

# BOND PARAMETERS AND ELECTRONIC STRUCTURE OF V, Nb AND Ta METALS<sup>①</sup>

Gao Yingjun<sup>1, 2</sup>, Chen Zhenghua<sup>1</sup>, Huang Peiyun<sup>1</sup> and Zhong Xiaping<sup>2</sup>

*1 Research Institute for Non-equilibrium Material Science and Engineering*

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

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

**ABSTRACT** Using the new developed one-atom-state method of pure metals, the electronic structures of the outer shell electrons of V, Nb and Ta metals have been analyzed systematically, and been determined to be  $(4s_f)^{0.27}(4s_e)^{1.24}(3d_e)^{3.49}$ ,  $(5s_f)^{0.32}(5s_e)^{0.39}(4d_e)^{4.29}$  and  $(6s_f)^{0.43}(6s_e)^{0.17}(5d_e)^{4.40}$ , respectively. The bond length and strength of these metals have also been determined. The conductivity of V, Nb and Ta metals discussed qualitatively and relative magnitude of resistivity were well explained.

**Key words** V, Nb and Ta metals one-atom-state method electronic structure bond parameter

## 1 INTRODUCTION

In recent years, a great progress has been made in the Pauling's valance bond (VB) theory in designing and determining the atomic state, and in establishing the relations between the atomic state and crystal structure in physical property. First, on the basis of the Pauling's valance bond theory, Yu set up the relations<sup>[1]</sup> between bond parameter and crystal cohesive energy. Second, Xie determined the corresponding relations<sup>[2]</sup> between electronic structures of crystal and characteristic properties (spacing constant and cohesive energy). Furthermore, he proposed an one-atom-state method<sup>[2]</sup> and gave a new many-atom-interaction potential<sup>[3]</sup>. In this paper we use the one-atom-state method systematically to determine bond parameter and electronic structures of B V element V, Nb and Ta metals in Periodic Table, and also discuss conductivity of these metals qualitatively.

## 2 BASIC ATOMIC STATES

In the new developed valance bond theory, the electronic structures of crystal are illustrated

by (OAS)<sup>[2]</sup>. Each OAS  $\Psi_a$  consists of some basic atomic state  $\Phi_k$ :

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

These coefficients  $C_k$  determined by characteristic properties of pseudo-crystal are best identical with that of real crystal. In this paper, following the principle of Ref. [2] to construct a set of basic atomic states of V, Nb and Ta.

All possible basically atomic states which contain no more than two numbers of non-valence electrons are shown in Table 1. If  $s_k^c$  and  $d_k^c$  denote respectively, the number of covalent electron of the outer  $s$  and  $d$  shells in the  $k$  basic atomic state,  $d_k^n$  and  $s_k^f$  denote respectively, the number of non-valence electrons and free electrons, the state parameters of atomic state may be obtained from the following expressions:

$$\left. \begin{aligned} s^c &= \sum_k C_k s_k^c, & d^c &= \sum_k C_k d_k^c, \\ s^f &= N^f = \sum_k C_k s_k^f, & N^c &= s^c + d^c \\ N^n &= d^n = \sum_k C_k d_k^n, & N^v &= N^c + N^f, \\ N_{\text{I}} &= N^c + N^f + N^n, & R &= \sum_k C_k R_k \end{aligned} \right\} \quad (2)$$

where  $R_k$  is the single-bond radius of the  $k$ th

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basic atomic state which can be obtained from Pauling equation<sup>[4]</sup>; for V, Nb and Ta metals, they are respectively as below:

$$\left. \begin{aligned} R_k^V &= 1.335 - 0.15 \delta_k, \\ R_k^{Nb} &= 1.471 - 0.15 \delta_k, \\ R_k^{Ta} &= 1.471 - 0.15 \delta_k, \\ \delta_k &= d_k^c / (s_k^f + D_k^c + d_k^c) \end{aligned} \right\} \quad (3)$$

