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Electronic structures and properties of pure vanadium①

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Abstract: By the one-atom theory the electronic structure of bcc-V has been determined to be [Ar] $(3d_n)^{1.7998}(3d_c)^{2.6578}(4S_c)^{0.1711}(4s_f)^{0.3713}$. According to this electronic structure of bcc-V, its potential curve, cohesive energy, lattice parameter, elasticity and linear thermal expansion coefficient were calculated. The electronic structures of the primary state crystals of fcc-V, hcp-V and the primary state liquid—V have also been studied.

Key words: vanadium; electronic structure; physical properties **Document code:** A

1 INTRODUCTION

To design new alloys scientifically Xie, the second author of the paper, has established a systematic alloy theory frame, which can give diagrams of thermodynamic properties, lattice parameters, electronic structure and properties of alloy systems as functions of composition; for binary alloy systems, their general functions are

$$G_\alpha = x_A G^0_{A\alpha} + x_B G^0_{B\alpha} + \Delta G(x_A, x_B)_\alpha \quad (1)$$

$$\psi_\alpha = x_A \psi^0_{A\alpha} + x_B \psi^0_{B\alpha} + \Delta \psi(x_A, x_B)_\alpha \quad (2)$$

$$a_\alpha = x_A a^0_{A\alpha} + x_B a^0_{B\alpha} + \Delta a(x_A, x_B)_\alpha \quad (3)$$

$$Q_\alpha = x_A Q^0_{A\alpha} + x_B Q^0_{B\alpha} + \Delta Q(x_A, x_B)_\alpha \quad (4)$$

where $G^0_{A\alpha}$, $G^0_{B\alpha}$, $\psi^0_{A\alpha}$, $\psi^0_{B\alpha}$, $a^0_{A\alpha}$, $a^0_{B\alpha}$, $Q^0_{A\alpha}$ and $Q^0_{B\alpha}$ denote respectively Gibbs energy, electronic state, lattice parameter and properties of pure components A and B in the α phase, between which the relations are described with the one-atom theory of pure metals (OA theory)[1,2]; and ΔG_α, $\Delta\psi_\alpha$, Δa_α, ΔQ_α denote respectively the interaction functions of the energy, state, lattice parameter and properties of component A and B, which are described with the characteristic crystal theory of the alloys (CC theory)[3~6]. In this paper, the electronic structures, lattic parameters and properties of primary state crystals of bcc-V, fcc-V, hcp-V and primary state liquid-V have been studied.

2 BASIC ATOMIC STATES OF V-METAL

In the OA theory the electronic state of a pure metal is illustrated with quasi-electron-occupation(QEO) number of one-atom state ψ_a consisting of some basic atomic states Φ_k:

$$\psi_a = \sum_k C_k \Phi_k \quad (5)$$

In the outer shell of atoms of metals and alloys, there are covalent electrons n_c, near free electrons n_f and non-valence electrons n_n. In each basic atomic state the electrons obey Pauli exclusion principle. If s^c_k and d^c_k denote respectively the number of covalent electrons of the s and d orbitals in the k basic atomic state, d^n_k and s^f_k denote respectively the number of non-valence d-electrons and free s-electrons, parameters of one-atom state of the pure metal can be obtained from the following expressions:

$$\begin{cases} s_c = \sum_k C_k s^c_k,\ d_c = \sum_k C_k d^c_k,\ p_c = \sum_k C_k p^c_k \\ n_c = s_c + p_c + d_c,\ n_v = n_c + n_f \\ n_n = \sum_k C_k d^n_k,\ \sum_k C_k = 1,\ R = \sum C_k R_k \end{cases} \quad (6)$$

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where R_k is the single bond redius which can be obtained from Pauling's equation slightly modified. For vanadium, it is

$$\begin{cases} R_k = (0.1610 - 0.0550\,\delta_k) \\ \delta_k = d_k^c/(s_k^c + s_k^f + p_k^c + d_k^c) \end{cases} \quad (7)$$

The characteristic properties of the relative pseudo-crystals formed by atoms in each kind of basic atomic state can be calculated by a series of equations of OA theory (See Table 1).

