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Ab initio calculations for properties of laves phase V₂M (M = Zr, Hf, Ta) compounds

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Abstract: A first-principles plane-wave pseudopotentials method based on the density functional theory (DFT), is used to investigate the structural, mechanic and electronic of Laves phase V_2M (M = Zr, Hf, Ta) compounds. It is found that V_2Hf is mechanically unstable because this compound do not satisfy the condition $C_{11} - C_{12} > 0$ below 6.27 GPa, it becomes stable beyond this pressure, the bulk modulus B revealing the largest B values for V_2Ta compound which are the stable ground state phases according to the total energies. Also there is a strong interaction between V and V, the interaction between M (M = Zr, Hf, Ta) and V is more strong and between M and M is the strongest.

Keywords: Ab Initio Calculation, Electronic Structure, Structural Properties

1. Introduction

Intermetallic phases are materials composed of two or more types of metal atoms, which crystallizes with a structure other than those of its components. Intermetallic compounds have been attracted candidates for high temperature structural materials because of their desirable intrinsic properties. There have been many investigations carried out on various compounds, but mostly on structures that are ordered from of fcc, bcc and hcp metals.

Most of the 4*d* and 5*d* elements are not soluble in the 3*d* elements, but they can form intermetallic compounds. Among them the Laves phase compound, AB_2, is the most important one. In particular, Laves phase compounds, which are the most abundant intermetallic compound class, have been investigated extensively for high-temperature structural applications and extensively studied in respect of magnetism if containing Fe or Co. The V-based Laves-phase compounds V_2Zr, V_2Hf and V_2Ta are of considerable current interest because of their relatively low densities and high melting temperatures, high electronic density of states at the Fermi energy and the strong influence of spin fluctuations [1]. V_2Zr, V_2Hf and V_2Ta have superconducting transition temperatures of 8K, 9K and 4K respectively, and

a martensitic phase transition around 120 K [2]. B. Lüthi et al [3] present experimental results for the low-temperature specific heat, electrical resistivity, elastic constants, ultrasonic attenuation and thermal conductivity of the C15 Laves phases V_2Hf. C-W. Zhang [4] studied theoretically the electronic structure and bonding properties for Laves-phase RV_2 (R= Ti, Nb, Hf, and Ta) compounds, using the full-potential linearized augmented plane-wave method (FLAPW) with the local density approximation (LDA). M. H.F. Sluiter [5] computed using electronic density functional theory, the enthalpies at zero Kelvin, for the nonmetals and semimetals in columns IV, V and VI of the periodic table. The lattice stabilities have been compared with other ab initio computed. For Ta-V system C. A. Danon et al. [6], based on the Calphad-Thermocalc approach the Gibbs energy functions of the liquid, the bcc solid solution and the Laves phases were determined, and the calculated phase equilibria were compared with experimental data. J. Pavlů et al. [7] present the thermodynamic modeling of Laves phases in the Ta-V system, using first-principles.

In order to further understand the physical properties of these compounds, a detailed investigation of the effect of pressure on the elastic constants, using the Perdew-Burke-

Ernzerhof (PBE) method. In our study we consider the most common crystal structures of Laves phases. The C15 structure is face-centered cubic with two AB_2 formula units per unit cell with space group Fd-3m, No.227.

In the present work we are interested in cubic V_2M (M = Zr, Hf, Ta) compounds. They present a C15-type structure with a Fd-3m space group. The paper is organized as follows. The computational method is described in section 2. In section 3, the results are presented and compared with available experimental and theoretical data. Conclusion is given in section 4.

