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BOND PARAMETER AND ELECTRONIC STRUCTURE OF Sc, Y, Ti, Zr AND Hf METALS①

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ABSTRACT Using the new developed one-state-method of pure metal, the electronic structures of the outer shell electrons of B Ⅲ and B Ⅳ group element metals, i. e. Sc, Y, Ti, Zr, Hf, have been analysed systematically, and the bond length and strength of these metals have been determined. The conductivity of Sc, Y, Ti, Zr and Hf metals are discussed qualitatively and the relative magnitude of conductivity are well explained. This shows that these results of electronic structure are reasonable.

Key words Sc, Y, Ti, Zr, Hf metals one-atom-state method electronic structure bond parameter

1 INTRODUCTION

In recent years, the Pauling's valence bond (VB) theory has been made a great progress in designing and determining the atomic state, and in establishing the relation between the atomic state as well as crystal structure and physical property. First, Yü[1] developed the pauling's valence theory to calculate the electronic structure of crystal and set up the two-hybrid-state model. Then, Lü[2] established the relation between bond parameter and crystal cohesive energy. Second, Xie determined the corresponding relation between electronic structure of crystal and characteristic properties (spacing constant and cohesive energy), furthermore, he proposed an one-atom-state method[3] and gave a new many-atom-interaction potential[4] which makes it possible to further analyse the electronic structure of metals and alloys as well as physical properties with these new progresses[5]. In this paper we use the one-atom-state method systematically to determine bond parameter and electronic structure of B Ⅲ and B Ⅳ element metals in periodic table with the same hcp crystal structure, and also discuss conductivity of these metals qualitatively.

2 BASIC ATOMIC STATE OF Sc, Y, Ti, Zr, Hf METALS

In the new developed valence bond theory, the electronic structure of crystal is illustrated by one-atom-state[3]. Each one-atom-state Ψ_a consists of some basic atomic states Φ_k:

$$\Psi_a = \sum_k C_k \Phi_k \qquad (1)$$

In this paper, following the principle of Ref. [3] to construct a set of basic atomic states of Sc, Y, Ti, Zr, Hf metals.

All possibly basic atomic states which contain no more than two numbers of non-valence electrons are listed in Table 1 and Table 2. Here the case of electrons transiting to $4p$, $5p$, $6p$ level are not considered, for these transition possibility is very small.

If S_k^c and d_k^c denote, respectively, the number of covalent electrons of the outer s and d shell in the kth basic state, d_k^n and S_k^f denote, respectively, the number of non-valence electrons and free electrons. The state parameters of one atomic state may be obtained from the formula below:

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Table 1 Basic atomic state of Sc, Y metals

Basic atomic state	Outer shell electronic structure
Φ_1^*	$(S_f)^2(d_c)^1$
Φ_2^*	$(S_c)^2(d_c)^1$
Φ_3^*	$(S_f)^1(d_c)^2$
Φ_4^*	$(S_c)^1(d_c)^2$
Φ_5^*	$(d_c)^3$
Φ_6^*	$(S_f)^1(d_n)^2$
Φ_7^*	$(S_c)^1(d_n)^2$

Table 2 Basic atomic state of Ti, Zr and Hf metals

Basic atomic state	Outer shell electronic structure
Φ_1	$(S_f)^2(d_c)^2$
Φ_2	$(S_c)^2(d_c)^2$
Φ_3	$(S_f)^1(d_c)^3$
Φ_4	$(S_c)^1(d_c)^3$
Φ_5	$(d_c)^4$
Φ_6	$(S_f)^1(d_n)^2(d_c)^1$
Φ_7	$(S_c)^1(d_n)^2(d_c)^1$
Φ_8	$(S_f)^2(d_n)^2$
Φ_9	$(S_c)^2(d_n)^2$

$$\left.\begin{aligned}
&S^c = \sum_k C_k S_k^c,\ \ d^c = \sum_k C_k d_k^c,\\
&S^f = N^f = \sum_k C_k S_k^f,\\
&N^c = S^d + d^c,\ \ N^n = \sum_k C_k d_k^n,\\
&N_t^v = N^c + N^f,\ \ N_t = N^c + N^f + N^n,\\
&R = \sum_k C_k R_k \qquad\qquad e\ ,
\end{aligned}\right| \tag{2}$$

