ELECTRONIC STRUCTURE AND PROPERTIES OF Au METAL①

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ABSTRACT

Using the new developed valence bond theory of metals, the electronic structure, crystal structure and physical properties of Au metal have been systematically analysed. It has been determined that its electronic structure is $(5d_n)^{4.65}(5d_c)^{4.71}(6s_c)^{0.62}(6s_f)^{1.02}$. According to this electronic structure, lattice constant, cohesive energy, potential curve, bulk modulus and temperature dependence of liner thermal expansion coefficient have been calculated. The theoretical values of properties are all in good agreement with experimental results. This electronic structure has been verified in part by linear rigorous cellular method of band theory. It shows that the valence bond theory has been reached perfectly.

Key word: Au electronic structure potential function lattice constant cohesive energy thermal expansion coefficient

1 INTRODUCTION

The study of H_2 molecule with quantum mechanics by Heitler-London started the modern chemical structure theory[1]. After that it has been gradually developed into approximate molecular orbital theory and approximate valence bond theory, hereafter the latter is refered as VB theory.

Pauling made a great contribution to the establishment of VB theory. Using the concepts of hybrization, resonance, electronegativity etc, he made extensive studies on a great number of molecules, metals and alloys. One of the basic equations in the VB theory is the bond length equation[2]

$$r = 2R - \beta \lg n \qquad (1)$$

where $n = n_c / I$; n_c— the number of covalent electrons; I— coordination number; $\beta = 0.600$.

According to Eq.(1), Pauling determined the number of covalent electrons and the single bond radii of elements in the Periodic Table[3,4]. Because no one has made breakthrough progress in design and determination of atomic states and relations between atomic states and properties for metals and alloys, the VB theory of metals and alloys was at standstill. Since 1978, the VB theory has been on the upgrade in China and has made a series of new advances owing to Yü's initiation: the Eq.(1) has been developed into a new bond length equation[5] and a lattice constant equation[6]; the cohesive energy equation and the potential function have been established[7,8]; recently, we have proposed the principles of

①Project supported by China National Nonferrous Metals Industry Corporation; manuscript received July 29,1991.

construction of atomic states known as the one-atom state (OAS) method, proved that the electronic structure of the crystal may be correctly determined only by both cohesive energy and lattice constant, and established a new potential function with many-atom interactions in solid known as MAI potential. The purpose of this paper is to systematically analyse Au metal.

2 CONSTRUCTION OF ONE-ATOM STATE OF Au METAL

In the new developed VB theory, the electronic structure of a crystal is characterized by quasi-electron-occupation (QEO) number of one-atom state which consists of some basic atomic states φ_k

$$\psi_a = \sum_k C_k \varphi_k \tag{2}$$

The coefficients C_k can be found by requiring that the characteristic properties (lattice constant and cohesive energy) of the pseudo-crystal with these coefficients are as much as possible in agreement with relative experimental values of Au metal.

The metallic bonds should be mixed bonds consisting of covalent electronic bonds and free eletronic bonds. So there are at least some covalent electrons (n_c) responsible for the formation of the bond network of the crystal and free electrons (n_f) responsible for the conductivity. Besides these electrons, in the QEO number of the outer shell there may be some non-valent eletrons (n_n) which can be treated as "chemically inert" ion core. According to the Pauli exclusion principle, no two electrons can be in exactly the same state as defined by three orbital quantum numbers, n, l and m_l, together with the spin quantum number m_s. From this, the electrons in the outer shell of the basic atomic state should fulfil the following equation:

$$\left.\begin{aligned} &0 \leqslant n_{n,l} < 2(2l+1) \\ &\sum_n \sum_l n_{n,l} = n_c + n_f + n_n = N_T \end{aligned}\right\} \tag{3}$$

Because the non-valent electrons are pairs of electrons with spin opposite to each other, the number of non-valent electrons must be even in each basic atomic state. Besides this, it is also supposed that the free electrons should be in the s state. According to these principles above, some basic atomic states of Au metal have been designed and listed in Table 1.

