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Phase Stability and Elasticity of C15 Transition-Metal Intermetallic Compounds

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Abstract

First-principle quantum mechanical calculations based on the local-density-functional theory have been performed to study the electronic, physical and metallurgical properties of C15 intermetallics MV_2 ($M=Zr, Hf, \text{ or } Ta$). The elastic constants of C15 HfV_2+Nb were measured by the resonant ultrasound spectroscopy technique. The phase stability of C15 HfV_2+Nb was studied by specific heat measurements and by transmission electron microscopy in a low temperature specimen holder. The total energies and their lattice volume dependence were used to obtain the equilibrium lattice constants and bulk modulus. The band structures at the X-point near the Fermi level were employed to understand the anomalous temperature dependence of shear modulus of the C15 intermetallics. It was found that the double degeneracy with a linear dispersion relation of electronic levels at the X-point near the Fermi surface is mainly responsible for the C15 anomalous elasticity. The density of states at the Fermi level, $N(E_F)$, and the Fermi surface geometry were obtained to understand the low temperature phase instability of C15 HfV_2 and ZrV_2 and the stability of C15 TaV_2 . It was proposed that the large $N(E_F)$ and Fermi surface nesting are the physical reasons for the structural instability of the C15 HfV_2 and ZrV_2 at low temperatures. The relationship between the anomalous elasticity and structural instability of C15 HfV_2 and ZrV_2 were also discussed.

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Introduction

Intermetallic compounds have been attractive candidates for high temperature structural applications because of their desirable intrinsic properties [1]. There have been many investigations carried out on various compounds, but mostly on structures that are ordered forms of fcc, bcc and hcp metals. If new intermetallics are to be selected on the basis of low density and high melting temperature, then the attraction of two groups of materials becomes apparent: topologically close-packed (TCP) compounds [2] and silicide-based compounds [3].

In the group of TCP intermetallics, the Laves phases constitute the single largest group. Laves phases have either the cubic C15(MgCu₂), hexagonal C14(MgZn₂) or mixed C36(MgNi₂) structure. Generally speaking, they have high melting temperatures and fairly low densities, and therefore could be attractive candidates for high temperature structural materials if their toughness could be increased at low temperatures. Among three Laves phases, C15 Laves phases are expected to show better deformability than the other two Laves phases because of their fcc based structure. For C15 Laves phases, early transition metal compounds, e.g., HfV₂+Nb, have been very interesting and subjected to comprehensive experimental studies [4-5], because they show high melting temperature, high strength and low temperature deformability. Other C15 Laves phase alloys have also been the subject of recent experimental studies, for example, NbCr₂ [6-7], HfCr₂ [8-9], ZrFe₂ [10] and TiCr₂ [11].

In order to improve the mechanical properties of this C15 alloy, it is necessary to understand its fundamental physical properties, e.g., phase equilibria, phases stability, elastic properties, and thermal properties.

Stability of transition metal Laves phases has been subjected to both theoretical and experimental studies [12, 13, 14]. The different roles played by size and electronic factors in stabilizing the transition metal Laves phases and the martensitic transformation associated with the transition metal Laves phases have been investigated particularly. Elastic properties of Laves phases are important because they relate to various fundamental solid-state phenomena such as interatomic potentials, equations of state, and phonon spectra. Elastic properties are also linked thermodynamically with specific heat, thermal expansion, Debye temperature, and Gruneisen parameter. Most importantly, knowledge of elastic constants is essential for many practical applications related to the mechanical properties of Laves phases as well: load-deflection, thermoelastic stress, internal strain (residual stress), sound velocities, dislocation core structure and fracture toughness. This paper summarizes our work on phase stability and elastic properties of C15 intermetallic compounds HfV₂+Nb, including some of our results which have been reported.

Review of Previous Work

For the binary C15 Laves phase compound HfV₂, the phase stability and elastic properties have been studied. In the investigation of phase stability, a low temperature phase transformation, occurring around 110K, in HfV₂ has been reported by a variety of experiments, e.g., neutron diffraction [15], elastic constants measurement [16] and specific heat measurement [17]. For the examination of elastic properties, it has been found that C15 HfV₂ shows anomalous elastic behavior at both low and high temperatures (even up to the melting temperature), i.e., the shear and Young's moduli of C15 HfV₂ increase with increasing temperature [18]. Especially, near the phase transformation temperature, there is a V-shaped softening of the shear and Young's modulus.