2. Computational Method

Our first-principles calculations are performed within a Plane Wave Pseudo Potential (PWPP) method which has been implemented in the CASTEP (Cambridge Serial Total Energy Package) simulation program [8]. Calculations were performed within Density Functional Theory (DFT) which is, in principle an exact theory of the ground state, using the Perdew-Burke-Ernzerhof scheme, known as PBE scheme [9], a Generalized Gradient Approximation (GGA) is made for the electronic exchange-correlation potential energy. Coulomb potential energy caused by electron-ion interaction is described within an ultra-soft scheme, in which the V ($3d3$ $4s2$), Zr ($4d2$ $5s2$), Hf ($4f14$ $5d2$ $6s2$) and Ta ($4f14$ $5d3$ $6s2$) orbitals are treated as valence electrons. According to an ultrasoft condition, the pseudo-wave function which is related to the pseudo potential matches the plane-wave function expanded with Kohn-Sham beyond cut-off energy. Using high cut-off energy, at the price of spending long computational time, can actually provide accurate results. The cut-off energy for the plane-wave expansion was set at 330 eV and the Brillouin zone sampling was carried out using the 6x6x6 set of Monkhorst-Pack mesh [10]. Atomic positions are optimized with a density mixing scheme using the Conjugate Gradient (CG) method for eigenvalues minimization. The equilibrium lattice parameter is then computed from a structural optimization, using the Broyden-Fletcher-Goldfarb-Shenno (BFGS) minimization technique. This technique provides a fast way of finding out the lowest energy structure out of all the converged structures, with the following thresholds: energy change per atom less than 2 x 10-5 eV, residual force less than 0.05 eV/Å, displacement of atoms during the geometry optimization less than 0.002Å, and maximum stress within 0.1 GPa. The crystal structures are reported (Table 1). The large and small balls represent M and V atoms Fig. (1).

Table 1. *Calculated V_2Zr, V_2Hf and V_2Ta structures: lattice parameters in Å; volumes per formula unit (f.u.) in Å³; Z is the number of formula units in the unit cell, the space group and enthalpies of formation ΔH in eV and compared with experimental data.*

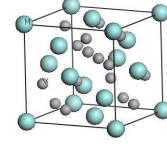|	Space group	A	V	Z	ΔH
V_2Zr	Fd-3m	7.36	399.39	8	1.25
V_2Hf	Fd-3m	7.35 7.38[a] 7.31[b]	397.95	8	0.21
V_2Ta	Fd-3m	7.17 7.22[b]	369.75	8	-0.22

[a][3], [b][4].

Fig. 1. *V_2M (M = Zr, Hf, Ta) structure.*

3. Results and Discussion

3.1. Structural Properties Phase Stability

The results for lattice parameters *a* are reported in Table. 1. and compared with experimental and previous theoretical calculations. Our calculated value for lattice parameter *a* of V_2Hf compound agrees well with that of the experimental value of 7.38 Å [3] and the theory work 7.34, 7.31 and 7.22 for V_2Zr, V_2Hf and V_2Ta compounds respectively [4]. The relative deviation may be attributed to the fact that our calculation corresponds to the perfect bulk material at zero temperature, whereas the experimental sample was synthesized at high temperature (1550°C). In general, the discrepancy between our GGA calculations and theoretical values given by W. Zhang was attributed to shortcomings of the local exchange-correlation approximations of LDA potential.

We are now interested in the pressure effect. We calculate the pressure-versus-volume equation of state (EOS) in the range from 0 to 30 GPa, which is fitted to a third-order Birch-Murnaghan equation [11], as follows:

$$P = \frac{3}{2}B_0\left[\left(\frac{V}{V_0}\right)^{-\frac{7}{3}} - \left(\frac{V}{V_0}\right)^{-\frac{5}{3}}\right]\left[1 + \frac{3}{4}(4-B')\left\{\left(\frac{V}{V_0}\right)^{-\frac{2}{3}} - 1\right\}\right]$$

With V_0 corresponding to the value determined from the zero pressure data. Our results are depicted in Fig. 2. For V_2Zr and V_2Ta compounds to the best of our knowledge, no experimental data are available to date, our results can be considered as prediction for future investigations.
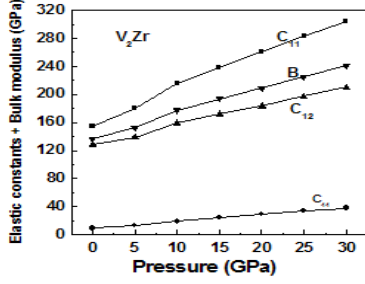
Fig. 2. *V/V0 equation of state versus pressure. V0 is the equilibrium volume of V2M (M = Zr, Hf, Ta) compounds.*

