

Review

Recent Progress in Phase Stability and Elastic Anomalies of Group VB Transition Metals

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Abstract: Recently discovered phase transition and elastic anomaly of compression-induced softening and heating-induced hardening (CISHIH) in group VB transition metals at high-pressure and high-temperature (HPHT) conditions are unique and interesting among typical metals. This article reviews recent progress in the understanding of the structural and elastic properties of these important metals under HPHT conditions. Previous investigations unveiled the close connection of the remarkable structural stability and elastic anomalies to the Fermi surface nesting (FSN), Jahn–Teller effect, and electronic topological transition (ETT) in vanadium, niobium, and tantalum. We elaborate that two competing scenarios are emerging from these advancements. The first one focuses on phase transition and phase diagram, in which a soft-mode driven structural transformation of BCC→RH1→RH2→BCC under compression and an RH→BCC reverse transition under heating in vanadium were established by experiments and theories. Similar phase transitions in niobium and tantalum were also proposed. The concomitant elastic anomalies were considered to be due to the phase transition. However, we also showed that there exist some experimental and theoretical facts that are incompatible with this scenario. A second scenario is required to accomplish a physically consistent interpretation. In this alternative scenario, the electronic structure and associated elastic anomaly are fundamental, whereas phase transition is just an outcome of the mechanical instability. We note that this second scenario is promising to reconcile all known discrepancies but caution that the phase transition in group VB metals is elusive and is still an open question. A general consensus on the relationship between the possible phase transitions and the mechanical elasticity (especially the resultant CISHIH dual anomaly, which has a much wider impact), is still unreached.

Keywords: phase stability; elastic anomalies; structural transition; group VB transition metals; high pressure and high temperature



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1. Introduction

The group VB transition metals (vanadium, niobium, and tantalum) have extensive applications because of their excellent mechanical and physical properties. Vanadium is well known as a kind of metallic “vitamin”, which is commonly added to iron or steel to increase their toughness, strength, and abrasion resistance. Moreover, vanadium plays an excellent role in titanium alloys, which greatly promotes the development of the aerospace industry. With the progression in science and technology, there are higher requirements for advanced materials, with the application of vanadium becoming more and more extensive, which covers batteries, pharmaceuticals, optics, and many other fields. Niobium and tantalum belong to refractory metals because of their melting point is higher than 2700 K [1]. One can increase a material's strength at high temperature and improve the processing performance by adding niobium or tantalum as alloying elements. On the

other hand, tantalum is also a widely used pressure standard and high technology material due to its strong stability in chemistry and mechanics, as well as the very high melting point (3269 K) [2].

Due to their important applications, group VB transition metals have always attracted much attention. However, most studies in early days mainly focused on their superconducting properties [3–10] because their superconducting transition temperature is quite high at ambient conditions. Theoretical studies show that the superconducting transition temperature of vanadium and niobium depends on the pressure; and the density of electron states at Fermi level has a significant impact on the relationship [11]. In 1997, Struzhkin et al. [10] measured the superconducting T_c of niobium and tantalum up to 100 GPa through a highly sensitive magnetic susceptibility technique. The results showed that T_c in tantalum remains nearly constant at 4.38 K in the range of 0–45 GPa. However, they observed T_c anomalies in niobium around 5–6 GPa and 60–70 GPa, where T_c increases by 0.7 K and decreases by about 1.0 K, respectively. Struzhkin et al. suggested that the anomalies in niobium arise from stress-sensitive ETT. Later, Tse et al. [12] calculated the Fermi surface of niobium by the density functional theory (DFT) method and found that the Fermi surface does undergo a topological transformation under pressure, confirming the results of Struzhkin et al. [10].

Unlike niobium and tantalum, vanadium has a large positive pressure coefficient of T_c . Smith [13] measured the T_c of vanadium under pressure up to 2.4 GPa and found a linear increase in T_c with $dT_c/dP = 0.062$ K/GPa. Subsequently, Brandt et al. [14] also observed a monotonic increase in T_c up to 18 GPa using ice bombs and mechanical presses. After that, Akahama et al. [15] carried out electrical resistance measurements of vanadium up to 49 GPa to investigate the upper bound of the monotonically increased T_c with pressure. They found that T_c increases linearly with a coefficient of $dT_c/dP = 0.096$ K/GPa and reaches a value of 9.6 K at about 18 GPa, the maximum pressure in their experiment. This value of T_c is comparable to that of niobium at ambient pressure. With the development of experimental technology, Ishizuka et al. [16] studied the superconducting properties of vanadium under higher pressure by using a vibrating coil magnetometer. The results showed that T_c increases from 5.3 K to 17.2 K from zero pressure to 120 GPa, and the superconducting transition temperature increases almost linearly.