To understand the mechanism(s) of the low temperature phase instability and anomalous elasticity and the relationship between the two phenomena for C15 HfV₂, theoretical approach has been performed based on the electronic structure consideration. It has been proved that for any C15 compound there is a double degenerate electronic energy levels with a linear dispersion relation at the X-point in the irreducible Brillouin zone (IBZ), because of the crystal symmetry of C15 (Fd3m) [19]. It was also hypothesized that for the C15 HfV₂, the Fermi level is filled by electrons in such a way that it just passes through the double degenerate point [19]. If this is true, it can be proved that the negative electronic contribution from these two bands to the

trigonal shear modulus, c_{44}^e , is anomalous in the entire temperature region. It was suggested that this is the physical mechanism of the observed anomalous elasticity for C15 HfV₂. Based on this suggestion, the HfV₂ phase instability mechanism was rationalized as the result of the total c_{44} softening, resulting from the cancellation of the negative and anomalous electronic contribution (c_{44}^e) to the positive and normal ionic contribution (c_{44}^i) [19]. Therefore, the C15 structural instability is directly related to the c_{44} anomaly induced by the electronic effect.

The questions remaining in these studies are (1) Is it necessarily true that the Fermi surface of C15 HfV₂ exactly passes through the double degenerate point? (b) If this is not true, how to understand the anomalous elastic properties of C15 HfV₂? and (c) If this is not true, what is the physical mechanism for the low temperature phase instability of C15 HfV₂? Bearing these questions in mind, we studied the phase stability and elastic properties of transition metal C15 Laves phases by a combination of experimental and theoretical approaches, using the C15 HfV₂+Nb as an example.

Experimental Procedure and Calculation Method

Arc-melted buttons were used in the studies of phase stability and elastic properties of C15 HfV₂+Nb. The arc-melted buttons were made using elemental Hf, V, and Nb with nominal purities 99.99%, 99.9% and 99.7%, respectively. For examining the C15 phase stability, five single phase samples, with compositions of V/Hf=2 and Nb at.%=0.0, 0.5, 1.0, 2.0, and 5.0, respectively, were chosen in this study based on the Hf-V-Nb ternary phase diagram [20]. The samples cut from arc-melted buttons were homogenized at 1200°C for 120 h in an argon atmosphere in order to produce a high degree of atomic ordering. The specific heat, C_p , was measured from 15K to 250K to investigate any phase transformation, in steps of 0.3K, using the semi-adiabatic heat pulse method in zero field in a closed cycle refrigeration system. Further examination on the low temperature structural transformation was performed by transmission electron microscopy, using a CM-30 Philip and in a low temperature specimen holder. We also measured the elastic constants of the polycrystalline C15 Hf₂₅V₆₀Nb₁₅ using the resonant ultrasound spectroscopy technique (RUS) [21]. The polycrystalline Hf₂₅V₆₀Nb₁₅ specimen was cut into a rectangular parallelepiped with dimensions $a=2.086$ mm, $b=1.886$ mm, and $c=1.449$ mm. The mass-density of the specimen was determined from its dimensions and mass. To study the temperature dependence of the elastic properties of the ternary C15 compound, the measurements were carried out from room temperature to 70K, using boil-off gas of a liquid helium storage dewar and a temperature controller [22].

In the first-principle calculations, the total energy and the electronic structure of the C15 phases MV₂ (M=Zr, Hf, or Ta) were determined self-consistently using the linear muffin-tin orbital (LMTO) method with the atomic sphere approximation (ASA). The C15 (AB₂) structure, as a TCP structure with the space group Fd3m (O_h^7), has 71% of the volume filled by touching spheres and high site symmetry for the two constituent elements. These facts make the C15 phase suitable for studies with the LMTO method using the atomic sphere approximation (ASA). The basis set included s, p and d orbitals ($l_{\max}=2$) for each site. The self-consistent iterations used 14 points in reciprocal k space along Γ -X direction in the irreducible Brillouin zone (IBZ). The total energy and the electronic band structure were determined at 372 independent k points within the IBZ. The overlapping Wigner-Seitz (WS) spheres used for these LMTO (ASA) calculations were chosen by scaling touching muffin-tin (MT) spheres so that the total volume of all spheres equals that of the unit cell and the ratio rule of the C15 Laves phase, $r_A/r_B=(3/2)^{1/2}$, is satisfied. Consequently, the WS spheres are $0.2426a_0$ for M (M=Zr, Hf and Ta) sites and $0.1981a_0$ for V sites, where a_0 is the experimental lattice parameter. The valence states were treated in a semi-relativistic scheme, and the spin-orbit coupling term was neglected for the early transition metal elements. The core states were treated fully relativistically. The exchange and correlation potential used in the calculations was the von Barth-Hedin local density formalism. The details of the calculation were presented in Ref. [23]. The electronic energy eigenvalues at 372 k points of the IBZ and LMTO parameters obtained from the equilibrium configuration were employed to determine the final band structures, densities of states and the Fermi surfaces of the C15 phases.

