The analysis of Fe-B-P valence electron structures by the empirical electron theory

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Abstract. The empirical electron theory (EET) of solids and molecules provides methods and basic data for calculating the valence electrons structure of group atoms. It makes it possible to calculate the valence electron structure of the alloy phase. Therefore, the essential relationship between the composition, structure properties, and valence electron structure of materials can be revealed. The valence electrons structure of amorphous Fe-B-P compounds are calculated by the bond length difference (BLD) method within the EET framework. The atomic states of the four selected crystal cells are possible states of the Fe-B-P.

1. Introduction

On the basis of the energy band theory and Pauling’s electron theory, Yu [1] put forward empirical electron theory of solids and molecules (EET) in 1978. By distinguishing the s, p, d valence electron of and the d electron equivalent to s and p of transition metal atoms, EET unifies the contradiction between Pauling’s chemical bond and Hume-Rothery’s metal bond of transition element atoms. At the same time, it expounds the physical substance, which the metal valence of the transition element in Hume-Rothery’s electron concentration rule is zero. Starting from the summary of experimental data, according to the double-state hybridization of atoms by induction, Yu [1] proposed the method of bond length difference (BLD) by describing Pauling’s covalent bond distance relation and four basic assumptions, which define the fine structure of valence electrons in molecules and solids, in order to obtain the hybrid state of each atom and the valence electron distribution between crystals, whose lattice constants are known. And then, the valence electron of crystals or molecules could be assessed by the theory.

The empirical electron theory has been widely used in many fields of the material research for steels intermetallic compounds, aluminum and magnesium alloys, ceramics, diamonds, and so on. At present, it is mainly used to calculate the valence electronic structure [2], phase-change dynamics [3], material mechanical properties [4], magnetism, conductivity, phase transition, binding energy, etc. Since 2008, Chao et al. [5-7] calculated the valence electron structure and magnetism of amorphous and nanocrystalline materials by EET.

In this paper, the valence electron structure of the Fe-B-P amorphous particles is calculated by the BLD method in EET. It extends the application scope of this theory.
2. Experimental materials and calculation methods

The Fe-B-P amorphous particles are prepared by the chemical method [8]. The BLD method is used to calculate the valence electron structure of molecules and solids, which need to calculate the atomic states of various constituent atoms and the covalence bond-net formed by the component atoms within the appointed system. The precondition for calculating the valence electron structure of molecules and solids by BLD method is that the crystal structure in the calculated system must be known. At the same time, you also need to know the spatial arrangement of each atom, which is crystal structure, lattice constant and coordinate parameter of atom et al. Based on the short range ordered structure model of amorphous alloy, the relative to the calculation size macroscopic amorphous alloy is treated as the crystal structure model approximately, but the electronic structure is different from the microscopic one. The valence electronic structure of the original Fe-B-P amorphous phase is calculated by EET. Because Fe-B-P amorphous alloy contains three elements like Fe, B, P, meanwhile, the content of B and P is very small in the sample, it is possible that there exist three types of unit cell such as α-Fe, α-Fe-P and α-Fe-B.

The theoretical basis for the calculation by BLD is the covalent bond distance formula by the third assumption in EET, as follows:

\[ D_{n_{\alpha}v}^{\mu-v} = R_{\alpha}(1) + R_{\nu}(2) - \beta|gn_{\alpha} | \]  

(1)

where \( \mu \) and \( \nu \) are two identical or different atoms, \( n_{\alpha} \) is the number of electron pairs of the valence bond, \( \alpha \) is a different valence bond in the structure; \( \alpha = A, B, C, D \ldots \)

\[ |\Delta D_{n_{\alpha}v}^{\mu-v}| = |\overline{D}_{n_{\alpha}v}^{\mu-v} - D_{n_{\alpha}v}^{\mu-v}| \]  

(2)

where the \( D_{n_{\alpha}v}^{\mu-v} \) is the experimental bond distance, the \( \overline{D}_{n_{\alpha}v}^{\mu-v} \) is the theoretical value. Yu applied \( |\Delta D_{n_{\alpha}v}^{\mu-v}| < 0.005nm \) as discrimination order to judge whether or not the assumed atomic state coincides with the actual one. The assumed atomic hybridization states are considered to be consistent with the actual one if the difference between the theoretical bond spacing and experimental one the assumed valence bonds meets the above requirement. There is more than one possible hybridization. If none of atomic hybridizations and the actual one are matching, the difference between the theoretical and experimental bond distances needs to be recalculated after adjusting the \( \beta \) value.