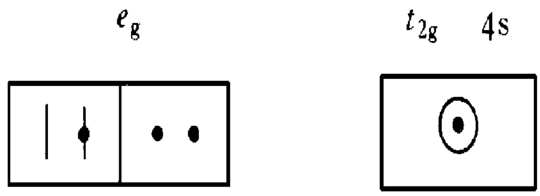
3 ELECTRONIC STRUCTURE, CRYSTAL STRUCTURE AND PHYSICAL PROPERTIES OF bcc-V

3.1 Electronic structure of bcc-V

In nature, V-metal is of body-centred cubic (bcc) crystal below its melting point. By the OA theory, the precise solution ϕ_α has been obtained from combination of three basic atomic states: $\Phi_7(c_7 = 0.7288)$, $\Phi_6(c_6 = 0.1001)$, $\Phi_{12}(c_{12} = 0.1711)$. The calculated results are listed in Table 2. From this atomic state ϕ_α, it can be known that as free V-atoms with [Ar]$4s^2 3d^3$ approach, the s and d bond overlap, and about 1.4576 s-electrons per atom is transformed into d-electrons. The electronic structure of bcc-V is [Ar] $(3d_n)^{1.7998}$ $(3d_c)^{2.6578}$ $(4s_c)^{0.1711}$ $(4s_f)^{0.3713}$.

3.2 Relation between crystal structure and electronic structure of bcc-V

According to OA theory, the d-electrons over p^6 shell first fill the deep potential holes in the e_g state, forming the lobes in the eight ⟨111⟩ directions. Atoms in this state form the bcc crystal. As the number of d-electrons in the e_g state increases, the bcc structure stablized greatly. The electronic configuration [Ar] $(3d_n)^{1.7998}$ $(3d_c)^{2.6578}$ $(4s_c)^{0.1711}$ $(4s_f)^{0.3713}$ of one-atom state of bcc-V can be described as



where •, and | denote respectively the covalent electron, and non-valence electron; ⊙ denots that one part of the electron is covalent and

Table 1 Basic atomic states and relative pseudo-crystals' characteristic properties of V-metal

K number	Electronic structure in outer shell	Lattice constant a/nm			Cohesive energy E_c/(kJ.mol^{-1})		
		bcc	fcc	hcp*	bcc	fcc	hcp*
1	$(3d_c)^4(4s_f)^1$	0.29570	0.37174	0.26279	621.49	611.91	621.45
2	$(3d_c)^4(4s_c)^1$	0.28914	0.36355	0.25700	915.84	907.97	908.34
3	$(3d_c)^5$	0.26438	0.33261	0.23511	912.45	905.46	905.88
4	$(3d_c)^3(4s_c)^1(4s_f)^1$	0.32056	0.40275	0.28472	623.12	613.37	622.16
5	$(3d_c)^3(4s_c)^2$	0.31398	0.39455	0.27892	816.88	809.19	809.48
6	$(3d_c)^3(4s_f)^2$	0.32905	0.42295	0.29899	433.50	408.82	432.08
7	$(3d_n)^2(3d_c)^3$	0.27935	0.36116	0.25525	519.11	499.32	499.61
8	$(3d_n)^2(3d_c)^2(4s_f)^1$	0.34218	0.43023	0.30413	270.66	263.72	274.22
9	$(3d_n)^2(3d_c)^2(4s_c)^1$	0.32075	0.41264	0.29169	487.94	471.03	471.20
10	$(3d_n)^2(3d_c)^1(4s_c)^2$	0.36232	0.46427	0.32821	380.07	367.73	367.86
11	$(3d_n)^2(3d_c)^1(4s_f)^2$	0.40782	0.51207	0.36201	163.09	150.75	175.44
12	$(3d_n)^2(3d_c)^1(4s_c)^1(4s_f)^1$	0.38360	0.48191	0.34068	246.94	240.50	249.83