Where R_k, which is the single-bond radius of the kth basic atomic state and can be obtained from Pauling's equation slightly modified by author. For Sc, Y, Ti, Zr, Hf, they are listed respectively as below:

$$\left.\begin{aligned}
&R_k^{\mathrm{Ti}} = 1.327 - 0.03\,\delta_k,\\
&R_k^{\mathrm{Hf}} = 1.5211 - 0.04\,\delta_k,\\
&R_k^{\mathrm{Y}} = 1.661 - 0.06\,\delta_k\\
&R_k^{\mathrm{Zr}} = 1.4786 - 0.05\,\delta_k,\\
&R_k^{\mathrm{Sc}} = 1.539 - 0.15\,\delta_k,\\
&\delta_k = d_k^c/(d_k^c + S_k^c + S_k^f)
\end{aligned}\right| \tag{3}$$

3 MAIN EQUATIONS

3.1 Bond parameters of crystal

For hcp structural crystal, we have bond-length relation[6]

$$\left.\begin{aligned}
I_1 &= 6,\\
r_1 &= a\\
&= 2R - \beta\lg n_1\\
I_2 &= 6,\\
r_2 &= \sqrt{a^2/3 + c^2/4}\\
&= 2R - \beta\lg n_2\\
I_3 &= 6,\\
r_3 &= \sqrt{4a^2/3 + c^2/4}\\
&= 2R - \beta\lg n_3\\
I_4 &= 2,\\
r_4 &= c\\
&= 2R - \beta\lg n_4
\end{aligned}\right| \tag{4}$$

where $\beta = 0.6$ is determined by Pauling. The total numbers of covalent electrons are $N^c = \sum_\alpha I_\alpha n_\alpha$, where n_α are the α covalence bond strength, I_α represents the number of the same kind of α bond, r_1, r_2, r_3, r_4 are the bond length. The a, c is spacing constant.

3.2 Bond capacity[6]

To $s-d$ hybridization, we have

$$\left.\begin{aligned}
f &= \sqrt{\alpha} + \sqrt{5\gamma},\\
\alpha &= S^c/N_t^v,\\
\gamma &= d^c/N_t^v\\
f' &= \sqrt{2\alpha'},\\
\alpha' &= N^f/N_t^v
\end{aligned}\right| \tag{5}$$

where f and f' are the bond capacity of the hybrid covalent electrons and free electrons, respectively.

3.3 Cohesive energy

In equilibrium state $(r = r_0)$ the cohesive energy[4] of crystal can be written as

$$E_c = A\left(\sum_\alpha I_\alpha n_\alpha \cdot f/r_\alpha + N^f \cdot f'/\overline{r}_0'\right) \tag{6}$$

For Sc, Y, Ti, Zr, Hf metals with hcp structure, we only consider the nearest, second nearest, third and fourth nearest neighbour atomic interaction, then the detail of cohesive energy formula is expressed as below:

$$E_c = A[(\frac{6n_1}{a} + 6n_2(\frac{a^2}{3} + \frac{c^2}{4})^{-1} + 6n_3(\frac{4a^2}{3} + \frac{c^2}{4})^{-1} + 2n_4/c)f + \frac{n^f \cdot f'}{\bar{r}_0'}] \qquad (7)$$

where $A = 314/(n - 0.36\delta)$, which denote the effect of the outer shell electrons screening nuclear charge. The value of n and δ depend on the period and group of the Sc, Y, Ti, Zr, Hf in element periodic table. $\bar{r}_0 = \sum_\alpha I_\alpha r_\alpha / \sum_\alpha I_\alpha$.

4 CALCULATION RESULTS OF ELECTRONIC STRUCTURE AND BOND PARAMETER

The coefficient C_k in equation (1) can be found by requiring that the characteristic properties of the psuedo-crystal are the most possible in agreement with that of real-crystal of Sc, Y, Ti, Zr, Hf, metals, such as the experiment value of cohesive energy and spacing constant. In addition, the normalization condition of coefficient C_k is needed. Here we only consider the three basic atomic state combinations. The calculation results of bond parameter as well as electronic structure of Sc, Y, Ti, Zr, Hf metals are listed in Table 3.

