Ti} + d_{k,c}^{Al})$$

$$n_{s_1}^A = n_1^A \cdot 10^{(r_1^A - r_{s_1}^A)/\beta}$$

$$n_{s_2}^B = n_1^B \cdot 10^{(r_2^B - r_{s_2}^B)/\beta}$$

$$n_{s_3}^{AB} = n_1^{AB} \cdot 10^{(r_2^{AB} - r_{s_3}^{AB})/\beta} \tag{5}$$

where $I_{s_1}^A$, $I_{s_2}^B$ and $I_{s_3}^{AB}$ represent the number of the same $n_{s_1}^A$, $n_{s_2}^B$ and $n_{s_3}^{AB}$ bond respectively. For a certain pseudo-crystal, the bond length can be expressed by its lattice constant:

$$r_{s_1}^A = G_{s_1}^A a \qquad r_{s_2}^B = G_{s_2}^B a$$

$$r_{s_3}^{AB} = G_{s_3}^{AB} a \tag{6}$$

To simplify the calculation for $\gamma$-TiAl with $L1_0$ crystal structure, (see Fig. 1) taking $\bar{a} = \bar{c} = (a + c)$, i.e., the crystal cell as fcc structure, therefore,

$$G_{s_1}^A = 1/\sqrt{2}, \quad G_2^A = 1, \quad G_1^B = 1/\sqrt{2},$$

$$G_2^B = 1, \quad G_1^{AB} = 1/\sqrt{2}, \quad G_2^{AB} = \sqrt{3}/\sqrt{2},$$

$$\cdots\cdots \tag{7}$$

Combining Eqns. (4), (5), (6), and (7), we produce

$$a = \frac{\beta}{G^{AB}} \cdot$$

$$\lg\left[\left\{\begin{array}{l}\left[\sum_{s_1} I_{s_1}^A \cdot 10^{-(G_{s_1}^A - G_1^{AB})\cdot a/\beta}\right] \times 10^{2R_k^A/\beta} + \\ \left[\sum_{s_2} I_{s_2}^B \cdot 10^{-(G_{s_2}^B - G_1^{AB})\cdot a/\beta}\right] \times 10^{2R_k^B/\beta} + \\ \left[\sum_{s_3} I_{s_3}^{AB} \cdot 10^{-(G_{s_3}^{AB} - G_1^{AB})\cdot a/\beta}\right] \times 10^{(R_k^A + R_k^B)/\beta}\end{array}\right\}/n_c\right] \tag{8}$$

Similar to method of Ref. [5], it can be proved that Eqn. (8) is a convergent transcendental equation of the lattice constant, and there is a unique lattice constant, namely a unique set of bond lengths for a certain cell state as forming a crystal.