3. Results and discussion

The calculation process of valence electron structure of α-Fe unit cell is described below, while other cases are omitted for brevity.

The crystal structure type of α-Fe is body centered cubic (bcc) structure. The number of atoms in a single cell is 2. The equivalent point positions are 0, 0, 0, 1/2, 1/2, 1/2. The lattice constant \( a_{0} \) is 0.28664nm. There are two kinds of bond in the unit cell (A and B). The values of the experimental bond distance are shown as follows.

\[ D_{n_{A}Fe}^{Fe-Fe} = \frac{\sqrt{3}}{2}a_{0} = 0.24824nm \]  

(3)

\[ D_{n_{B}Fe}^{Fe-Fe} = a_{0} = 0.28664nm \]  

(4)

The bonds of the same distance formed by the same atoms are called equivalent bonds in molecules or crystals. In a molecular or crystalline structural unit, the total number of equivalent bonds with the bond order of α is represented by the symbol \( I_{\alpha} \).

\[ I_{\alpha} = I_{M}I_{S}I_{K} \]  

(5)

where \( I_{M} \) is the number of the resource atom, \( I_{S} \) is the symmetry of the resource atom. The value of \( I_{K} \) is 1 when two bonding atoms are identical. The value of \( I_{K} \) is 2 when the bonding atoms are heterogeneous atoms.

The number of equivalent bonds can be calculated via equation (5).

\[ I_{A} = I_{A}^{I_{A}I_{S}I_{K}} = 1 \times 8 \times 1 = 8 \]  

(6)

\[ I_{B} = I_{B}^{I_{B}I_{S}I_{K}} = 1 \times 6 \times 1 = 6 \]  

(7)

According to the covalent bond distance formula given by EET, the bond distance equation can be written as follows:

\[ D_{n_{A}Fe}^{Fe-Fe} = 2R_{Fe}(1) - \beta|gn_{A} | \]  

(8)

\[ D_{n_{B}Fe}^{Fe-Fe} = 2R_{Fe}(1) - \beta|gn_{B} | \]  

(9)
Considering that molecules or solids are normally electrically neutral, the EET assumes that all covalent electrons of all atoms in a structural formula should be fully distributed in all covalent bonds in this structural unit. That is, the total number of valence electrons in all covalent bonds in a structure unit is equal to the total number of valence electrons in all atoms in the structure unit. The total number of covalent electrons supplied by all j atoms in a structural unit is denoted by \( \sum_j n_{cj} \). The total number of covalent electrons in all covalent bonds in a structural unit is derived as follows.

\[
n_A l_A + n_B l_B + \cdots n_N l_N = n_A \sum_i l_A r_a
\]

Therefore, the conservation equation of charge in the crystal cell is:

\[
n_A \sum_i l_A r_a = \sum_j n_{cj}
\]

The sum \( \sum_j n_{cj} \) can be found in the hybridization table when the hybridization has been selected. The value of \( r_a \) can be obtained from the following equation.

\[
lg r_a = lg n_A - lg n_{gA} = \left[ D_{na}^{Fe-Fe} - D_{na}^{Fe-Fe} \right] / \beta
\]

It is noteworthy that the selection of \( \beta \) value depends on whether the system is metallic or nonmetallic. The value of the strongest bond \( n_A \) can be obtained from the conservation equation. Then, the theoretical bond distance can be derived from equations (8) and (9).

\[
\frac{D_{na}^{Fe-Fe}}{D_{nb}^{Fe-Fe}} = 2R_{Fe}(1) - \beta lg n_A = 2 \times 0.11059 - 0.06 \times lg 0.4026 = 0.24489nm
\]

\[
\frac{D_{nb}^{Fe-Fe}}{D_{nb}^{Fe-Fe}} = 2R_{Fe}(1) - \beta lg n_B = 2 \times 0.11059 - 0.06 \times lg 0.922 = 0.28329nm
\]

The bond length difference \( \Delta D_{na}^{Fe-Fe} \) can be calculated from equation (2).

\[
\Delta D_{na}^{Fe-Fe} = \left[ 0.24489 - 0.28264 \right] = 0.03835nm
\]

\[
\Delta D_{nb}^{Fe-Fe} = \left[ 0.28329 - 0.28664 \right] = 0.00335nm
\]

The results of the above calculation are summarized in table 1. Table 1 shows the valence electron structures of \( \alpha \)-Fe. Similar to the above calculation process, the valence electron structures of \( \alpha \)-Fe-P, \( \alpha \)-Fe-B, and \( \alpha \)-Fe-B-P are given in tables 2 and 3, respectively.