C15 Phase Stability

Using the phase diagram of the Hf-V-Nb system [20], the phase stability of the C15 intermetallic compound based on HfV_2 was studied. Sensitive specific heat measurements from the five single phase samples, with the compositions of V/Hf=2 and Nb at. %=0.0, 0.5, 1.0, 2.0, and 5.0, respectively, at low temperatures are shown in Fig. 1. Figure 1 reveals that the binary C15 Laves phase HfV_2 is unstable at low temperatures. A structural phase transformation occurs at about 115K. This is basically consistent with previous work on HfV_2 , e.g., neutron diffraction [15], elastic constants measurement [16] and specific heat measurement [17]. Further transmission electron microscopy study using a liquid nitrogen stage unambiguously shows that this is indeed a structural transformation, because of the appearance of superlattice spots in diffraction patterns as shown in Fig. 2. A detailed analysis of the diffraction patterns of different zone axis is in progress, by which the crystal symmetry of the low temperature phase could be revealed. Most importantly, Fig. 1 reveals in the first time that Nb ternary alloying can reduce the transition temperature and heat absorption in the structural transformation of the C15 Laves phase HfV_2+Nb , and in fact small Nb additions of 2-3 at. % eliminate this structural phase transformation entirely. This means that the role played by the Nb ternary alloying is to stabilize the structure of C15.

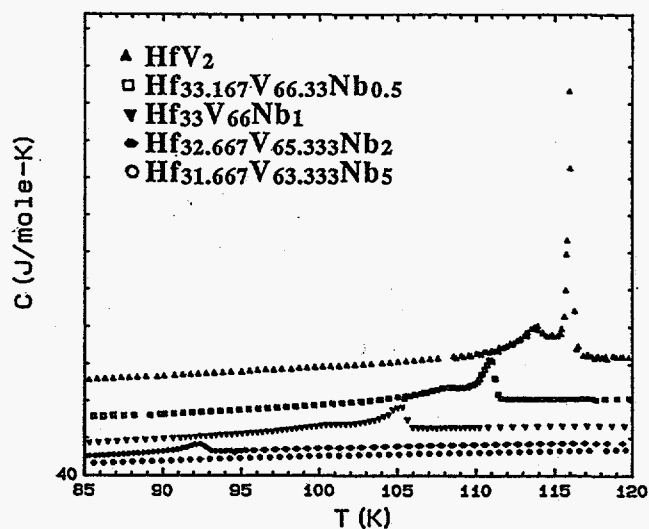


Figure 1. Heat capacity vs. temperature curves for five ternary C15 Laves compounds based on HfV_2 in the vicinity of the lattice transformation temperature.