**Table 1** Natural basis-cell-state and pseudo-crystal characteristic properties of TiAl

| Basic State | Electronic configuration | Lattice constants/Å | Cohesive energy /(kJ·mol⁻¹) |
|---|---|---|---|
| $\varphi_1^0$ | $(1, 0, 3)^2_{Ti}(1, 0, 2)^2_{Al}$ | 4.0717 | 331.48 |
| $\varphi_2^0$ | $(0, 1, 3)^2_{Ti}(1, 0, 2)^2_{Al}$ | 4.0047 | 429.96 |
| $\varphi_3^0$ | $(1, 1, 2)^2_{Ti}(1, 0, 2)^2_{Al}$ | 4.1108 | 344.36 |
| $\varphi_4^0$ | $(1, 0, 3)^2_{Ti}(0, 1, 2)^2_{Al}$ | 4.0047 | 412.18 |
| $\varphi_5^0$ | $(0, 1, 3)^2_{Ti}(0, 1, 2)^2_{Al}$ | 3.9480 | 557.88 |
| $\varphi_6^0$ | $(1, 1, 2)^2_{Ti}(0, 1, 2)^2_{Al}$ | 4.0438 | 426.09 |
| $\varphi_7^0$ | $(1, 0, 3)^2_{Ti}(0, 2, 1)^2_{Al}$ | 4.1031 | 387.56 |
| $\varphi_8^0$ | $(0, 1, 3)^2_{Ti}(0, 2, 1)^2_{Al}$ | 4.0465 | 504.97 |
| $\varphi_9^0$ | $(1, 1, 2)^2_{Ti}(0, 2, 1)^2_{Al}$ | 4.1388 | 400.72 |
| $\varphi_{10}^0$ | $(1, 0, 3)^2_{Ti}(0, 0, 3)^2_{Al}$ | 3.9190 | 402.22 |
| $\varphi_{11}^0$ | $(0, 1, 3)^2_{Ti}(0, 0, 3)^2_{Al}$ | 3.8624 | 537.82 |
| $\varphi_{12}^0$ | $(1, 1, 2)^2_{Ti}(0, 0, 3)^2_{Al}$ | 3.9615 | 418.50 |
| $\varphi_{13}^0$ | $(0, 2, 2)^2_{Ti}(1, 0, 2)^2_{Al}$ | 4.0438 | 393.94 |
| $\varphi_{14}^0$ | $(0, 2, 2)^2_{Ti}(0, 1, 2)^2_{Al}$ | 3.9871 | 499.14 |
| $\varphi_{15}^0$ | $(0, 2, 2)^2_{Ti}(0, 2, 1)^2_{Al}$ | 4.0822 | 483.10 |
| $\varphi_{16}^0$ | $(2, 0, 2)^2_{Ti}(1, 0, 2)^2_{Al}$ | 4.1929 | 246.15 |
| $\varphi_{17}^0$ | $(2, 0, 2)^2_{Ti}(0, 1, 2)^2_{Al}$ | 4.1495 | 287.27 |
| $\varphi_{18}^0$ | $(2, 0, 2)^2_{Ti}(0, 2, 1)^2_{Al}$ | 4.2059 | 312.98 |
| $\varphi_{19}^0$ | $(2, 0, 2)^2_{Ti}(2, 0, 1)^2_{Al}$ | 4.3938 | 275.69 |
| $\varphi_{20}^0$ | $(1, 1, 2)^2_{Ti}(2, 0, 1)^2_{Al}$ | 4.2880 | 280.69 |
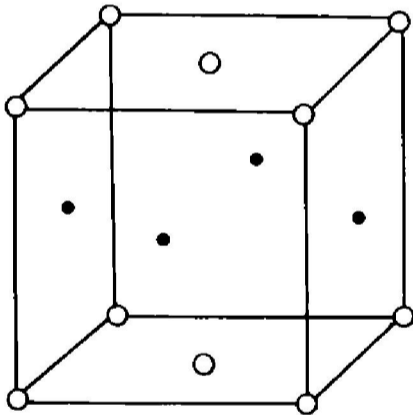


**Fig.1** $LI_0$ crystal structure

## 3.2 Potential function

Combining the calculation formula of cohesive energy $E_c^T$ for intermetallic compound in Ref. [6] with the potential in Ref. [7], the new potential function can be written as below:

$$U(r) = E_c^T \cdot \left[ -n\left(\frac{r_0}{r}\right)^x + (n-1)\left(\frac{r_0}{r}\right)^{nx/(n-1)} \right]$$

(9)

where $E_c^T$ is the cohesive energy in equilibrium

state, the $x$ and $n$ are constants determined by experiments. Since the charge transfer in TiAl can be neglected, the ionic energy and the chemical affinity are not considered here. So $E_c^T$ can be simplified and written as

$$E_c^T = b_A \left[ \sum_{s_1} \frac{I_{s_1}^A n_{s_1}^A}{r_{s_1 0}^A} f_A \right] +$$

$$b_B \left[ \sum_{s_2} \frac{I_{s_2}^B n_{s_2}^B}{r_{s_2 0}^B} f_B \right] +$$

$$\sum_s \overline{B}_{AB} \cdot \frac{I_{s_3}^{AB} n_{s_3}^{AB}}{r_{s_3 0}^{AB}} \cdot F_{AB} +$$

$$B'_{AB} \cdot \frac{n_f \cdot f'}{r_0}$$

(10)

Where $b_A$, $b_B$, $B_{AB}$, $f_A$, $f_B$, and $f'$ are given in Refs. [6, 8].

## 4 ELECTRONIC STRUCTURE AND BOND PARAMETER

Analogous to the OA theory[2], equations (8) and (10) can be considered as one of the two characteristic properties($a$ and $E_c^T$) in potential energy equation (9) of a pseudo-crystal in equilibrium. It has been found that a most satisfactory solution is the combination of $\varphi_{14}$ ( $C_{14} = 0.5839$), $\varphi_{20}$ ( $C_{20} = 0.1971$) and $\varphi_{10}$ ( $C_{10} = 0.2190$). The coefficients of this solution, atom (or cell) state parameters, bond parameters, theoretical and experimental values of characteristic properties are listed in Table 2. According to the cell state parameter in Table 2, the electronic structure of TiAl can be easily expressed as below:

TiAl: $[ (4s_f)^{0.416}(4s_c)^{1.365}(3d_c)^{2.219} ]_{Ti}$

and $[ (3s_f)^{0.394}(3s_c)^{0.584}(3p_c)^{2.002} ]_{Al}$

(11)

The electronic structure of pure metals Ti and Al by OA method are given in Ref. [9, 10]. Here we write it out in order to compare with that of TiAl as below:

Ti: $[ (4s_f)^{0.30}(4s_c)^{1.05}(3d_c)^{2.65} ]_{Ti}$ and

Al: $[ (3s_f)^{0.885}(3s_c)^{0.546}(3p_c)^{1.570} ]_{Al}$ (12)

Comparing Eqns. (11) and (12), we can see that the free electronic numbers of Al atom in

TiAl is less about $0.885 - 0.394 \approx 0.5$ than that of Al atom in pure Al metal, and the free electrons decrease and become the $p_c$ orbital covalence electrons of Al atom in TiAl. We can also see that the $d_c$ electron of Ti atom in TiAl is less than that of Ti atom in pure Ti metal. This can be explained by the cohesive energy(434 kJ/mol) of TiAl, which is less than the cohesive energy (468 kJ/mol) of Ti metal, so that TiAl needs less $d_c$ electrons to form strong covalence bond. Table 2 also shows the Ti-Ti bond ( $n_1 = 0.4918$) is greater than that of Ti-Al bond( $n_2 = 0.2330$), and the result is agreement with that of Refs.[11,14] which give the charge distribution of Ti atom in TiAl.

## 5  RELATIONSHIP BETWEEN CRYSTAL AND ELECTRONIC STRUCTURES

Here we consider lattice constants $a = c$ being approximately held in order to simplify calculation, so the $L1_0$ structure becomes fcc structure, but in the latter the Ti atoms alternate with that of Al atoms. The $d_c$ electron of Ti atom in TiAl should occupy the $t_{2g}$ state in order to form the lobe, i. e., $d_{xy}$ bond state , along the $<110>$ bisectors in atomic layer of TiAl, where the Ti-Al p-d bond can be formed between the alternated plane of Ti and Al atom. The trunk of Al atomic layers is found by the dumb-bell-shaped lobe of p electron in TiAl. We can see from the nearest neighbor coordination atoms, that there are not only d-d bond but also p-d bond in environment of Ti atom, therefore the bond net surrounding Ti atom is unsymmetrical distribution. The bond net surrounding Al

atom is also unsymmetrical distribution because of existence of both p-d bond and p-p bond in environment of Al atom. Table 2 shows that the Ti-Ti bond ( $n_1 = 0.4918$) is much greater than Ti-Al bond( $n_2 = 0.2330$). This is the main reason that the two-dimension structure with alternating layer of Ti and Al atom is formed in TiAl.

The valence electronic bonding state of Ti and Al atom in TiAl written in formula (11) can be approximately expressed by following pictorial formula.
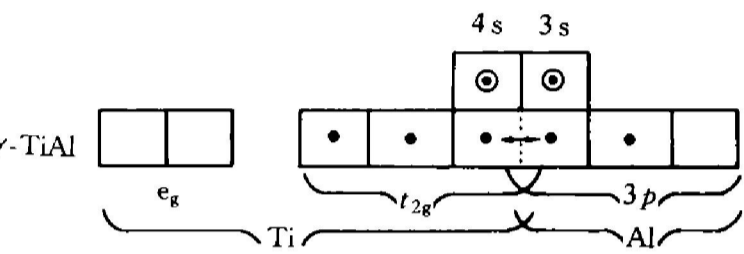


where the symbol $\leftrightarrow$ expresses the p-d bond, $\cdot$ denotes the covalent electron, and $\odot$ denotes that one part of electron is covalent and another electron is free.

## 6  PHYSICAL PROPERTY OF TiAl

### 6.1  Potential function and thermal expansion coefficient

Fig. 2 and Fig. 3 show the theoretical potential energy function and theoretical temperature dependence of linear thermal expansion coefficient for TiAl.