5 DISCUSSION

5.1 Outer shell electronic distribution of B III and B IV group metals

Table 3 shows that the one-atom-state of Sc and Y metals consists of φ_2^*, φ_3^* and φ_4^*. The electronic distribution of Sc and Y atoms are $(S_f)^{0.24}(S_c)^{0.97}(d_c)^{1.79}$ and $(S_f)^{0.19}(S_c)^{1.05}(d_c)^{1.76}$, respectively. The results show that when atoms cohere together to form crystal, the outer electronic distribution (s^2d^1) in free atoms of Sc and Y change very much. The d-occupation number of electrons are on great increase. There are about 0.77 and 1.55 S-state electrons transfer to d-occupation state to become d electrons. This is due to s-d hybridization, in order to form the stronger covalent bond. The free electrons in the outer shell electron distribution are very little, about 0.22.

The Table 3 also shows that the one-atomic state of B IV group metal of Ti and Zr, consist of basic atom state φ_2, φ_3, φ_4, while one-atom-state of Hf metal is composed of φ_1, φ_2, φ_4. The outer shell electronic structure of these metals are, Ti: $(S_f)^{0.30}(S_c)^{1.05}(d_c)^{2.65}$, Zr: $(S_f)^{0.38}(S_c)^{1.00}(d_c)^{2.62}$, Hf: $(S_f)^{0.67}(S_c)^{0.97}(d_c)^{2.36}$, respectively. Because of S-d hybridization, when free atoms cohere together to form metals, the outer shell electronic distribution (s^2d^2) of free atoms change greatly, there are some $S-$ state electron transfer to $d-$ state electrons. For example, there are about 0.6 electrons to become $d-$ state electron of Ti and Zr atom, about 0.36 electrons to $d-$ state electrons of Hf. In $S-$ state electrons, the covalent electrons take great part, while free electrons are take small part, about 0.3~ 0.6.

5.2 Single-bond radius and atomic valence of B III and B IV group element metals

From the point of view of valence bond theory, the single bond radius[9] given by Pauling of Sc, Y, Ti, Zr, Hf metals, respectively, are 1.439, 1.616, 1.327, 1.454 and 1.442 (Å), agreeing with our calculation results which are 1.448, 1.6148, 1.3071, 1.4484 and 1.4265 (Å) respectively. Pauling points the valence of Sc and Y to be 3, of Ti, Zr, Hf to be 4, agreement with the total numbers of free and covalent electronic number of our calculations results, i.e. $N_T^v = N^f + N^c$. They are all to make a contribution to the atomic valence, when atoms cohere together to form metals. So we think the more reasonable result is that the atomic valence is expressed by the value of total N^c and N^f electrons in outer shell.

5.3 Electrical conductivity of Sc, Y, Ti, Zr, Hf metals

Up to now, it is still difficult to quantitatively discuss the electric conductivity with the newly developed valence bond theory of metals, but we can use the simple electrical conductive model qualitatively to discuss the conductivity.

Table 3 Calculation results of bond parameter and electronic structure of Sc, Y, Ti, Zr and Hf metals