Table 2 Atomic state parameter, bond parameter and characteristic properties of bcc-V

Atomics state prameters	$d_n = 1.7998$	$d_c = 2.6578$	$s_c = 0.1711$
	$s_f = 0.3713$	$n_c = 2.8289$	$n_V = 3.2002$
Bond parameters	$r_1 = 0.26163$ nm	$r_2 = 0.30210$ nm	$r_3 = 0.42724$ nm
	$n_1 = 0.3045$	$n_2 = 0.0644$	$n_3 = 0.0005$
	$R = 0.11532$ nm		

Properties	a	E_c
Theo. value	0.30210 nm	470.28 kJ/mol
Expt. value	0.30238 nm[7]	470.28 kJ/mol[8]

another part is near free, and † denotes that one part of the electron is covalent and another part is noncovalent.

3.3 Physical properties of bcc-V

3.3.1 Theoretical potential curve of bcc-V According to the one-atom state ψ_a, the theoretical potential curve of bcc-V can be obtained by OA theory (see Fig.1).

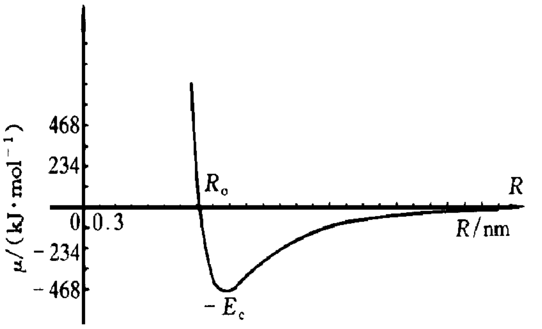


Fig.1 Theoretical potential curve of bcc-V
$n = 2.6$, $j = 5.3$, $x = 3.7143$
$E_c = 470.28$ kJ/mol, $R_0 = 0.26163$ nm

3.3.2 Thermal expansion coefficient of bcc-V

The temperature dependence of linear thermal expansion coefficients of bcc-V can be obtained by OA theory (see Fig.2).

3.3.3 Elasticity of bcc-V

According to the one-atom state ψ_a, bulk modulus (B), Young's modulus (Y), shear modulus (μ) and Poisson's ratio (σ) have been calculated by OA theory. The theoretical and experimental values are listed in Table 3[10].

4 ELECTRONIC STRUCTURE OF fcc-V

The V-metals with face-centred cubic (fcc) and hexagonal closed-packed (hcp) structures can not exist naturally. But it is necessary to study fcc-V and hcp-V for the studies of the structure and properties of V-alloy systems containing fcc and hcp phases.

Under the isopiestic condition, the Gibbs energy of pure metal is a function of specific heat $C_p(T)$ and volume $V(T)$:

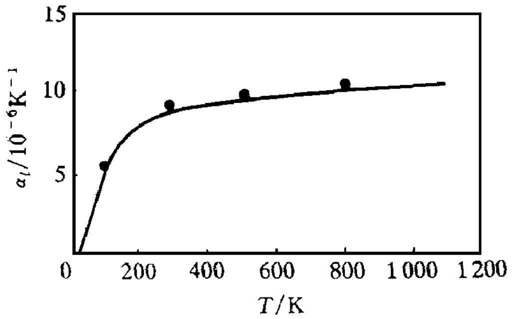


Fig.2 Temperature dependence of linear thermal expansion coefficients of bcc-V
(• —experimental values[9])
$K = 2.26$, $Q = 896.93$ kJ/mol, $\theta = 380$ K

Table 3 Elasticity of bcc-V

Property	Theo. value /(10^2 GPa)	Expt. value /(10^2 GPa)
B	1.646	1.651
Y	1.637	1.34
μ	0.617	0.475
σ	0.33	0.36

$$G = E + \int_0^T C_p(T)\,dT + p\int_0^T V(T)\,dT - T\int_0^T (C_p(T)/T)\,dT \quad (8)$$

G is also represented as a power series in terms of temperature T in the SGTE database[11]:

$$G' = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1}, \quad (9)$$

where a, b, c, d, e and f are coefficients.