**Table 1 Basic atomic state of V, Nb and Ta metals**

Basic atomic state	Outer shell electronic structure
$\Phi_1$	$(s_f)^1(d_c)^4$
$\Phi_2$	$(s_c)^1(d_c)^4$
$\Phi_3$	$(s_f)^2(d_c)^3$
$\Phi_4$	$(s_c)^2(d_c)^3$
$\Phi_5$	$(d_c)^5$
$\Phi_6$	$(s_f)^1(d_n)^2(d_c)^2$
$\Phi_7$	$(s_c)^1(d_n)^2(d_c)^2$
$\Phi_8$	$(s_f)^2(d_n)^2(d_c)^1$
$\Phi_9$	$(s_c)^2(d_n)^2(d_c)^1$

### 3 MAIN EQUATIONS

#### 3.1 The bond parameters of crystal

For bcc structural crystal, we have bond length relation<sup>[5]</sup> as

$$\left. \begin{aligned} r_1 &= \frac{\sqrt{3}}{2}a = 2R - \beta \lg n_1 \\ r_2 &= a = 2R - \beta \lg n_2 \end{aligned} \right\} \quad (4)$$

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

#### 3.2 The bond capacity<sup>[6]</sup>

The the bond capacities of the hybrid covarence electrons and free electrons,  $f$  and  $f'$  are as follows:

$$\left. \begin{aligned} f &= \sqrt{\alpha} + \sqrt{5\gamma}, \quad \alpha = s^c/N_1^v, \quad \gamma = d^c/N_1^v \\ f' &= \sqrt{2\alpha'}, \quad \alpha' = N^f/N_1^v \end{aligned} \right\} \quad (6)$$

#### 3.3 Cohesive energy

In equilibrium state ( $r = r_0$ ) the cohesive energy<sup>[3]</sup> of crystal can be written as

$$E_c = A \left( \sum_{\alpha} n_{\alpha} f / r_{\alpha} + n^f \cdot f' / \bar{r}_0 \right)$$

for V, Nb, Ta metals with bcc structure, we only consider the nearest and the second nearest neighbour atom interaction, then the detail of cohesive energy formula is expressed in

$$E_c = (A/a) [(16n_1/\sqrt{3} + 6n_2) \cdot f + 0.923n^f \cdot f'] \quad (7)$$

where  $A = 314/(n - 0.36\delta)$ , which denote the effect of the outer shell electrons screening nuclear charge. The value of  $n$  and  $\delta$  depend on the period and group of the V, Nb, Ta in the Element Periodic Table.

### 4 CALCULATION RESULTS

The coefficient  $C_k$  in Eqn(1) can be found by requiring that the characteristic properties of the pseudocrystal are the most possible agreement with that of real crystal of V, Nb, Ta metals. To meet these condition, the one-atom state of real crystal should be combined with no less than three basic atomic states. In all the possible three basic atomic state combinations, we can only find the combination of  $\Phi_1$ ,  $\Phi_2$ ,  $\Phi_4$  to give satisfactory solution for V metal, and  $\Phi_1$ ,  $\Phi_2$ ,  $\Phi_5$  for Nb and Ta metals. We do not consider the case of more than three basic atomic state combination, because the results are the same. These calculation results are listed in Table 2.

### 5 DISCUSSION

#### 5.1 The one-atom state of V, Nb, Ta metals

Table 2. shows that the one-atom-state of V metals consists of the  $\Phi_1$ ,  $\Phi_2$  and  $\Phi_4$ , while that of Nb and Ta metals consists of  $\Phi_1$ ,  $\Phi_2$  and  $\Phi_5$ . The main distinction between the constructions of the one-atom-state of the Nb and Ta metals is that the weightings of the three basic atomic state are different in  $C_1$ ,  $C_2$  and  $C_5$ . As for the difference between combination of basic atomic state of V and that of Nb and Ta metals, it comes from their greatly different magnitude

of cohesive energy.