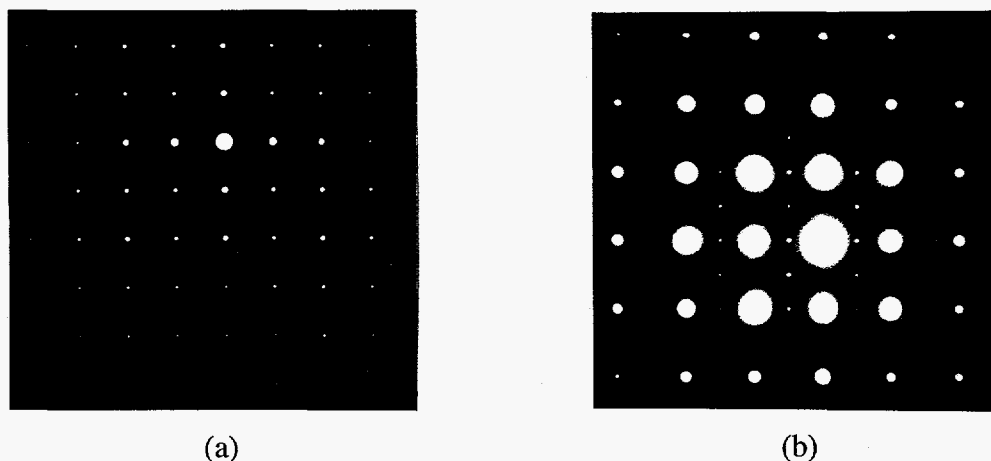


Figure 2. Diffraction patterns of HfV_2 along $\{100\}$ zone axis: (a) at room temperature, and (b) at 83K, showing the superlattice spots after the structural transformation in HfV_2 .

Elastic Properties

The shear modulus, Young's modulus, Bulk modulus and Poisson's ratio of the ternary C15 Hf₂₅V₆₀Nb₁₅ are shown as a function of temperature in Fig. 3. It can be seen from Fig. 3 that the shear and Young's moduli of C15 Hf₂₅V₆₀Nb₁₅ are anomalous, i.e., they increase with increasing temperature. The bulk modulus is virtually constant, and the Poisson's ratio (above 0.4) is higher than observed for most materials and decreases with increasing temperature. These results indicate that an anomaly in elastic properties still exists in ternary C15 compounds, although there is no low temperature structural instability in the ternary compounds. This suggests that the shear modulus anomaly is not directly related to such a phase transformation in C15 transition metal Laves phases.

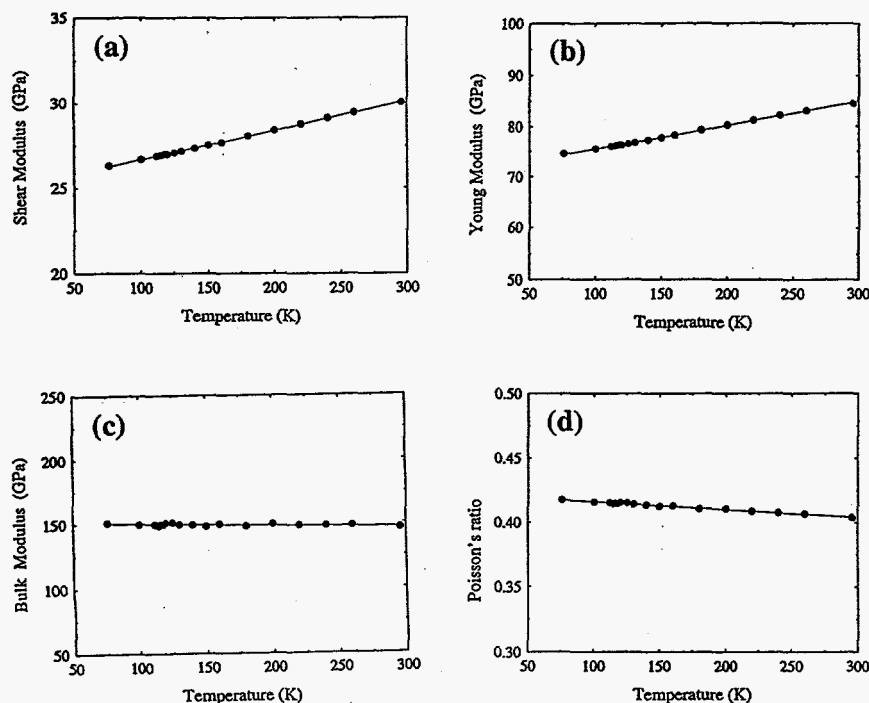


Figure 3. Temperature dependence of elastic constants of C15 Hf₂₅V₆₀Nb₁₅: (a) shear modulus G vs. T , the error is ± 0.02 GPa, (b) Young's modulus E vs. T , the error is ± 0.13 GPa, (c) bulk modulus B vs. T , the error is ± 0.87 GPa, and (d) Poisson's ratio ν vs. T , the error is ± 0.001 (from Ref. [22]).