The relative Gibbs energy G' is not equal to G. At 0 K, their difference should be

$$G - G' = E - a \quad (10)$$

According to the cohesive energy of bcc-V ($E_{c\ bcc-V}$ = 470.28 kJ/mol) and the G' values of bcc-V, fcc-V, hcp-V and liquid V(L-V) in SGTE database, the cohesive energies of the primary state crystals of fcc-V, hcp-V and primary liquid V(L-V) can be obtained:

E_{fcc-V} = 462.78 kJ/mol, $E_{c\ hcp-V}$ = 466.28 kJ/mol, $E_{c\ L-V}$ = 449.52 kJ/mol。

The lattice constant of the primary state crystal of fcc-V can not be measured experimentally. To calculate it, V-Ni system containing fcc phase can be chosen. According to experimental lattice constants of V-Ni alloys in the fcc phase[12], the lattice constant of fcc-V has been calculated to be 0.39416 nm by trapolation method. The electronic structure of fcc-V can be determined by OA theory to be [Ar]$(3d_n)^{2.0000}(3d_c)^{2.4058}(4s_c)^{0.4252}(4s_f)^{0.1690}$. The atomic state parameter, bond parameters and characteristic properties are listed in Table 4.

5 ELECTRONIC STRUCTURE OF hcp-V

$E_{c\ hcp-V}$ has been caluclated to be 466.28 kJ/mol as above, but up to now we can not find enough data to calculate the lattice constant of hcp-V, so its electronic structure can be determined only by the cohesive energy. Two possible electronic structures and their state parameters, bond parameters and characteristic properties are listed in Table 6.

6 ELECTRONIC STRUCTURE OF V-LIQUID

$E_{c\ L-V}$ has been calculated to be 449.52 kJ/mol as above. X-ray diffraction experiments finds that liquid metals are like short-range ordered crystals. The volume expands about 10.09 %[13] when V-metal is transformed from solid into liquid. It may be supposed that the primary state V-liquid is a quasi-crystal with bcc structure. Below the melting point its crystal volume is 0.013 786 nm^3, and after melting it increases to 0.015 173 nm^3. So the lattice constant of L-V can be calculated to be 0.311 94 nm. Then its electronic structure can be determined by OA theory to be [Ar]$(3d_n)^{2.0000}(3d_c)^{2.4220}(4s_c)^{0.2890}(4s_f)^{0.2890}$. Its atomic state parameters, bond parameters and characteristic properties are listed in Table 5.

7 CONCLUSION

(1) As free V atoms approach to form bcc-V the electronic structure [Ar]$4s^2 3d^3$ is transformed into [Ar]$(3d_n)^{1.7998}(3d_c)^{2.6578}(4s_c)^{0.1711}(4s_f)^{0.3713}$.

(2) According to the electronic structure of bcc-V, its potential curve, cohesive energy, lattice parameter, elasticity and linear thermal expansion coefficient are calculated, and the calculated values agree well with the experimental

Table 4 Atomic state parameters, bond parameters and characteristic properties of fcc-V

Coefficients	C_{10} = 0.2126	C_7 = 0.6184	C_8 = 0.1690
Atomic state	d_n = 2.0000	d_c = 2.4058	s_c = 0.4252
parameters	s_f = 0.1690	n_c = 2.8310	n_v = 3.0000
Bond	r_1 = 0.278 77 nm	r_2 = 0.394 23 nm	r_3 = 0.482 84 nm
prameters	n_1 = 0.2325	n_2 = 0.0055	n_3 = 0.0003
	R = 0.11689 nm		
Properties	a		E_c
Theo. value	0.39423 nm		462.78 kJ/mol