If s_k^c and d_k^c denote respectively the number of covalent electrons of s and d shells in k basic atomic state, and d_k^n and s_k^f denote respectively the number of non-valent electrons and free electrons, the state parameters of the one-atom state can be obtained by following expressions:

$$\left.\begin{aligned} &s_c = \sum_k C_k s_k^c \ , \quad d_c = \sum_k C_k d_k^c \\ &s_f = n_f = \sum_k C_k s_k^f \ , \quad n_c = s_c + d_c \\ &n_n = \sum_k C_k d_k^n \ , \quad R = \sum_k C_k R_k \\ &n_T^v = n_c + n_f \ , \quad n_T = n_c + n_f + n_n \end{aligned}\right\} \tag{4}$$

where R_k is the single bond radius which can be obtained by Pauling's equation[2] slightly modified by the authors. For Au, it is

$$\left.\begin{aligned} &R_k = 1.520 - 0.497\delta_k \\ &\delta_k = d_k^c / (s_k^f + s_k^c + d_k^c) \end{aligned}\right\} \tag{5}$$

From the state parameters of the one-atom state, the characteristic properties of the relative pseudo-crystal consisted of atoms in each kind of basic atomic state can be calculated by a series of equations in the following section (see Table 1).

Table 1 The basic atomic states and the characterisitic properties of relative pseudo-crystals of Au metal

b.a.state	electronic structure	lattice constant(Å)	cohesive energy / kJ · mol^{-1}
φ_1	$(5d_n)^6(5d_c)^3(6s_f)^2$	4.477,9	174.21
φ_2	$(5d_n)^6(5d_c)^3(6s_c)^2$	4.194,3	343.36
φ_3	$(5d_n)^6(5d_c)^4(6s_f)^1$	4.133,5	248.36
φ_4	$(5d_n)^6(5d_c)^4(6s_c)^1$	4.051,5	367.77
φ_5	$(5d_n)^4(5d_c)^5(6s_f)^2$	4.112,7	310.20
φ_6	$(5d_n)^4(5d_c)^5(6s_c)^2$	3.989,0	517.99
φ_7	$(5d_n)^4(5d_c)^6(6s_f)^1$	3.943,7	394.65
φ_8	$(5d_n)^4(5d_c)^6(6s_c)^1$	3.887,1	536.66

3 THE MAIN EQUATIONS

3.1 *Lattice Constant*

Supposing that the Pauling's bond length equation may be suitable to the various bonds in the pseudo-crystal, we have

$$\left.\begin{aligned} r_{1,0} &= 2R - \beta \lg n_1 \\ r_{2,0} &= 2R - \beta \lg n_2 \\ &\cdots\cdots\cdots \\ r_{s,0} &= 2R - \beta \lg n_s \end{aligned}\right\} \quad (6)$$

where $r_{1,0}$, $r_{2,0}\cdots$, $r_{s,0}$ denote respectively the lengths of the first, the second$\cdots$ the s neighbouring bonds; $n_1, n_2\cdots, n_s$ denote respectively the numbers of covalent electrons on the relative bonds; β is 0.6 for Au metal.

From Eq.(6), the following equations may be derived as

$$\left.\begin{aligned} n_c &= \sum I_s n_s \\ n_s &= n_1 \times 10^{(r_{s,0} - r_{1,0})/\beta} \\ n_1 &= n_c / [\sum_s I_s \times 10^{(r_{1,0} - r_{s,0})/\beta}] \end{aligned}\right\} \quad (7)$$

where I_s represents the number of the same kind of the s bond.

For certain pseudo-crystals, the bond lengths may be expressed by its lattice constant:

$$r_s = G_s a \quad (8)$$

For a crystal with fcc structure, $G_1 = 1/\sqrt{2}$, $G_2 = 1$ and $G_3 = \sqrt{6}/2$.

Combing Eq.(7) and Eq.(8), we have

$$a = (1/G_1)\{2R - \beta \lg [n_c / \sum_s I_s \times 10^{(G_1 - G_s)a/\beta}]\} \quad (9)$$

We have proved that it is a convergent transcendental equation of the lattice constant[6].

3.2 *The* MAI *Potential Function*

Considering contributions of the covalent electrons and free electrons to cohesive energy of the crystal the MAI potential for pure metals has been proposed. It is (in kJ / mol)

$$W(r) = A[\sum_s \frac{I_s n_s}{r_{s,0}} f + \frac{n_f}{\bar{r}_0} f'] \times [-n(\frac{r_0}{r})^x + (n-1)(\frac{r_0}{r})^{nx/(n-1)}] \quad (10)$$

where

$$\left.\begin{aligned} f &= \sqrt{\alpha} + \sqrt{3\beta} + \sqrt{5\gamma} \\ \alpha &= s_c / n_T^v, \quad \beta = p_c / n_T^v \\ \gamma &= d_c / n_T^v, \quad A = 314/(n' - 0.36) \\ f' &= \sqrt{2\alpha'}, \quad \alpha' = n_f / n_T^v \\ \bar{r}_0 &= \sum_s I_s r_{s,0} / \sum_s I_s \end{aligned}\right\} \quad (11)$$

The $r_0 = r_{1,0}$ and $r = r_1$ are respectively the shortest bond lengths of the crystal at the equilibrim and the unequilibrium state. The bonding capacities (f and f') of the hybrid covalent electron and free electron were proposed by Lü *et al*[7]. We have found that the n'

constant is taken as 4 for Cu, Ag and Au metals. The details of this potential will be introduced in another paper.