### Table 1. The valence electron structures of \( \alpha \)-Fe.

| Bond name | \( I_\alpha \) | \( D_{na}^{Fe-Fe}/nm \) | \( D_{nb}^{Fe-Fe}/nm \) | \( n_\alpha \) | \( \Delta D_{na}^{Fe-Fe}/nm \) |
|-----------|----------------|-----------------|----------------|----------------|----------------|
| \( D_{na}^{Fe-Fe} \) | 8 | 0.24489 | 0.24824 | 0.4026 | 3.35 \times 10^{-3} |
| \( D_{nb}^{Fe-Fe} \) | 6 | 0.28329 | 0.28664 | 0.0922 | 3.35 \times 10^{-3} |

\[
\sum I_\alpha r_\alpha : 9.3745 \quad \sum n_C : 3.7743 \quad \beta : 0.06 \text{ nm}
\]

### Table 2. The valence electron structures of \( \alpha \)-Fe-P.

| Bond name | \( I_\alpha \) | \( D_{na}^{Fe-P}/nm \) | \( D_{nb}^{Fe-P}/nm \) | \( n_\alpha \) | \( \Delta D_{na}^{Fe-P}/nm \) |
|-----------|----------------|-----------------|----------------|----------------|----------------|
| \( D_{na}^{Fe-P} \) | 8 | 0.24824 | 0.24657 | 0.3989 | 1.67 \times 10^{-3} |
| \( D_{nb}^{Fe-P} \) | 6 | 0.28664 | 0.28497 | 0.1013 | 1.67 \times 10^{-3} |

\[
\sum I_\alpha r_\alpha : 18.2266 \quad \sum n_C : 7.090 \quad \beta = 0.06
\]
Table 3. The valence electron structures of $\alpha$-Fe-B.

| Bond name       | $I_\alpha$ | $D_{n\alpha}$ $/ nm$ | $D_{n\alpha}^*$ $/ nm$ | $n_\alpha$ | $\Delta D_{n\alpha} / nm$ |
|-----------------|-------------|-----------------------|-------------------------|------------|---------------------------|
| $D_{n\alpha}^{Fe-B}$ | 4           | 0.18259               | 0.1814                  | 1.0842     | 1.19×10^{-3}              |
| $D_{n\alpha}^{Fe-B}$ | 8           | 0.19092               | 0.1897                  | 0.8775     | 1.22×10^{-3}              |
| $D_{n\alpha}^{Fe-B}$ | 16          | 0.26417               | 0.2630                  | 0.2116     | 1.17×10^{-3}              |
| $D_{n\alpha}^{Fe-B}$ | 8           | 0.269998              | 0.2688                  | 0.1793     | 1.20×10^{-3}              |
| $D_{n\alpha}^{Fe-B}$ | 16          | 0.26417               | 0.2630                  | 0.1652     | 1.17×10^{-3}              |
| $D_{n\alpha}^{Fe-B}$ | 8           | 0.269998              | 0.2688                  | 0.1574     | 1.20×10^{-3}              |
| $D_{n\alpha}^{Fe-B}$ | 16          | 0.32594               | 0.3249                  | 0.0123     | 1.22×10^{-3}              |
| $D_{n\alpha}^{Fe-B}$ | 2           | 0.36517               | 0.3640                  | 0.0089     | 1.17×10^{-3}              |
| $D_{n\alpha}^{Fe-B}$ | 4           | 0.36517               | 0.3640                  | 0.0072     | 1.17×10^{-3}              |

$\sum I_\alpha r_\alpha : 18.8492 \quad \sum n_c : 20.4332 \quad \beta = 0.071$

After calculating the valence electron structure of the amorphous Fe-B-P particles via the EET, it can be seen that the atomic states of three types of unit cell correspond to Fe-B-P.

4. Conclusion
The valence electron structures of Fe-B-P were calculated via the empirical electron theory. The atomic states of the three types of unit cell are Fe-B-P. The unit cells are $\alpha$-Fe, $\alpha$-Fe-P and $\alpha$-Fe-B, respectively.

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