In order to understand these experimental results, Suzuki et al. [17] further studied the superconducting properties of vanadium under pressure by first-principles calculations. It was found that the T_c of vanadium shows an obvious upward trend with the change of pressure, and the increasing rate of T_c decreases gradually at about 80 GPa, which is qualitatively consistent with the experimental results. Moreover, they interpreted such characteristic behavior of T_c under pressure by attributing it to a significant frequency softening of the transverse mode near the Γ -H line as pressure increased. According to their results, when the pressure is above 130 GPa, the transverse acoustic mode (TA) even has imaginary frequency, indicating that the BCC phase of vanadium becomes dynamically unstable and there is an opportunity of structural phase transformation. However, at that time, the research on vanadium was limited to its superconducting properties and did not pay much attention to its structural instability under high pressure. This softening was subsequently confirmed by calculated elastic constants [18,19], in which C_{44} continuously decreased to negative values, indicating mechanical instability of the BCC structure, but the crystalline structure of the high-pressure phase was not proposed at that time.

Until 2007, Ding et al. [20] performed X-ray diffraction (XRD) experiments on vanadium using diamond anvil cell (DAC) up to 150 GPa. They discovered a novel rhombohedral (RH) phase appearing around 63–69 GPa. This novel high-pressure structural phase transition had not been detected in any of the earlier experiments. After that, the focus of investigation on group VB transition metals has been gradually shifted to study their structural stability and phase transition.

In addition to the structural transformation, the group VB transition elements also exhibit striking anomalous elastic softening under pressure, which is quite different from other transition metals. According to existing literature reports [18,21,22], the pressure-

induced shear elastic softening of vanadium, niobium, and tantalum originates from the electronic structure, which is closely related to the FSN and ETT. Furthermore, the elastic softening in vanadium and niobium were discovered to gradually diminish with increased temperature, effectively giving rise to a heating-induced *hardening* phenomenon, which is very rare (if any) to our knowledge. These elastic anomalies might be taken as due to the phase transition. However, some experimental and theoretical facts that are incompatible with this scenario.

During the past two decades, the structural stability and elastic anomalies of the group VB transition elements have been the subject of numerous theoretical and experimental studies [23–76]. The progress is tremendous; regardless, there are still many controversies on some key issues. In this paper, we review the current understanding of the structural and mechanical anomalies of these important metals under high temperature and high pressure. It is hoped that this paper will significantly promote the understanding of the physical properties for more broad types of metals under extreme conditions.

2. Phase Stability and Elastic Anomalies in V, Nb, Ta

2.1. Pressure Effect on Structure Stability

The first direct evidence of a phase transition in vanadium came from the static compression experiment by Ding et al. [20]. They observed a new type of high-pressure structural transition from BCC to an RH phase at 63–69 GPa, which once was thought of as a second-order transition and was not found in any of the earlier experiments with elements or compounds. In general, the phase transition sequence of transition metals under pressure is hexagonal close packed (HCP)→body centered cubic (BCC)→HCP→face centered cubic (FCC). Based on this sequence, the stability of the BCC phase has long been predicted to be very high [77]. Therefore, the discovery of a phase transition in vanadium below 70 GPa is very remarkable.

Soon after, Lee et al. [36] confirmed this phase transition with DFT calculations and showed that a metastable RH structure is formed at 73 GPa and becomes the ground state at 84 GPa. This low-pressure RH phase is termed as “RH1”, which has an angle of $\alpha = 110.25^\circ$. Furthermore, Lee et al. predicted two other transformations that were not detected in Ding et al.’s experiment: the second transformation to a high-pressure structure “RH2” with an angle $\alpha = 108.14^\circ$ at 120 GPa, and the third transformation back to the high-symmetric BCC structure ($\alpha = 109.47^\circ$) at 280 GPa. As the pressure continues to increase, the BCC phase becomes the only stable structure at 315 GPa. Since the latent heat of BCC→RH transition is much smaller than the thermal fluctuation at room temperature, Lee et al. [36] suggested that this transformation is first-order, which contradicts the second-order transition proposed by Ding et al. [20]. To verify this result, Lee et al. [37] further studied the elastic constants and volume changes associated with two high-pressure RH phase transitions in vanadium. The results shown are that there were small discontinuities in shear modulus and other elastic properties in the phase transitions even at zero temperature, indicating that the phase transitions should be first-order.