The nearest-neighbor distance DV-M and DV-V in V$_2$M (M = Zr, Hf, Ta) compounds decrease and the bulk modulus increase. Fig. 3. shows the trend of volumes and bulk modulus B revealing the largest B values for V$_2$Ta compound which are the stable ground state phases according to the total energies. For the two latter compounds, the smaller difference between the volumes values yielding larger bulk moduli. The calculated equilibrium enthalpies of formation with respect to the equilibrium bulk phases of the pure constituents are defined by
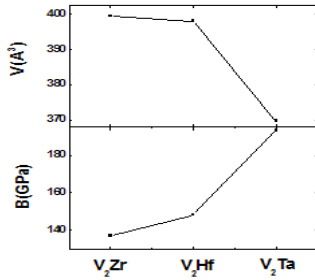

Fig. 3. *Ab initio equilibrium volumes V and bulk modulus B for the V$_2$Zr, V$_2$Hf and V$_2$Ta compounds.*

$$\Delta H = UDFT(V2M) - [2UDFT(V) + UDFT(M)]$$

As the difference between the corresponding total energies U of the DFT calculation. Table. 1. lists the calculated formation energies of V$_2$M (M = Zr, Hf, Ta) at identical levels of theory. It should be noted that V$_2$Ta is the most stable one of about -0.224 eV. V$_2$Zr is less stable than V$_2$Hf by about 1 eV. No experimental values are available for the V$_2$M Laves phase for a comparison with the calculated results.

3.2. Elastic Constants

The elastic constants of solids provide a link between mechanical and dynamical behaviors' of crystals, and give important information concerning the nature of forces operating in solids. In particular, they provide information on stability and stiffness of materials. It is well known that first-order and second-order derivatives of the potential give forces and elastic constants. Therefore, it is an important issue to check the accuracy of the calculations for forces and elastic constants.

Let us recall here that pressure is an important thermodynamic parameter since it allows an increase of matter density by reducing volume. The reduction of volume by applying high pressures leads to an overall decrease of interatomic and intermolecular distances that allows exploring in detail atomic and molecular interactions, and effect upon elastic constants is essential, at least for understanding interatomic interactions, mechanical stability and phase transition mechanism. Therefore, high-pressure research has improved our fundamental understanding of these interactions in solids, liquids and gasses. The study of the structure of matter under compression is a rapid developing field that is receiving increasing attention especially due to continuous experimental and theoretical developments.

Both V$_2$M (M = Zr, Hf, Ta) are cubic structures characterized by three independent elastic constants (C_{11}, C_{12}, and C_{44}) as well as the bulk modulus, which we determine as a function of pressure up to 30 GPa (Fig. 4 and 5). All elastic constants and the bulk modulus linearly increase with respect to pressure. Fig. 5. show other the linearity of the elastic moduli *vs.* pressure of V$_2$Hf compound. The inset shows an enlarged view of (Cij + B) near the pressure stability.
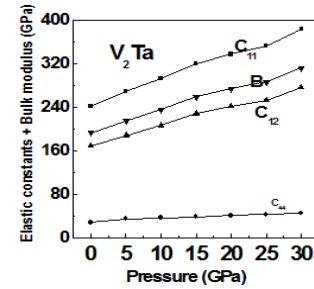

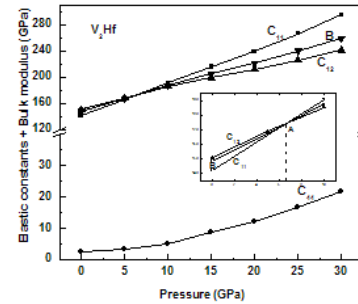**Fig. 4.** *Elastic constants Cij and bulk modulus B, (Cij + B) vs. pressure of V$_2$Zr and V$_2$Ta compounds.*

Fig. 5. *Elastic constants Cij and bulk modulus B (Cij + B) vs. pressure of V$_2$Hf compound. The inset shows an enlarged view of (Cij + B) near the pressure stability.*