## 5.2 The distribution of the outer shell electrons of atom in V, Nb, Ta metals

We can see in Table 2, when free atoms which outer shell electronic structure is  $s^2d^3$  cohere together to form metals, due to  $s$ - $d$  hybridization of electrons, there are about 0.5  $s$ -shell electrons to become  $d$ -state electrons in V metal and about 1.3  $s$ -shell electrons to  $d$ -state electrons in Nb and Ta metals. We also can see the  $d$ -state electrons in these metals are all in the state of covalence electrons  $d^c$ , no nonvalence electrons  $d^n$ . This is because the cohesive energy is much great for BV group element metals, so all  $d$ -shell electrons occupy the  $d$ -bond orbital in order to meet the much great cohesive energy.

## 5.3 The single bond radius and atomic valence of V, Nb, Ta metals

From the point of view of valence bond theory, Pauling obtained the single bond radii<sup>[4]</sup> of V, Nb, Ta metals respectively to be 1.224, 1.342 and 1.343 (Å), in agreement with our calculation results which are 1.230, 1.3423 and

1.339 (Å), respectively. Pauling pointed the valence of V, Nb and Ta to be 5, as the same results we obtained are expressed in  $N^v = N^f + N^c = 5$ . This shows that the atomic valence consists of  $N^c$  and  $N^f$ , which are all to make a contribution to the atomic valence. 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.

## 5.4 Electric conductivity of V, Nb, Ta metals

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

On the basis of the simple conductive model<sup>[5]</sup> of VB 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

**Table 2 Calculation results and analysis of bond parameters as well as electronic structure**

Metal	V (bcc)	Nb (bcc)	Ta (bcc)
Screen coefficient / $\text{kJ} \cdot \text{Å} \cdot \text{mol}^{-1}$	$A = 314 / (n - 0.36\delta) = 118.9$ $n = 3, \delta = 1$	$A = 314 / (n - 0.36\delta) = 191.5$ $n = 2, \delta = 1$	$A = 314 / (n - 0.36\delta) = 215.1$ $n = 2, \delta = 1.5$
Bond length/ Å	$R_k = 1.335 - 0.15\delta_k$	$R_k = 1.471 - 0.15\delta_k$	$R_k = 1.471 - 0.15\delta_k$
Modifying term	$\delta_k = d_k^c / (s_k^f + s_k^c + d_k^c)$	$\delta_k = d_k^c / (s_k^f + s_k^c + d_k^c)$	$\delta_k = d_k^c / (s_k^f + s_k^c + d_k^c)$
Construction of one atom state	$\Psi_a^V = C_1\Phi_1 + C_2\Phi_2 + C_4\Phi_4$ $C_1 = 0.2712, C_2 = 0.2217$ $C_4 = 0.5071$	$\Psi_a^{\text{Nb}} = C_1\Phi_1 + C_2\Phi_2 + C_5\Phi_5$ $C_1 = 0.3214, C_2 = 0.3875$ $C_5 = 0.2911$	$\Psi_a^{\text{Ta}} = C_1\Phi_1 + C_2\Phi_2 + C_5\Phi_5$ $C_1 = 0.4330, C_2 = 0.1715$ $C_5 = 0.3955$
Bond parameter	$n_1 = 0.5244, n_2 = 0.1150$ $r_1 = 2.619(\text{Å}), r_2 = 3.024(\text{Å})$	$n_1 = 0.5142, n_2 = 0.0943$ $r_1 = 2.835(\text{Å}), r_2 = 3.294(\text{Å})$	$n_1 = 0.5091, n_2 = 0.0920$ $r_1 = 2.858(\text{Å}), r_2 = 3.300(\text{Å})$
State parameter	$N^f = 0.271, N^c = 4.729$ $R = 1.230(\text{Å}), R^* = 1.224(\text{Å})$	$N^f = 0.321, N^c = 4.679$ $R = 1.342(\text{Å}), R^* = 1.342(\text{Å})$	$N^f = 0.433, N^c = 4.567$ $R = 1.339(\text{Å}), R^* = 1.343(\text{Å})$
Property Parameter	Theory value		
	$a = 3.0236(\text{Å})$ $E_c = 511.3(\text{kJ/mol})$	$a = 3.2999(\text{Å})$ $E_c = 730.5(\text{kJ/mol})$	$a = 3.2997(\text{Å})$ $E_c = 780.6(\text{kJ/mol})$
Property Parameter	Experimental <sup>[8,9]</sup>		
	$a = 3.024(\text{Å})$ $E_c = 512(\text{kJ/mol})$	$a = 3.294(\text{Å})$ $E_c = 730(\text{kJ/mol})$	$a = 3.300(\text{Å})$ $E_c = 782(\text{kJ/mol})$
Electronic structure	$(4s_f)^{0.27}(4s_c)^{1.24}(3d_c)^{3.49}$	$(5s_f)^{0.32}(5s_c)^{0.39}(4d_c)^{4.29}$	$(6s_f)^{0.43}(6s_c)^{0.17}(5d_c)^{4.40}$