The prediction of RH1 and RH2 phases in vanadium was supported by phonon calculations of Luo et al. [35]. They found that the lattice dynamical instability of vanadium starts at 62 GPa and phonon softening leads to a phase transition of BCC→RH1 ($\alpha = 110.5^\circ$). At about 130 GPa, the angle of RH1 phase changes to 108.2° , and the electronic structure changes drastically. At a pressure of 250 GPa, lattice dynamics calculations show that the stability of BCC structure is restored. Luo et al. [35] suggested that the dramatic change in the electronic structures of vanadium under pressure are the driving force behind the structural phase transitions. Later, Verma et al. [38] and Qiu et al. [39] further investigated the structural stability of vanadium under high pressure through first-principles calculations. Both confirmed the existence of the RH1 and RH2 phases, as well as the pressure-induced structural transition sequence of BCC→RH1→RH2→BCC reported by Lee et al. [36]. Meanwhile, detailed electronic structure analysis by Verma et al. showed that the phase transition of BCC→RH1 is caused by the Jahn–Teller mechanism. Although different theoretical studies

have reached a consensus on the phase transition sequence of vanadium under pressure, there is still disagreement on the exact value of the phase transition pressure. For example, Qiu et al. reported a BCC→RH1 transition pressure of 32 GPa, while all other theoretical transition pressures were located between 60 and 84 GPa.

To trace the possible origin of the discrepancy between these calculations, two different methods were exploited by Wang et al. [54] to evaluate the phase transition pressures of vanadium. The first method is to choose RH1 and RH2 as the initial structure, and directly optimize them under different pressures without any symmetry constraints. The calculated enthalpy difference with respect to the BCC phase as a function of pressure is shown in Figure 1 (taken from [54]). It can be seen clearly that the BCC→RH1 transition is not at 30 GPa, where RH1 is dynamically unstable and spontaneously collapses to BCC phase. According to Wang et al. [54], the relaxation of the RH1 phase to the BCC phase is far from being perfect, and the angle is about 109.51° at 20–40 GPa, which reflects a possibility that non-hydrostatic loading can easily drive vanadium towards RH-like deformations. It is worth noting that another RH phase (RH2) transforms to a similar twisted BCC structure with $\alpha = 109.39^\circ$ when below 110 GPa. In addition, when the pressure is about 98 GPa, the RH1 phase becomes the ground state with an angle of $\alpha = 110.17^\circ$. With the further increase of pressure, the RH1 phase transforms into another RH phase (RH2) at about 128 GPa. At the pressure of 211 GPa, RH2 reaches the maximum stability, with $\alpha = 108.23^\circ$. As compression increases, the RH2 phase eventually collapses to the BCC phase at about 300 GPa.

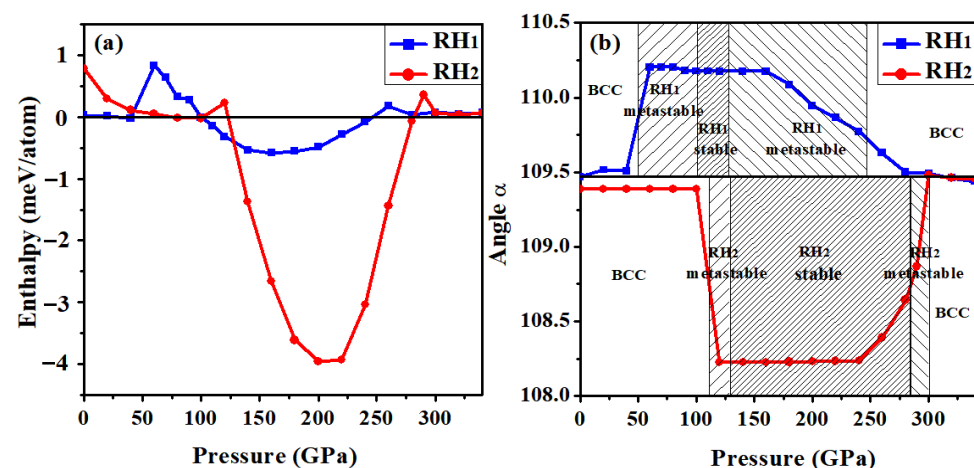


Figure 1. (a) Enthalpy difference of vanadium in RH1 and RH2 structures at zero Kelvin with respect to the BCC phase as a function of pressure. (b) Variation of angle α in RH1 and RH2 structures as a function of pressure at zero Kelvin. Note that $\alpha = 109.47^\circ$ corresponds to the perfect BCC structure. (By the courtesy of Ref. [54]).