For a cubic crystal, the generalized elastic stability criteria in terms of elastic constants [12]:

$$(C_{11} + 2C_{12})/3 > 0 \quad C_{44} > 0$$

$$(C_{11} - C_{12})/2 > 0$$

There is another relation between C_{11} and C_{12}, that is

$$B = (C_{11} + 2C_{12})/3$$

where B is the bulk modulus. In the Voigt average, the shear modulus is given by

$$G_V = (C_{11} - C_{12} + 3C_{44})/5$$

The Young's modulus, Poisson's ratio and elastic anisotropy ratio are given by

$$E = 9B/(1 + 3B/G)$$

$$\nu = (B - 2G/3)/2(B + G/3)$$

$$A = 2C_{44}/(C_{11} - C_{12})$$

For V_2Zr and V_2Ta, these criteria are satisfied in the studied pressure, whereas V_2Hf do not satisfy the condition $C_{11} - C_{12} > 0$ below 6.27 GPa, V_2Hf becomes stable beyond this pressure. The single-crystal elastic moduli constants at the equilibrium constants of V_2M (M = Zr, Hf, Ta) are listed in Table 3.

Table 3. *Enthalpies of formation E (eV), zero pressure elastic moduli (Cij) in GPa of cubic V_2Zr, V_2Hf and V_2Ta. The polycrystalline bulk moduli (B), shear moduli (G), Young's moduli (Y), and Poisson's ratio v were obtained using the Voigt approximation. All the elastic constants are in GPa except for the dimensionless v.*

Material	E	C_{11}	C_{12}	C_{44}	B	G	B/G	Y	v
V_2Zr	-10467	154.09	128.61	9.18	137.11	10.60	12.80	37.07	0.455
					134.70[b]				
V_2Hf	-8723	142.30	151.19	2.63	148.23	-0.20	-740	-13.49	0.515
		128[a]	102[a]	17[a]	140.50[b]				
V_2Ta	-32724	240.92	169.19	28.63	193.10	31.52	6.12	101.33	0.412
					202.60[b]				

[a][3], [b][4].

Also Young (E) and shear (G) moduli are two important quantities for technological and engineering applications and provide fundamental description for mechanical behavior. The former is defined as the ratio between stress and strain. The latter, which is related to bond bending, depends on the nature of the bond and decreases as a function of onicity. $(C_{11} - C_{12})$, as well as Young's modulus E, are also very significant quantities to characterize mechanical properties of materials [13]. For comparison, the calculated bulk modulus for V_2Ta is about 193.6 GPa, 137.11 GPa and 148.23 GPa respectively for V_2Zr and V_2Hf respectively, slightly different than those obtained by W. Zhang [4], this discrepancy was attributed to the local exchange-correlation approximations of LDA potential. Note that bulk modulus for V_2Ta is larger than that of all compounds. Auther comparison, we compare our compound V_2Zr with the C15 Laves phases of Cr_2Zr [14] compounds because it

appears to be similar ($[C_{11} - C_{12}; E] = [102; 150]$ GPa) our V_2Zr compound presents lower $(C_{11} - C_{12})$ [26 GPa] and E [37 GPa] than in Cr_2Zr, and at least a lower E implying better plasticity. V_2Zr has a large bulk modulus (137 GPa), then for Cr_2Zr it is equal to 180 GPa and 182 GPa [15]. For V_2Hf that is also comparable to $HfCr_2$ [15], B[199 GPa] our V_2Hf compound present lower B [148 GPa].

Unfortunately, there are no experimental results for comparing with the present work. However, it can be seen that they are much smaller than those found for Cr_2Zr compound. The reason of these deviations is not so clear; the computational methods and, especially, the various atomic bonding mechanisms operating between cations and anions affect the bulk modulus and elastic constants [16]. Since the bulk modulus is inversely proportional to the bond length, the smaller atomic size and shorten bond length can cause the bulk modulus to be larger, and consequently, the elastic constants.

