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Electronic bonding and property of FeAl ①

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Abstract: The electronic structure of FeAl was determined by one-cell-state method and the curve of potential energy, lattice constant, cohesive energy, bulk elastic modulus, and the variation of linear thermal expansion coefficient with temperature were calculated. It was found that most of the theoretical values of these properties above are in good agreement with experimental ones. The relationship between electronic bonding and crystal structure/brittleness was discussed by using the calculated electronic structure.

Key words: FeAl; electronic bonding; crystal structure; thermal expansion; brittleness **Document code:** A

1 INTRODUCTION

In order to advance materials science into a systematic science of materials and empirical design of materials into a scientific design of materials, Xie first established the one-atom-state theory (OA theory)[1] of pure metal by absorbing quintessences of the energy band theory[2] and the metal valence bond theory[3], and then combined the OA theory with the statistic thermodynamics to produce a characteristic crystals (CC) theory[4], and successfully used it to calculate the electronic structure of disorder alloy system. Now the OA theory has made a new progress and can be applied to intermetallic compound system[5~7] with charge transfer. The purpose of this paper is to make comprehensive analysis of FeAl with these new progresses.

2 BASIC CELL STATE OF FeAl

As far as intermetallic compounds are concerned, they are composed of different kinds of atoms. The unit that reflects the characteristic of intermetallic compounds is not the atom, but the primary cell or crystal cell, so electronic structure for intermetallic compound can be illustrated by one-cell-state[5] Ψ_c, which is composed of some basic cell state (BCS) $\varphi_k^{\mathrm{Cell}}$:

$$\Psi_c = \sum C_k \varphi_k^{\mathrm{Cell}} \qquad (1)$$

According to whether there are charge transfer or not between atoms, the BCS can be divided into two states[5], one of which is called neutral BCS (NBCS), and the other is called polar BCS (PBCS). FeAl is a nonferromagnetic intermetallic compound, its crystal structure is of B_2 type, and a crystal cell of it contains two atoms. One of them is an Fe atom, the other is an Al atom. In nonferromagnetic compounds, there are covalent electrons n_c, near free-electrons n_f and non-bond electrons n_n in its atoms. Electronic distributions in BCS obey the Pauli exclusion principle. Then the BCS can be expressed by the following form[5]:

$$\varphi_k^{\mathrm{Cell}} = [(s_f, s_c, d_c, d_n)_{\mathrm{Fe}} \cdot (s_f, s_c, p_c)_{\mathrm{Al}}]_k \qquad (2)$$

The experimental results show that there is charge transfer[8] from Al atom to Fe atom in FeAl intermetallic compounds. Therefore the BCS should include the polar basic-cell-state (PBCS)[5]. If s_k^c, p_k^c and d_k^c denote respectively the number of convalent electrons of s, p and d shell in kth BCS, d_k^n and s_k^f denote respectively the number of non-bond electrons and near free electrons, then the parameters of cell state can be obtained by the following formula:

$$s_c^{\mathrm{Cell}} = \sum_k C_k S_{k,c}^{\mathrm{Cell}} = \sum_k C_k (S_{k,c}^{\mathrm{Fe}} + S_{k,c}^{\mathrm{Al}})$$

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

$$d_c^{\mathrm{Cell}} = \sum_k C_k d_{k,c}^{\mathrm{Fe}}$$

$$d_n^{\mathrm{Cell}} = \sum_k C_k d_{k,n}^{\mathrm{Fe}}$$

$$s_f^{\mathrm{Cell}} = \sum_k C_k (s_{k,f}^{\mathrm{Fe}} + s_{k,f}^{\mathrm{Al}})$$

$$n_c = s_c^{\mathrm{Cell}} + p_c^{\mathrm{Cell}} + d_c^{\mathrm{Cell}}$$

$$R^{\mathrm{Fe}} = \sum_k C_k R_k^{\mathrm{Fe}}$$

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

$$R_k^{\mathrm{Fe}} = (1.395 - 0.30\,\delta_k^{\mathrm{Fe}})$$

$$R_k^{\mathrm{Al}} = (1.308 - 0.25\,\delta_k^{\mathrm{Al}})$$

where R_k^{Fe} and R_k^{Al} are single-bond radii. For a cer-

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tain cell state, the characteristic properties of the corresponding pseudo-crystal can be calculated by a series of equations established in Refs. [1, 5]. The detail results are listed in Tables 1 and 2.