Table 5 Atomic state parameters, bond parameters and characteristic properties of L-V

Coefficients	$c_7 = 0.7110$	$c_{12} = 0.2890$	$c_{11} = 0$
Atomic state parameters	$d_n = 2.0000$ $s_f = 0.2890$	$d_c = 2.4220$ $n_c = 2.7110$	$s_c = 0.2890$ $n_v = 3.0000$
Bond parameters	$r_1 = 0.26646$ nm $n_1 = 0.2908$ $R = 0.11660$ nm	$r_2 = 0.30768$ nm $n_2 = 0.0629$	$r_3 = 0.43512$ nm $n_3 = 0.0006$
Properties	a		E_c
Theo. value	0.30768 nm		449.57 kJ/mol

Table 6 Two possible electronic structure and their parameter and characteristic properties of hcp-V($c/a = 1.632$)

	State	$\phi_a(1)$ $s_f \to s_c$	$\phi_a(2)$ $s_f \to d_c$
Atomic state parameters	s_f	0.3259	0.3269
	s_c	0.2165	0.1711
	d_n	1.7998	1.7998
	d_c	2.6578	2.7022
	n_c	2.8743	2.8733
	n_v	3.2002	3.2002
Bond parameters	R/nm	0.11532	0.11456
	r_1/nm	0.27496	0.27346
	r_2/nm	0.27508	0.27357
	r_3/nm	0.38894	0.38681
	r_4/nm	0.44892	0.44647
	n_1	0.2367	0.2365
	n_2	0.2358	0.2357
	n_3	0.0059	0.0060
	n_4	0.0008	0.0004
Properties	a/nm	0.27508	0.27357
	E_c/kJ·mol^{-1}	466.28	466.28

values.

(3) The electronic structure of the primary state crystal of fcc-V has been determined to be [Ar] $(3d_n)^{2.0000}$ $(3d_c)^{2.4058}$ $(4s_c)^{0.4252}$ $(4s_f)^{0.1690}$.

(4) Two probable electronic structures of the primary state hcp-V are respectively: [Ar] $(3d_n)^{1.7998}(3d_c)^{2.7022}(4s_c)^{0.1711}(4s_f)^{0.3269}$ and [Ar] $(3d_n)^{1.7998}$ $(3d_c)^{2.6578}$ $(4s_c)^{0.2165}$ $(4s_f)^{0.3259}$.

(5) The electronic structure of the primary state V-liquid has been determined to be [Ar] $(3d_n)^{2.0000}(3d_c)^{2.4220}(4s_c)^{0.2890}(4s_f)^{0.2890}$.

REFERENCES

1 Xie Y Q, Science in China(A), 1993, 36(1):90.
2 Xie Y Q. Acta Metall Mater, 1994, 42(11):3705.
3 Xie Y Q. Science in China(E), 1998, 41(2):146.
4 Xie Y Q, Zhang X D. Science in China(E), 1998, 41(2): 156.
5 Xie Y Q, Zhang X D. Science in China(E), 1998, 41(3): 225.
6 Xie Y Q, Zhang X D. Science in China(E), 1998, 41(4): 348.
7 Bulletin of Alloy Phase Diagrams, 1981, 2(3): 402.
8 Bulletin of Alloy Phase Diagrams, 1981, 2(2): 261.
9 Kaye G W C and Laby T H. Tables of Physical and Chemical Constants and Some Mathematical Function. London and New York: Longman, 31.
10 Frederick Seitz, David Turnbul. Solid State Physics, Vol.16, New York and London: Academic Press, 281 ~ 340.
11 Dinsdale A T. SGTE Date for Pure Element, CALPHAD, 1991, 15(4): 412.
12 Bulletin of Alloy Phase Diagrams, 1982, 3(3): 343.
13 CRC Handbook of Chemistry and Physics, 70th ed. Florida: CRC Press Inc. 1989, B219.

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