3.3 *Cohesive Energy*

At the equilibrium, $r = r_0$, the absolute values of one molar potential energy of the crystal is equal to cohesive energy

$$E_c = -W(r_0) = A(\sum_s \frac{I_s n_s}{r_{s,0}} f + \frac{n_f}{r_0} f') \quad (12)$$

For the crystal with fcc structure, the Eq.(12) may be written as

$$E_c = (A/a)\{(12\sqrt{2}n_1 + 6n_2 + 8\sqrt{6}n_3)f + [7n_f/(1+\sqrt{2}+2\sqrt{6})]f'\} \quad (13)$$

where a is the lattice constant.

3.4 *Bulk Modulus*

The bulk modulus equation of the crystal has been derived from MAI potential function

$$B = \frac{4\theta^2 K_B^2 r_0^2 m}{9\hbar V_0} \cdot \frac{1}{j^2}(1-2\varepsilon) \quad (14)$$

where θ is the Debye temperature; K_B is the Boltzmann's constant; $\hbar$ is Planck's constant; j is the multiple of the half cutoff wave length; m is the atomic mass; V_0 is the molar volume of the crystal and ε is the volumetric strain.

3.5 *Thermal Expansion*

The MAI potential function can be simplified to have analogy with Lennard-Jones potential. The Grüneisen equation calculating linear thermal expansion coefficient of the cubic crystals

$$\alpha = C_v / \{3Q[1-K(U/Q)]^2\} \quad (15)$$

can be still used here[9]. C_v is the molar specific heat at constant volume; U is the energy of the lattice vibration. If the Debye temperature θ is known, both C_v and U may be calculated at any temperature.

Comparing the MAI potential with the Lennard-Jones potential, the parameters (K and Q) can be obtained:

$$K = \frac{\theta K_B r_0}{3\hbar j}(2n-1) \times \sqrt{\frac{m}{n(n-1)E_c}} + \frac{1}{2} \quad (16)$$

$$Q = m(\frac{2\theta K_B r_0}{3\hbar j})^2 / [\frac{1}{3}(\frac{\theta K_B r_0}{\hbar j}\sqrt{\frac{m}{E_c}} \cdot \frac{n}{n-1} + 1)] \quad (17)$$

4 RESULTS

4.1 *The Electronic Structure of* Au *Metal*

The equations (9) and (12) may be considered as ones of two characteristic properties (a and E_c) in the MAI potential of the pseudo-crystal at equilibrium states. To determine electronic structure of Au metal means that the atomic state parameters of the pseudo-crystal should be found by fitting equations (9)and (12) to the characteristic properties of Au metal. It can not be found that the characteristic properties of a pseudo-crystal consisted of two kinds of basic atomic states listed in Table 1 can be in good agreement with that of Au metal. But the satisfactory solution has been found from combination of φ_1, φ_6 and φ_7 basic atomic states. The coefficients are listed in Table 2. From the atomic state parameters, it can be known that the electronic structure of Au metal is

$$(5d_n)^{4.65}(5d_c)^{4.71}(6s_c)^{0.62}(6s_f)^{1.02}$$

4.2 *Theoretical Potential Curve of* Au *Metal*

According to experimental values of the

Table 2 Atomic state parameters, bond parameters of Au metal

coefficients	$c_1=0.325,2$	$c_6=0.326,0$	$c_7=0.365,8$
Atomic state parameters	$s_f=0.618,0$	$s_c=1.162$	$d_c=4.715,4$
	$d_n=4.650,4$	$n_c=5.333,5$	$n_T^v=6.349,7$
	$R=1.335,5$ / Å		
Bond parameters	$r_1=2.883,7$ / Å	$r_2=4.078,2$ / Å	$r_3=4.994,7$ / Å
	$n_1=0.441,9$	$n_2=0.004,5$	$n_3=0.000,1$

Table 3 Main physical properties of Au metal

Properties	a / Å	E_c / kJ · mol^{-1}	B / × 10^5 MPa	α_{293} / × 10^{-6}
Theo.values	4.0782	368.23	1.6524	14.26
Expt.values	4.0782	368.27[10]	1.7358[10]	14.2[9]

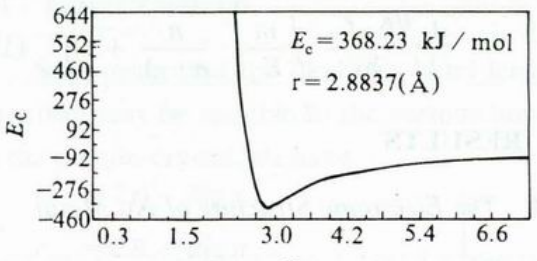

Fig.1 Theoretical potential curve of Au metal

linear thermal expansion coefficient at two temperatures, the parameters n, j and x in the MAI potential are repectively 1.3, 4.4 and 3.155; and Fig.1 shows the theoretical potential curve.