$R^*$ : Pauling's single radius.

order to move from one interspace to neighbour interspace. So the covalence bond is the barrier for the free electrons moving. If the covalence bond opens, then the barrier will disappear. At this time, the free electron very easily steps across the covalence bond. In this case, we call the site of the covalence bond the open “channel”.

According to VB theory<sup>[5]</sup>, the fractional covalence bond means the covalence electron shares with a number of covalence bonds, i. e. a covalence electron “resonates” within a number of covalence bonds. So as far as each covalence bond is concerned, there is a certain amount of “unoccupied orbital”, i. e., there is no covalence electron in some bonds at the moment. In this case, we consider the “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 difficulty the “channel” opens, and then the conductivity of metals is smaller. 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 reasons, it is easily to explain the relative magnitude of resistivity of these three metals.

Table 2 shows, the free electronic density of the V metals is the least in these three metals, i. e.,  $e/a = s^f = 0.27$ . The bond strength, which are  $n_1 = 0.5244$  and  $n_2 = 0.1150$ , respectively, are greatest. For these two reasons, the possibility of the opening “channel” and the capacity through the “channel” are all the least. So the resistivity of V metal in all these three metals is the greatest, i. e.,  $\rho^V = 18.2 (\mu\Omega \cdot \text{cm})^{[7]}$ . While the free electronic density in Ta metals,  $e/a = s^f = 0.43$  is the greatest and the bond strength ( $n_1 = 0.5019$ ,  $n_2 = 0.0920$ ) are the least, so  $\rho^{\text{Ta}} = 12.1 (\mu\Omega \cdot \text{cm})^{[8]}$  is least.

While the  $s^f$ ,  $n_1$  and  $n_2$  of Nb metal are all between that of V and Ta metals, so the resistivity of Nb metal,  $\rho^{\text{Nb}} = 13.5 (\mu\Omega \cdot \text{cm})^{[7]}$  is smaller than that of V metal, but greater than that of Ta metal. Therefore this is a good explanation of the relative magnitude of resistivity for V, Nb and Ta metals. This also shows these calculation results in this paper are reasonable.

## 6 CONCLUSIONS

(1) The one-atom-state in V metal is the combination of the three basic atomic state  $\Phi_1$ ,  $\Phi_2$  and  $\Phi_4$ , while that of Nb and Ta metals are  $\Phi_1$ ,  $\Phi_2$  and  $\Phi_3$ .

(2) The outer shell electronic structure of V, Nb and Ta metals are respectively  $(4s_f)^{0.27} (4s_c)^{1.24} (3d_c)^{3.49}$ ,  $(5s_f)^{0.32} (5s_c)^{0.39} (4d_c)^{4.29}$  and  $(6s_f)^{0.43} (6s_c)^{0.17} (5d_c)^{4.40}$ .

(3) To meet the much greater cohesive energy of Nb and Ta metals, the covalence electrons are as much as possible to occupy the  $d$ -bond state.

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