Total Energy and Electronic Structure of C15 MV₂ (M=Zr, Hf, or Ta)

The total energy vs. volume curves for the C15 Laves compounds, MV₂ (M=Zr, Hf, or Ta) were obtained. Based on these curves, the calculated lattice parameter (a) and bulk modulus (B) corresponding to the energy minimum obtained from these curves are tabulated in Table 1. It can be seen from Table 1 that the theoretical lattice parameter (a) is just 1-2 % off of the experimental value (a_0), which shows good agreement between the theoretical and the experimental results.

TABLE 1 The lattice parameters and bulk moduli of C15 MV₂ (M=Zr, Hf, or Ta).

C15 Phases	a_0 (Å)	a (Å)	B (GPa)
ZrV ₂	7.4440	7.5467	162
HfV ₂	7.4239	7.4740	172
TaV ₂	7.1570	7.2977	218

The energy-band structures of the C15 MV₂ (M=Zr, Hf, or Ta) along the high-symmetry directions in the Brillouin zone were obtained at the equilibrium configurations [23]. There is a large number of flat energy bands at or below the Fermi level, E_F, as is reflected also in the density of states. Figure 4 shows the detailed features of this band structure near the Fermi level and the X-point of the IBZ. There is, indeed, a double degeneracy of electron energy levels with a linear dispersion relationship in the vicinity of the X-point, which is related to the special symmetry Fd3m of the C15 structure [19]. However, we can see from Fig. 4 that the Fermi surface does not pass through the X-point of the IBZ exactly, but passes near the X-point so that there is an energy gap, Δε, between the double degeneracy point and the Fermi level. This is not consistent with the assumption by Izyumov et al. [19]. The Δε values for C15 MV₂ (M=Zr, Hf, or Ta) are listed in Table 2

TABLE 2 The energy gap, Δε, of C15 MV₂ (M=Zr, Hf, or Ta).

C15 Phases	Δε (mRyd)	Δε (K)
ZrV ₂	5.0	781
HfV ₂	4.8	750
TaV ₂	6.0	1000

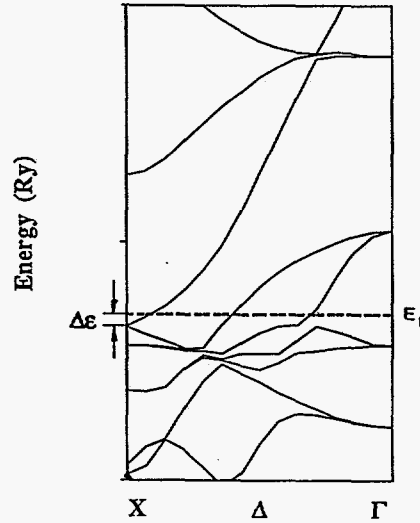


Figure 4. Detailed features of the band structure near the Fermi level for C15 MV₂, (M=Zr, Hf, or Ta), showing the double degeneracy with a linear dispersion relation and energy gap (Δε).

In this case, it can be shown that the electronic contribution to the shear modulus, c_{44}^e , follows the equation [23]:

$$c_{44}^{(e)} \propto - \int_0^{\omega} \frac{d\varepsilon}{\varepsilon} e^{\frac{\Delta\varepsilon}{T}} \left(\frac{e^{\frac{\varepsilon}{2T}}}{e^{-\frac{\varepsilon}{2T}} + e^{\frac{\Delta\varepsilon}{T}} e^{\frac{\varepsilon}{2T}}} - \frac{e^{-\frac{\varepsilon}{2T}}}{e^{\frac{\varepsilon}{2T}} + e^{\frac{\Delta\varepsilon}{T}} e^{-\frac{\varepsilon}{2T}}} \right)$$

Based on this formula, if the Fermi surface passes exactly through the double degenerate point (Δε=0), c_{44}^e obeys the following equation:

$$c_{44}^{(e)} \propto - \int_0^{\omega} \frac{d\varepsilon}{\varepsilon} \tanh \frac{\varepsilon}{2T}$$

The integral on the right hand side of the above equation gives the following temperature dependence of c_{44}^e :

$$c_{44}^{(e)} \propto - \sum_{n=1}^{\infty} B_n \frac{(-1)^{n-1} 2^{2n} (2^{2n} - 1)}{(2n-1)(2n)!} \left(\frac{\omega}{2T} \right)^{2n-1}$$

c_{44}^e is negative and anomalous in the entire temperature region. However, if the Fermi surface passes near the double degenerate point with an energy gap ($\Delta\epsilon$), as C15 MV₂ (M=Zr, Hf, or Ta) has, c_{44}^e is negative but anomalous only at high temperatures, depending on the value of $\Delta\epsilon$, as shown in Fig. 5.