3.3. Electronic Structures

DFT band structure calculations are conducted to understand the electronic structure of different materials. Figure. 6. shows the partial *s*-, *p*-, and *d*-Densities of States (DOS) for all V_2M (M = Zr, Hf, Ta) compounds. We show here only the vicinity of the Fermi energy level. The peaks corresponding to the lowest energy (not shown) are due to the contribution M-*s* and M-*p* for all compounds. There are two common features in the DOS profiles for these compounds: (1) V and M (M = Zr, Hf, Ta) have similar DOS profiles in the whole energy region, indicating the presence of hybridization between V and M (M = Zr, Hf, Ta) *d*-electrons; (2) The M-4*d* bands are nearly fully occupied and the states near the Fermi level are mainly the V 3*d* states. The DOS at the Fermi level, N(E_f), for all three compounds, which is often used as a good indicator for the structural stability. For each of these compounds considered here, except for the case of V_2Ta, the lowest energy structure is also found to have the lowest N(E_f) value. The DOS profiles and their N(E_f) values of V_2Zr and V_2Hf structures are very similar, which explains their tiny energy difference and suggests the possibility of the co-existence of both structures. The TDOS at the Fermi level E_f (N(E_f)) for all V_2M compounds is listed in Table 2. On the other hand near the Fermi level, the DOS mainly originates from the M-*d* states (M = V, Zr, Hf and Ta), this suggests that our compounds are all conductive, and the *d* bands of the transition metal play the dominant role in electrical transport.
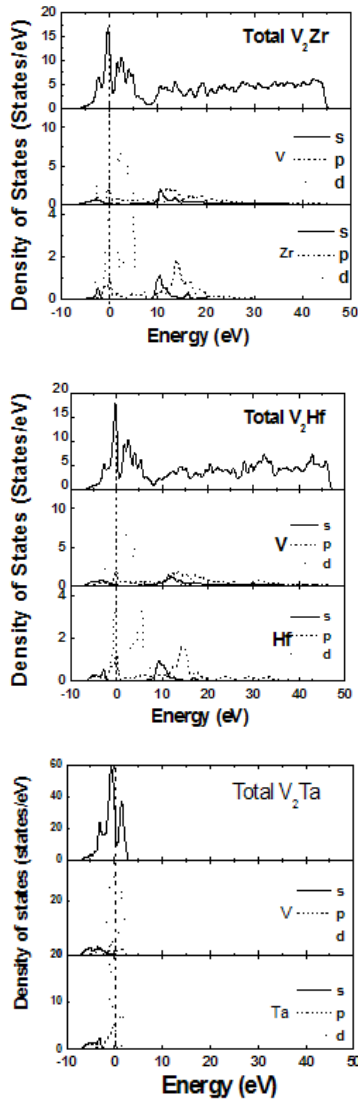
Fig. 6. *Partial state densities for V2M (M = Zr, Hf, Ta) structures.*

Table 2. *Distances between nearest-neighbored atoms and energy Fermi level of V_2M (M = Zr, Hf, Ta) compounds studied in this work.*

	V2Zr	V2Hf	V2Ta
E_f	11.882	13.020	33.115
D_{V-M}	3.053	3.049	2.976
D_{V-V}	2.604	2.602	2.538

4. Bond Orders between Atoms

Bond order is the overlap population of electrons between atoms, and this is a measure of the strength of the covalent bond between atoms. In Table 4., if the overlap population is positive (+) a bonding-type interaction is operating between atom, whereas if it is negative (-) an anti-bonding-type interaction is dominant between atoms. It is apparent that the bonding-type interactions are operating

between the M (M = Zr, Hf, Ta) (4d and 5d) and the V 3d electrons. Thus, there is a strong interaction between V and V, the interaction between M (M = Zr, Hf, Ta) and V is more strong and between M and M is the strongest.

Table 4. *Bond orders in the V2M (M = Zr, Hf, Ta) structures.*

	V₂Zr	V₂Hf	V₂Ta
V-V	0.02	0.04	0.10
V-M	0.06	0.19	0.16
M-M	0.99	1.57	0.54

5. Summary and Conclusion

* V₂Hf do not satisfy the condition $C_{11} - C_{12} > 0$, this compound is mechanically unstable below 6.27 GPa, V₂Hf becomes stable beyond this pressure.

* There is a strong interaction between V and V, the interaction between M (M = Zr, Hf, Ta) and V is more strong and between M and M is the strongest.

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