3 ELECTRONIC STRUCTURE OF FeAl

Using the one-cell-state method, the accurate solution of one-cell-state of FeAl can be determined and is composed of three BCS's: φ_6 (C_6 = 0.5311), φ_7 (C_7 = 0.4408), φ_7^* (C_7^* = 0.0281). Table 3 shows the calculated results of cell state parameters and physical properties in detail. These calculated properties are all in good agreement with experimental values. The r_1, r_2, r_3 and n_1, n_2, n_3 respectively denote the bond lengths and the pair numbers of covalent electrons on related bonds. The Δn_{Fe} and Δn_{Al} denote the charge transfer between Fe and Al atoms in FeAl.

According to the cell state parameters listed in Table 3, it can be seen that there are charge transfers from Al atom to Fe atom when free Fe atoms ([Ar] $4s^2 3d^6$) and Al atoms ([Ne] $3s^2 3p^1$) approach each other because of the overlaping between p and d bands. One Fe atom gains about 0.021 electron from Al atom. Therefore the electronic structures of Fe atom and Al atom in FeAl are respectively [Ar] $(3d_c)^{4.792}(3d_n)^{2.237}(4s_f)^{0.441}(4s_c)^{0.551}$ and [Ne] $(3s_f)^{0.531}(3s_c)^{0.470}(3p_c)^{1.972}$. Comparing the calculated electronic structures of pure metal Fe and Al in Refs. [9, 10], which gave out the [Ar] $(3d_c)^{4.47}(3d_m)^{2.39}(3d_n)^{0.02}(4s_f)^{0.52}(4s_c)^{0.60}$ and [Ne] $(3s_c)^{0.546}(3s_f)^{0.885}(3p_c)^{1.572}$ respectively, we can conclude that the magnetic electron d_m in Fe atom becomes a non-bond electrons d_n in FeAl.

Table 1 NBCS and characteristic properties of pseudo-crystals of FeAl

Basic state	Electronic configuration	Lattice constant/ Å	Cohesive energy/ (kJ· mol^{-1})
φ_1	$(1,0,5,2)_{Fe}(2,0,1)_{Al}$	3.0794	277.58
φ_2	$(0,1,5,2)_{Fe}(2,0,1)_{Al}$	3.0340	320.39
φ_3	$(1,0,5,2)_{Fe}(0,1,2)_{Al}$	2.8986	420.43
φ_4	$(0,1,5,2)_{Fe}(0,1,2)_{Al}$	2.8640	580.37
φ_5	$(1,0,3,4)_{Fe}(1,0,2)_{Al}$	3.0752	236.73
φ_6	$(0,1,3,4)_{Fe}(1,0,2)_{Al}$	3.0215	290.17
φ_7	$(1,0,7,0)_{Fe}(0,1,2)_{Al}$	2.8142	544.43
φ_8	$(0,1,7,0)_{Fe}(0,1,2)_{Al}$	2.7862	639.20

Table 2 PBCS and characteristic properties of pseudo-crystals of FeAl

Basic state	Electronic configuration	Lattice constant/ Å	Cohesive energy/ (kJ· mol^{-1})
φ_1^*	$(1,0,6,2)_{Fe}(1,0,1)_{Al}$	3.7463	375.36
φ_2^*	$(0,1,6,2)_{Fe}(1,0,1)_{Al}$	3.7292	410.32
φ_3^*	$(1,0,6,2)_{Fe}(0,1,1)_{Al}$	3.6957	440.40
φ_4^*	$(0,1,6,2)_{Fe}(0,1,1)_{Al}$	3.6684	527.29
φ_5^*	$(1,0,4,4)_{Fe}(1,0,1)_{Al}$	3.8030	318.40
φ_6^*	$(0,1,4,4)_{Fe}(1,0,1)_{Al}$	3.7832	354.00
φ_7^*	$(1,0,4,4)_{Fe}(1,1,0)_{Al}$	3.2138	191.08
φ_8^*	$(0,1,4,4)_{Fe}(1,1,0)_{Al}$	3.7101	431.66