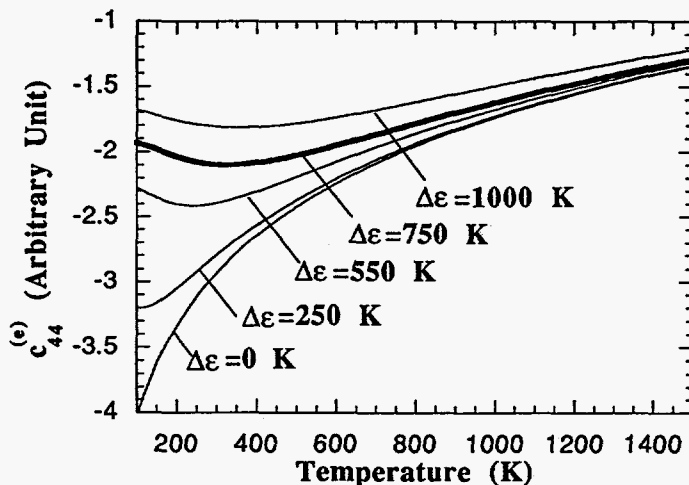


Figure 5. Temperature dependence of c_{44}^e for different $\Delta\epsilon$. The thick line corresponds to the case of C15 HfV₂.

These results suggest that for C15 HfV₂ the electronic contribution to the shear modulus, c_{44}^e , is *negative* and anomalous at high temperatures ($T > 300\text{K}$), i.e. c_{44}^e increases with increasing temperature at high temperatures. This can explain the experimentally observed anomalous behavior of shear modulus for C15 HfV₂ at high temperatures [17]. It is also suggested based on these arguments that the V-shaped low temperature behavior of c_{44} for C15 HfV₂ is not due to the electronic effect because c_{44}^e shows no stiffening in the low temperature region and, therefore, the low temperature phase transformation is not caused by the cancellation of the negative electronic contribution to the shear modulus with the corresponding positive modulus due to ion-ion interaction, c_{44}^i , as suggested by Izyumov et al. [18].

A further detailed analysis for the density of states and the Fermi surface of C15 MV₂ (M=Zr, Hf, or Ta) suggests a new mechanism for the phase instability of C15 HfV₂.

The density of states (DOS) of C15 MV₂ (M=Zr, Hf, or Ta) is shown in Fig. 6. It can be seen that for these systems, the density of states at the Fermi level, $N(E_F)$, is very large, as listed in Table 3. This results in a very strong electron-phonon coupling due to the contribution of a large number of electrons at the Fermi level.

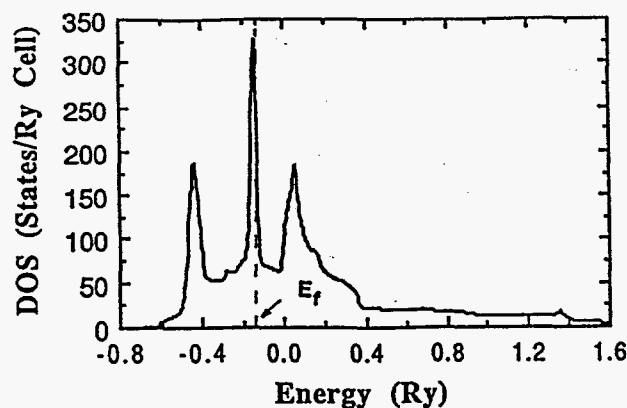


Figure 6. DOS of C15 MV₂ (M=Zr, Hf, or Ta).

TABLE 3 $N(E_F)$ of C15 MV_2 ($M=Zr, Hf, \text{ or } Ta$).