In the second method, Wang et al. [54] adopted the same method as Lee et al. [36], that is, twisting the BCC structure along a predetermined path. Note that the unit volume is conserved in this approach. Qiu et al. [39] argued that such a treatment would result in a higher phase transition pressure. According to Lee et al., the error caused by fixed volume can be corrected by the following formula

$$H(\delta, P_0) \approx U(\delta, V_0) + P_0 V_0 - \frac{1}{2B(\delta, V_0)} \Delta P(\delta, V_0)^2 V_0. \quad (1)$$

It is worth noting that only the first term was used in Lee et al.'s calculations [36]. After careful examination, Wang et al. [54] found that the correction of the third term is indeed small, which means that the contribution of volume relaxation can be safely ignored when studying the relative phase stability. This supports the assessment of Lee et al. [36]. In addition, the transition pressures of 'unrelaxed' calculations (method II) by Wang et al. [54]

are in good accordance with the full structural relaxation calculations (method I), therefore, Qiu et al.'s comment on Lee et al.'s results is inappropriate.

Wang et al. [54] further studied the influence of changing the position of Fermi level on the structural stability of vanadium by using a partial jellium model, see Figure 2 (taken from [54]). Here, the Fermi level is shifted by charge transfer (chemical doping) changing the orbital occupations. Since the RH2 phase reaches the maximal stability at 211 GPa, it should have the optimum orbital occupation. Thus, raising (adding electrons) or lowering (removing electrons/adding holes) the Fermi level pushes the system away from the optimum occupation, so the stability of RH2 phase will be weakened in both cases. However, Wang et al.'s calculations showed that moving the Fermi level down further stabilized the RH2 phase, while moving the Fermi level up greatly destabilized the RH2 phase. This is consistent with Landa et al.'s band-filling argument when alloying vanadium with the same transition series [41]; however, it is incompatible with Jahn–Teller mechanism.

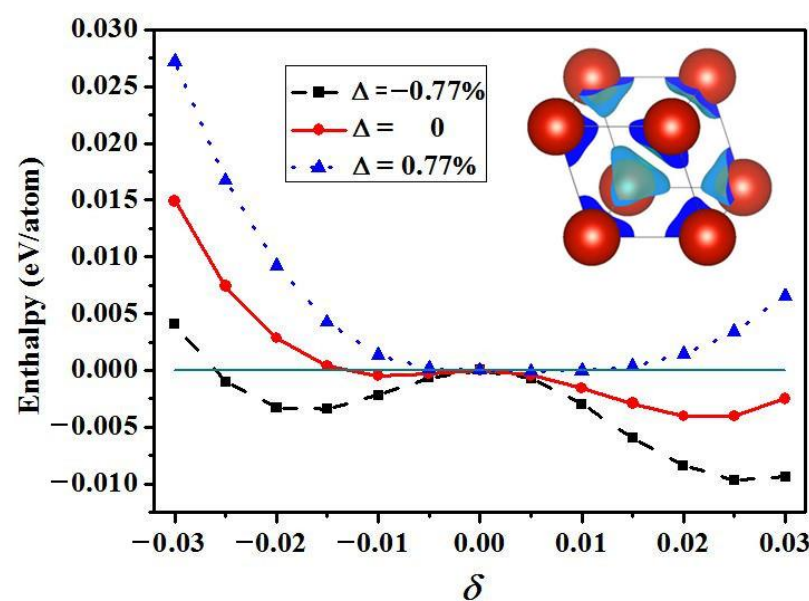


Figure 2. Calculated enthalpy difference with respect to BCC phase as a function of the RH deformation parameter δ when the Fermi level is shifted up or down at a pressure of 211 GPa. Inset: Calculated differential charge density between $\Delta = -0.77\%$ and $\Delta = 0$. (By the courtesy of Ref. [54]).

According to the calculation of Wang et al. [54], RH2 phase reaches the maximal stability at 211 GPa when $\Delta = -2.15\%$ (Δ represents the percentage of total charge added to /removed from the system). Further shifting down the Fermi level reduces the stability of RH phase. When $\Delta < -4.85\%$, BCC becomes stable again. In the inset of Figure 2, Wang et al. plotted the differential charge density between $\Delta = -0.77\%$ and $\Delta = 0$. As shown, the removed electrons/added holes are distributed around the nucleus and mainly exhibit d orbital characteristics. Since the d orbitals' delocalization results in lower electronegativity of the RH2 phase relative to the BCC phase, the localization (or delocalization) of d electrons has an important effect on the stability of the RH phase.