Table 3 Cell state parameters, bond parameters and physical properties

Coefficient	φ_6 = 0.5311			φ_7 = 0.4408				φ_7^* = 0.0281
Cell state	s_f^{Cell}	s_c^{Cell}	d_c^{Cell}	d_n^{Cell}	p_c^{Cell}	R^{Fe}	R^{Al}	$\Delta n_{Fe} = -\Delta n_{Fe}$
Parameters	0.972	1.021	4.792	2.237	1.972	1.154	1.145	0.021

Bond parameters	n_1	n_2	n_3	r_1	r_2	r_3
	0.4163	0.0972	0.0909	2.5193	2.9090	2.9090

Properties	a/ Å	E/ (kJ· mol^{-1})	B/ (10^{11} N· m^{-2})	α_{293}/ (10^{-6}K^{-1})
Theoretical	2.9195	401.1	1.541	16.9
Experimental[12]	2.9090	402.4	1.536	17.4

a: lattice; E: cohesive energy; B: bulk elastic module; α_{293}: thermal expansion coefficient

4 RELATIONSHIP BETWEEN ELECTRONIC BONDING AND CRYSTAL STRUCTURE

The unspilt p^6 shell in free atoms are spilt into two energy levels e_g and t_{2g}[11] with different energies and different symmetries, when there is interaction between Fe and Al atoms. Two four-lobed orbital e_g (d_{xyz}) are oriental along the diagonal d_{xyz} and have lower energy, while the three four-lobed t_{2g}(d_{xy}, d_{yz}, d_{zx}) orbits line in the three coordinate planes between p_x, p_y and p_z orbits and have higher energies. Having the strong hybridization between Fe and Al atom with d-p bond along the direction ⟨111⟩ in FeAl intermetallic compound, which is of B_2 type crystal structure, the d_{xyz} orbital energy level along the direction ⟨111⟩ are most possibly occupied by covalent electrons d_c, while the t_{2g} orbits are occupied by the non-bond electrons d_n.

According the electronic structure with p-d hybridization between Fe and Al atoms in FeAl calculated in this paper and using the denotation given in Ref.[9], we suggest that the electronic bonding state of Fe and Al in FeAl be approximately expressed as pictorial formula in Fig.1, where ®, |, ○ denote respectively the covalent electrons, non-bond electrons, near free electrons and ◄ denote that orbits are partly occupied by covalent electrons; |® or ⊙ denote that one part of the electronic is covalent and another part is nonvalent or free. There are about 0.792 covalent electron d_c and 2.237 non-bond electrons d_n in t_{2g}, and each orbit has 0.264 covalent electron and 0.746 non-bond electron on an average. The p-d electronic hybridization between Fe and Al atoms in FeAl is also shown in Fig.1. The bond net between Al and Fe atoms in FeAl intermetallic compound is shown in Fig.2.

5 PHYSICAL PROPERTY OF FeAl

5.1 Potential energy function and thermal expansion coefficient

Based on electronic structure of FeAl, using the potential function of the many-atom-interaction (DMAI)[10], the potential energy curve of interaction between atoms in FeAl with one cell state Ψ_c is calculated and shown in Fig.3. Using the formula of linear thermal expansion[10], Gao figured out, the curve of linear thermal expansion coefficient varies with temperature, taking the parameters of interactive function as $n = 1.214$, $x = 2.114$, Debye temperature $\theta_D = 500$ K.