### 6.2  Elasticity

According to the elastic formula given in

**Table 2**  Cell state parameters and pseudo-crystal properties

| Coefficient | $C_{10} = 0.2190$ | | | $C_{14} = 0.5839$ | | $C_{20} = 0.1971$ | |
|---|---|---|---|---|---|---|---|
| Cell state parameter | $s_f^{Ti} = 0.416$ | $s_c^{Ti} = 1.365$ | $d_c^{Ti} = 2.219$ | $R^{Ti} = 1.327(\text{Å})$ | $n_T^{Ti} = 4.00$ | $n_c^{Cell} = 6.190$ | |
| | $s_f^{Al} = 0.394$ | $s_c^{Al} = 0.584$ | $p_c^{Al} = 2.022$ | $R^{Al} = 1.140(\text{Å})$ | $n_T^{Al} = 3.00$ | $n_T^{Cell} = 7.00$ | |
| Bond parameter | $n_1 = 0.4918$ | $n_2 = 0.2330$ | $n_3 = 0.1132$ | $n_4 = 0.0021$ | | $n_5 = 0.0045$ | |
| | $r_1 = 2.8548(\text{Å})$ | $r_2 = 2.8548(\text{Å})$ | $r_3 = 2.8548(\text{Å})$ | $r_4 = 4.0373(\text{Å})$ | | $r_5 = 4.0373(\text{Å})$ | |
| Theoretical | $a = 4.031(\text{Å})$ | $E = 432.1(\text{kJ/mol})$ | | $B = 1.75\,\text{GPa}$ | | $\alpha = 10.5(10^{-6}/\text{K})$ | |
| Experimental[16] | $a = 4.037(\text{Å})$ | $E = 434.8\ (\text{kJ/mol})$ | | $B = 1.71\,\text{GPa}$ | | $\alpha = 11.0(10^{-6}/\text{K})$ | |

Ref. [7] and Deybe temperature $\theta_{TiAl}$ = 515 (K)[12], we can calculate the bulk elastic module (K), Young's E and shear module (G) and Poisson's ratio(v). The theoretical and experimental results are listed in Table 3.

**Table 3**    Elastic module of TiAl

| Elasticity/$10^{11}N\cdot m^{-2}$ | K | E | G | v |
|---|---|---|---|---|
| Theoretical | 1.72 | 1.72 | 0.64 | 0.33 |
| Experimental[16] | 1.71 | 1.74 | 0.70 | 0.25 |
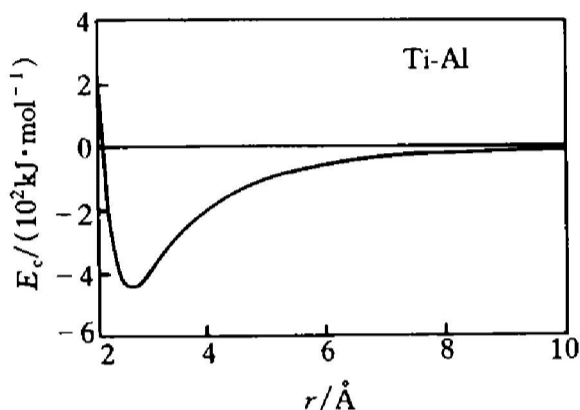


**Fig.2**    Potential energy function
$E_c$ = 434.8(kJ/mol),  $r_0$ = 2.8548(Å)
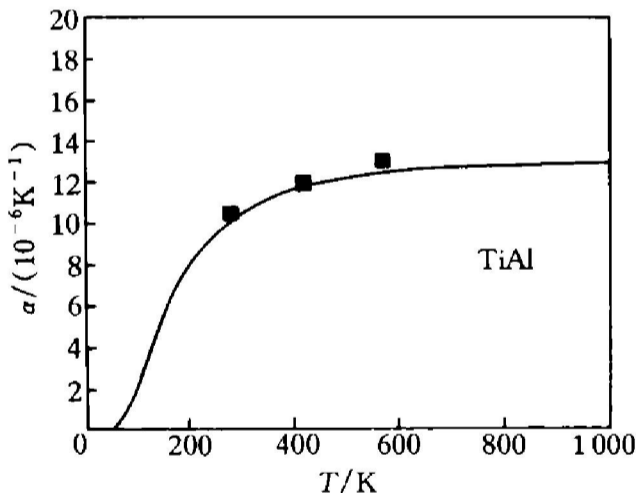


**Fig.3**    Temp. dependence of coefficient of linear thermal expansion for TiAl.
■ = Experiment values[15]

Table 3 shows that calculated results of bulk and Young's module are in agreement with ex-periment values, but the calculated results of shear module and Poisson's ratio comparing with the experiment values have some deviations. The cause is that the many-body pair potential is too simple to consider the interrelation between the bond angle. The TiAl has such a system of stronger covalence bond that the bond angle interrelation can not be neglected. Therefore, the interaction potential TiAl will be more accurately described by the BOP[13].

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