Metal		Ti(hcp)	Zr(hcp)	Hf(hcp)	Sc(hcp)	Y(hcp)
Screen coefficient /(kJ·Å·mol^{-1})		$A = 314/(n - 0.36\delta) = 157$ $n = 2,\ \delta = 0$	$A = 314/(n - 0.36\delta) = 226.3$ $n = 2,\ \delta = 1.7$	$A = 314/(n - 0.36\delta) = 226.3$ $n = 2,\ \delta = 1.7$	$A = 314/(n - 0.36\delta) = 191.5$ $n = 2,\ \delta = 1.0$	$A = 314/(n - 0.36\delta) = 226.3$ $n = 2,\ \delta = 1.7$
Bond length/ Å		$R_k = 1.327 - 0.03\delta_k$	$R_k = 1.4786 - 0.05\delta_k$	$R_k = 1.5211 - 0.04\delta_k$	$R_k = 1.539 - 0.15\delta_k$	$R_k = 1.661 - 0.06\delta_k$
Modifying term		$\delta_k = d_k^c/(S_k^f + s_k^c + d_k^c)$	$\delta_k = d_k^c/(S_k^f + s_k^c + d_k^c)$	$\delta_k = d_k^c/(S_k^f + s_k^c + d_k^c)$	$\delta_k = d_k^c/(S_k^f + s_k^c + d_k^c)$	$\delta_k = d_k^c/(S_k^f + s_k^c + d_k^c)$
Construction of one-atom state		$\Psi_a^{Ti} = C_2\Phi_2 + C_3\Phi_3 + C_4\Phi_4$ $C_2 = 0.3501$ $C_3 = 0.2971$ $C_4 = 0.3528$	$\Psi_a^{Zr} = C_2\Phi_2 + C_3\Phi_3 + C_4\Phi_4$ $C_2 = 0.3810$ $C_3 = 0.3789$ $C_4 = 0.2401$	$\Psi_a^{Hf} = C_1\Phi_1 + C_2\Phi_2 + C_4\Phi_4$ $C_1 = 0.333$ $C_2 = 0.302$ $C_4 = 0.365$	$\Psi_a^{Sc} = C_2\Phi_2^* + C_3\Phi_3^* + C_4\Phi_4^*$ $C_2 = 0.2051$ $C_3 = 0.2364$ $C_4 = 0.5585$	$\Psi_a^{Y} = C_2\Phi_2^* + C_3\Phi_3^* + C_4\Phi_4^*$ $C_2 = 0.1897$ $C_3 = 0.2645$ $C_4 = 0.5458$
Bond parameter		$n_1 = 0.2751$ $n_2 = 0.3394$ $n_3 = 0.0028$ $n_4 = 0.0004$ $r_1 = 2.9506$(Å) $r_2 = 2.8958$(Å) $r_3 = 4.1342$(Å) $r_4 = 4.6835$(Å)	$n_1 = 0.2712$ $n_2 = 0.3320$ $n_3 = 0.0019$ $n_4 = 0.00017$ $r_1 = 3.3216$(Å) $r_2 = 3.1789$(Å) $r_3 = 4.5330$(Å) $r_4 = 5.1475$(Å)	$n_1 = 0.2695$ $n_2 = 0.2861$ $n_3 = 0.0022$ $n_4 = 0.00021$ $r_1 = 3.1946$(Å) $r_2 = 3.1300$(Å) $r_3 = 4.4724$(Å) $r_4 = 5.0578$(Å)	$n_1 = 0.2061$ $n_2 = 0.2545$ $n_3 = 0.0014$ $n_4 = 0.0001$ $r_1 = 3.308$(Å), $r_2 = 3.2531$(Å) $r_3 = 4.6396$(Å) $r_4 = 5.276$(Å)	$n_1 = 0.1935$ $n_2 = 0.2750$ $n_3 = 0.0010$ $n_4 = 0.0001$ $r_1 = 3.6482$(Å) $r_2 = 3.5567$(Å) $r_3 = 5.0950$(Å) $r_4 = 5.7318$(Å)
State parameter		$N^f = 0.2971$, $N^c = 3.7029$ $R = 1.3071$(Å) $R^* = 1.327$(Å)	$N^f = 0.3789$ $N^c = 3.6211$ $R = 1.4484$(Å) $R^* = 1.454$(Å)	$N^f = 0.666$ $N^c = 3.334$ $R = 1.4265$(Å) $R^* = 1.442$(Å)	$N^f = 0.2364$ $N^c = 2.7939$ $R = 1.448$(Å) $R^* = 1.439$(Å)	$N^f = 0.1897$ $N^c = 2.8103$ $R = 1.6148$(Å) $R^* = 1.616$(Å)
Property parameter	Theory value	$a = 2.9505$(Å) $c = 4.6530$(Å) $E_c = 469.2$(kJ/mol)	$a = 3.2317$(Å) $c = 5.1535$(Å) $E_c = 603.2$(kJ/mol)	$a = 3.1947$(Å) $c = 5.0598$(Å) $E_c = 622.3$(kJ/mol)	$a = 3.3076$(Å) $c = 5.296$(Å) $E_c = 375.5$(kJ/mol)	$a = 3.6482$(Å) $c = 5.7225$(Å) $E_c = 421.9$(kJ/mol)
	Experimental [7, 8]	$a = 2.9506$(Å) $c = 4.6835$(Å) $E_c = 468$(kJ/mol)	$a = 3.2316$(Å) $c = 5.1475$(Å) $E_c = 603$(kJ/mol)	$a = 3.1946$(Å) $c = 5.0578$(Å) $E_c = 621$(kJ/mol)	$a = 3.308$(Å) $c = 5.267$(Å) $E_c = 376$(kJ/mol)	$a = 3.6482$(Å) $c = 5.7318$(Å) $E_c = 422$(kJ/mol)
Electronic structure		$(4S_f)^{0.30}(4S_c)^{1.05}(3d_c)^{2.65}$	$(5S_f)^{0.38}(5S_c)^{1.00}(4d_c)^{2.62}$	$(6S_f)^{0.67}(6S_c)^{0.97}(5d_c)^{2.36}$	$(4S_f)^{0.24}(4S_c)^{0.97}(3d_c)^{1.79}$	$(5S_f)^{0.19}(5S_c)^{1.05}(4d_c)^{1.77}$

R^*: Pauling single-bond radius.