5.2 Brittleness

Comparing the electronic structure calculated in this paper of FeAl with that of pure metal calculated in Ref.[9,10], we can see that when the free Fe atom and Al atom approach each other to form intermetallic compound, the free electrons s_f of Fe in FeAl are less then those in pure metal Fe, while covalent electrons d_c are more than those of pure metal Fe about 4.792 - 4.470 = 0.322. On the other hand, the free electron s_f of Al atom in FeAl is much less than that of pure metal Al, about 57 %, and the decreased part of free electrons s_f in Al atom is transfered to covalent electrons p_c in p orbits in FeAl. These show that free electrons s_f responsible for the conductivity and plasticity are much less, while the covalent electrons n_c responsible for mechanical properties such as brittleness and rigidity have the advantage of other part of electrons in FeAl.

Furthermore, the number of free electrons s_f of Al atom in FeAl decreases much greater than that of pure metal Al, and the decrease number of s_f is to increase the number of covalent electrons p_c in orbits, and strengthen the p-d bond in ⟨111⟩ direction. These are the important reasons to explain the brittleness for FeAl in room temperature.

6 CONCLUSIONS

1) The valent electronic structure of Fe and Al atoms in FeAl are respectively $[Ar](3d_c)^{4.792}(3d_n)^{2.237}(4s_f)^{0.441}(4s_c)^{0.551}$ and $[Ne](3s_f)^{0.531}(3s_c)^{0.470}(3p_c)^{1.972}$, where the covalent electrons d_c in Fe atom are occupied in e_g orbits and non-bond electrons in t_{2g} orbits.

2) Using the potential function (DMAI), the calculated results of potential energy curve, lattice constant, cohesive energy, the variation of linear thermal expansion coefficient with temperature, are all in good agreement with experimental values.

3) The number of covalent electrons n_c is the

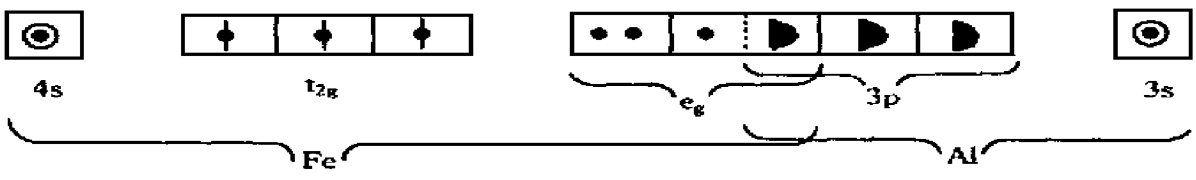

Fig.1 Pictorial formula of electronic bonding state of Fe and Al atoms in FeAl

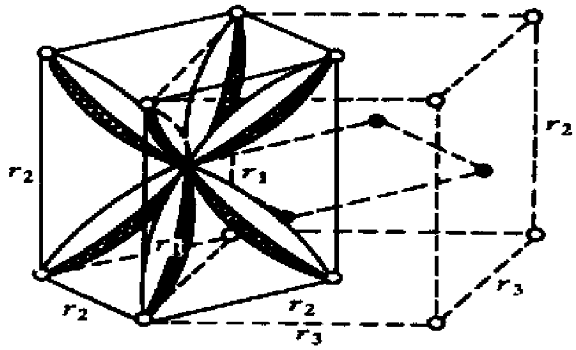

Fig. 2 Bond net between Fe atom and Al atom in FeAl

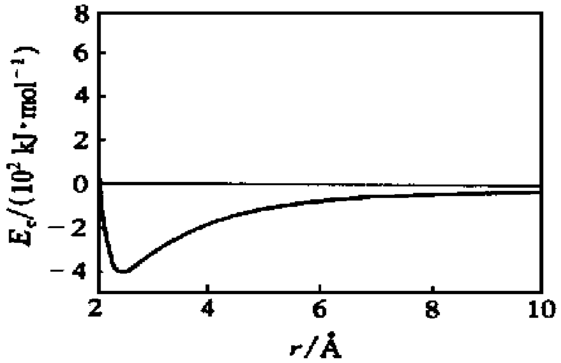

Fig. 3 Potential energy curve of FeAl

main part of valent electrons of FeAl, and there are much more covalent electrons p_c in Al atom of FeAl than in Al atom of pure metal, and form strong p-d hybridization. These are important reasons for brittleness.

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