C15 Phases	$N(E_F)$ (States/ Rdy Cell)
ZrV ₂	184.96
HfV ₂	196.84
TaV ₂	176.21

The Fermi surfaces of C15 MV_2 ($M=Zr, Hf, \text{ or } Ta$) are shown in Fig. 8. It can be seen from Fig. 8 that C15 HfV₂ and ZrV₂ have Fermi surface nesting with a $q//\langle 100 \rangle$ while C15 TaV₂ does not. The Fermi surface nesting results in a very large electronic susceptibility, which induces an electronic charge density wave (along $\langle 100 \rangle$ with a wavelength $\lambda \sim 1/q$). This electronic charge density wave may induce a structural modulation through the strong electron-phonon interaction due to the large $N(E_F)$ for C15 HfV₂ and ZrV₂ at low temperatures. We suggest that this could be the mechanism for the structural transformation in C15 HfV₂, as described above, and in C15 ZrV₂ [15-16]. In fact, both the susceptibility increase and the partial phonon softening have been experimentally observed around the phase transformation temperature for HfV₂ [17]. We believe that the low temperature structural instability for C15 transition metal Laves phases is driven by phonon softening ($\omega(\mathbf{q}), \mathbf{q}//\langle 001 \rangle$), resulting from the strong electron-phonon coupling due to the large $N(E_F)$ and Fermi surface nesting.

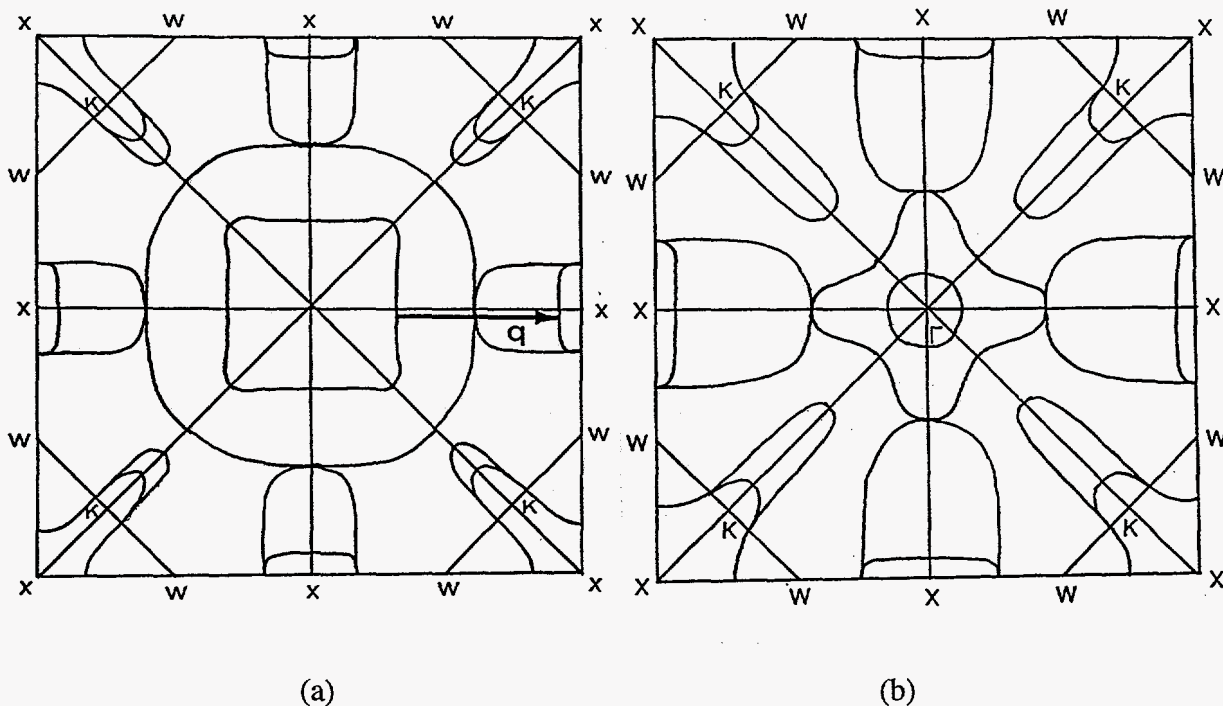


Figure 7. The Fermi surfaces of (a) C15 HfV₂ and ZrV₂, showing the Fermis surface nesting with $q//\langle 100 \rangle$, and (b) C15 TaV₂, showing the disappearance of the Fermi surface nesting.