4.3 *Theoretical Curve of Linear Thermal Expansion Coefficient of* Au *Metal*

Substituting $n=1.3$, $j=4.4$, $\theta=165$ K and $E_c=368.23$ (kJ / mol) into Eqs.(16) and (17), we can obtain $Q=613.28$ (kJ / mol) and $K=3.40$. The theoretical curve of linear thermal expansion coefficinent can be calculated from Eq.(15). Fig.2 shows that the theoretical values are in good agreement with experiment values (denoted by ·).

5 DISCUSSIONS

5.1 *The* QEO *Number of* Au *Metal*

Eckardt *et al*[11] studied the band structure of Au metal by the linear rigorous cellular LRC method. Their result of the band structure was in good agreement with experimetal data from angular-resolved photoemission. They also obtained the QEO number of Au metal. Table 4 shows the QEO numbers obtained by OAS method and LRC method respectively, and the analogous free atomic values n_1^0.

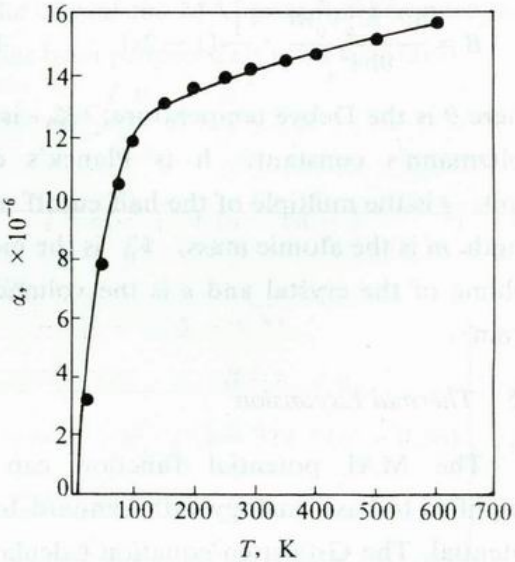

Fig.2 Theoretical tem.(T) dependence of linear thermal expansion coefficients (α) of Au metal experimental value [9]

From results of OAS method and LRC method, it can be known that there are very few electrons of d state about 0.6～0.7 jumping to up higher levels by the transition from

Table 4 The QEO numbers of Au metal and the analogous free atomic values n_1^0

method	l			
	0	1	2	3, 4, 5, 6
	(6s)	6P	(5d)	—
OAS	$s_f = 0.6180$ $s_c = 1.0162$	0	$d_c = 4.7154$ $d_n = 4.6504$	0
LRC	0.772	0.610	9.464	0.154
n_1^0	1	0	10	

the free atom to the metal atom. But the OAS method pointed out that the rest of the electrons of d state should be divided into two kinds of electrons: covalent electrons and non-valent electrons.

In Eckardt's opinion of that "as a result of the strong s–p hybridization the occupation of the formerly unoccupied p levels becomes practically equal to that of the s level", it is reasonable to consider electrons in the higher levels with l = 3, 4, 5 and 6 to that in the s level. Table 4 shows the good agreement between the total number (1.536) of n_0, n_1, n_3, n_4, n_5 and n_6 electrons obtained by LRC method and the total number (1.6342) of s_f and s_c electrons obtained by OAS method. It means that the energy band theory and valence bond theory can be linked up together.

5.2 *Single Bond Radius and Valency of* Au *Metal*

The single bond radius (1.34Å) of Au metal listed in the Periodic Table of the Elements[4] and obtained by Pauling is almost exactly equal to that (1.335,5 Å) obtained by authors. Pauling pointed out that the valency of Au metal was 5.56[3] which is more than covalent electrons (n_c = 5.333,5), but less than total valence electrons (n_T^v = 6.349,6). In our opinion it is reasonable to divide valence electrons into covalent electrons responsible for the formation of the bond network of crystals and free electrons responsible for conductivity of metals.

Because the electronic structure of Au metal presented here is obtained by systematic and comprehensive analysis, and the QEO number has been verified by band theory, it should be more complete, more accurate and more reliable than that obtained by Pauling.

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