On the basis of the simple conductive model[6] of valence bond theory, when exerted by external electric field, the free electrons in metals will move through the "channel" to form electric current. At equilibrium state without external electric field, free electrons in metals are inside the interspace surrounded by three or more atoms. When exerted by the external electric field, the electron has to step across one covalence bond in order to move from one interspace to neighbour interspace. So the covalence bond is the barrier for the free electron moving. If the covalence bond opens, then the barrier disappears. At this time, the free electrons can very easily step across the covalence bond. In the case, we call the site of the covalence bond the open "channel".

According to VB theory, the fractional covalence bond means a covelence electron shares with a number of covalenec bonds, i. e. a covalence electron "resonate" with a number of covalence bonds. So as far as each covalence bond is concerned, there is a certain moment of "unoccupied orbital", i. e., there is no covalence electron in some bond at the moment. In the case, we consider "channel" in the bond is opened. The possibility of opening channel has much closely relation with metal conductivity and is the main factor that influences the electric conductivity. The more the possibility of opening "channel" is, the easier the free electrons go through. On the other hand, the stronger the covalence bond is, the more difficultly the "channel" opens, and the smaller the conductivity of metals is. While the greater the density of free electrons in metals, the stronger the capacity of free electrons through "channel". On the basis of the two reason, it is easily to explain the relative magnitude of resistivity of these metals.

Table 3 shows, the free electronic density of atoms in Ti, Zr, Hf metal are respectively 0. 30, 0. 38, 0. 67, and the strongest bond strength n_2 which reflect the "channel" open easily or difficultly are respectively 0. 3394, 0. 3320, 0. 2861. Based on the two reasons above, we can easily see the resistivity of Hf is the smallest, that of Zr is the smaller, and that of Ti is greatest. This is the identity with the relative magnitude ordering of Ref. [7]. $\rho_{Hf}=$ 30. 6(μΩ. cm), $\rho_{Zr}=$ 42. 4 (μΩ. cm) and $\rho_{Ti}=$ 43. 1 (μΩ. cm). To Sc and Y metals, the free electron density of atom are 0. 24, 0. 18 respectively, and the stronger bond strength n_2 are 0. 2545 and 0. 2750 respectively. So we can easily guess that the resistivity of Sc are smaller than that of Y. The experimental results[7] are $\rho_{Sc}=$ 46. 8(μΩ• cm) and $\rho_{Y}=$ 58. 5(μΩ• cm), therefore the relative magnitude of resistivity for B III and B IV element metals are well explained. This also shows these calculation results of the valent electronic structure and bond perameter of B III and B IV group element metals are reasonable.

6 CONCLUSIONS

(1) The one-atom-state of Sc and Y element metals are the combination of the three basic atomic state φ_2^*, φ_3^*, φ_4^*, For B IV group metals, the one-atom-state of Ti, Zr metals are combination of φ_2, φ_3, φ_4, and that of Hf are combination of φ_1, φ_2, φ_4.

(2) The outer shell electronic distribution of B III and B IV group element metals are respectively. Sc: $(S_f)^{0.24}(S_c)^{0.97}(d_c)^{1.79}$ and Y: $(S_f)^{0.19}(S_c)^{1.05}(d_c)^{1.76}$, Ti: $(S_f)^{0.30}(S_c)^{1.05}(d_c)^{2.65}$, Zr: $(S_f)^{0.38}(S_c)^{1.00}(d_c)^{2.62}$, Hf: $(S_f)^{0.67}(S_c)^{0.97}(d_c)^{2.36}$.

(3) When free electrons cohere together to form metals, there are some S-state electrons to transfer d-state covalent electrons. The great part of the outer shell electrons are covalent electrons, free electrons are only take small part.

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