On the other hand, for C15 TaV₂, because Ta provide one more valence electron than Hf does, the Fermi level increases correspondingly. Based on the rigid-band assumption, this results in two effects: (a) the $N(E_F)$ for C15 TaV₂ is decreased, as shown in Table 3, and (b) the shape of the Fermi surface is dramatically changed, resulting in the disappearance of the Fermi surface nesting, due to the flattened bands near the Fermi level, as mentioned above. Due to the relatively weak electron-phonon coupling and the lack of Fermi surface nesting, the low temperature phase transformation could not occur in C15 TaV₂. In fact, this has been experimentally proved, as shown in Fig. 8. Based on this argument, the stabilization of the C15 structure in HfV₂+Nb by Nb alloying can be understood in the same way: Nb provides one more electrons than Hf does and the substitution of Hf site by Nb increases the Fermi level, resulting in a smaller $N(E_F)$ the disappearance of Fermi surface nesting. Therefore, there is no

such a transformation in C15 HfV_2+Nb induced by phonon softening ($\omega(\mathbf{q})$, $\mathbf{q} // \langle 001 \rangle$), resulting from the strong electron-phonon coupling due to the large $N(E_F)$ and Fermi surface nesting.

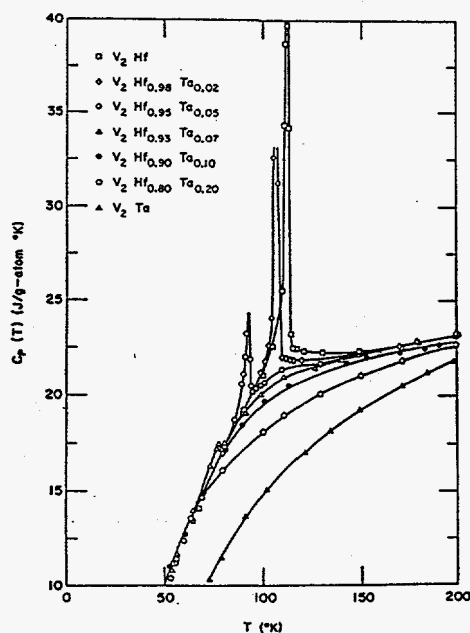


Figure 8. Heat capacity vs. temperature in the vicinity of the lattice transformation temperature for C15 $(\text{Hf}_{1-x}\text{Ta}_x)\text{V}_2$ compounds (from Ref. [16]), showing that there is no low temperature phase transformation in C15 TaV_2 .

It is necessary to point out that the recently-finished more precise total energy and electronic structure calculations, full-potential LMTO calculations, yield the similar results for C15 HfV_2 as mentioned above [24]. Therefore, the atomic sphere approximation in the present calculations may not bring ambiguity in the above arguments for the analysis of the phases stability and elasticity of C15 transition metal Laves phases.

Conclusions

Based on the combined experimental and theoretical study for the phase stability and elasticity of C15 HfV_2+Nb , we conclude:

1. The phase stability of the C15 Laves compounds HfV_2+Nb has been investigated. The binary C15 Laves phase HfV_2 is unstable at low temperatures. A structural phase transformation occurs at about 115K. Nb ternary alloying can reduce the transition temperature and heat absorption in the structural transformation of the C15 Laves phase HfV_2+Nb . A small amount of Nb doping (Nb at.%>2-3) can eliminate this phase transformation. This means that the role played by the Nb ternary alloying in HfV_2 is to stabilize the structure of C15. We suggest that low temperature structural instability of C15 HfV_2 and ZrV_2 is induced by phonon softening, resulting from a large $N(E_F)$ and Fermi surface nesting. The lack of structural instability of C15 TaV_2 and C15 HfV_2+Nb is due to the disappearance of Fermi surface nesting and a smaller $N(E_F)$, because of the increase in valence electrons.
2. Anomalous elastic properties exist in both binary and ternary C15 Laves compounds HfV_2+Nb . For ternary C15 compounds, the shear and Young's moduli increase with increasing temperature, the bulk modulus is virtually constant, and the Poisson's ratio is very high and decreases with increasing temperature. The special electronic structure at the X-point of IBZ near the Fermi level may be one of the reasons for the C15 anomalous temperature dependence of the shear modulus at high temperatures.
3. The low temperature structural instability of C15 HfV_2 and ZrV_2 may not be directly related to the anomalous shear modulus (c_{44}) induced by the electronic effect.

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