In addition, Wang et al. [54] found that even if the absolute convergence is achieved, the DFT method still has the problem of insufficient accuracy when exploring the phase transition of vanadium. Consider that the semi-local functional PBE may not be able to handle strong electron correlations in narrow-band systems, so they thought that the quality of the exchange-correlation (XC) functional may be an important factor affecting the results. For this reason, an evaluation of the advanced hybrid functionals in vanadium and niobium was further carried out by Wang et al. [66]. The results show that the common HSE06, PBE0, and B3LYP hybrid functionals are complete failures in describing the mechanical properties of these metals. The unexpected failure is due to the very rare localization error in these functionals, which is further supported by a similar failure of the DFT + U method.

To solve this problem, Wang et al. [66] proposed a DFT + J method to promote on-site electron exchange, which well reproduces the experimental shear modulus under ambient conditions. However, Wang et al. found that the PBE + J increases the BCC→RH transition pressure, and the correction of localization error weakens (or even eliminates) the RH phases. They concluded that RH phase could be unstable under more accurate calculation methods, which is a striking prediction and challenges the previously reported structural transition in vanadium.

Following this prediction, an independent XRD experiment was performed by Akahama et al. [73] to study the structural stability of vanadium. The results showed that BCC vanadium is stable up to 189 GPa at room temperature, while the RH phase ($\alpha > 109.47^\circ$) reported in previous studies should be a metastable phase induced by non-hydrostatic pressure. This supports the prediction of Wang et al. [66] that RH phase may be unstable in vanadium. Furthermore, they observed a new high-pressure phase after annealing at 242 GPa, which was also confirmed from a different experiment at room temperature. Akahama et al. interpreted the phase as RH phase with $\alpha < 109.47^\circ$. However, the pressure range does not agree with the previous theoretical [35–37,54] and experimental results [21,47,51,55].

At the same time, Stevenson et al. [74] re-performed the XRD experiment at pressures up to 154 GPa using polycrystalline (powder) and single crystal samples with various pressure transfer media (PTM). It was found that only the single-crystal samples reveal two RH phases, and the distortions from cubic symmetry are much smaller than previous results. That is to say, the observed RH phase is far from being perfect, and should be interpreted as a kind of lattice distortion rather than a phase transition. Moreover, Wang et al. [72] measured the sound velocity of vanadium through shock wave experiment recently. They found that when the pressure was above 79 GPa, the sound velocity of the shocked vanadium was closer to the RH phase rather than the BCC phase. The unexpected high-pressure phases along the Hugoniot can be seen as slight distortions of the BCC structure, which may be caused by the dynamic, nonequilibrium, and nonhydrostatic nature of planar shock waves. The above two experimental signatures are compatible with the experimental results of Akahama et al. [73] and further confirm the theoretical assessment of Wang et al. made in Ref. [66].

In other experimental research, Jenei et al. [47] performed DAC experimental studies and found that the BCC structure transformed to RH1 phase at about 30 GPa in non-pressure medium, while it was around 60 GPa when Ne pressure medium was used. In addition, the transition can occur at a much lower pressure if under nonhydrostatic conditions. Nonetheless, in Ding et al.'s experiments [20], the transition pressure of BCC→RH in non-pressure medium and He pressure medium was 69 GPa and 63 GPa, respectively. Thus, the deviation in transition pressure of BCC→RH might not be due to the non-hydrostatic condition. In addition, Antonangeli et al. [55] used inelastic X-ray scattering to detect the phonon dispersion of single crystal vanadium under pressure up to 45 GPa. Their results showed that the transverse acoustic mode has abnormally high-pressure behavior along (100) direction, and the softening of C_{44} causes the RH distortion around 34–39 GPa. It is obvious that the transition pressure is consistent with the diffraction results of 30 GPa in non-hydrostatic conditions by Jenei et al. [47]. It should be noticed that Antonangeli et al. [55] performed the measurements on relatively large single crystals, which are more susceptible to non-hydrostatic stress than powders. Moreover, according to the experimental study of Stevenson et al. [74], an RH high-pressure phase was indeed observed when using single crystal samples; but the high-pressure diffraction profiles from the polycrystalline samples is not suitable for RH lattice, regardless of the PTM used. Why there is such a big difference between the experimental data of powder and single crystal is still an open question that needs further study.

On the other hand, Yu et al. [51] recently measured the sound velocities and yield strength of vanadium through reverse impact experiments. They found an indication of the shock induced BCC→RH transition at about 60.5 GPa by the discontinuity of longitudinal sound velocity against shock pressure, which disagrees with the results of Jenei et al. [47]

and Antonangeli et al. [55] but remains consistent with both DAC measurements by Ding et al. [20]. The aforementioned experiment studies cautioned that the phase transition in group VB metals is elusive, which remains an open question and no general consensus on this issue has been achieved.

2.2. Temperature Effect on Structure Stability

In 2014, Landa et al. [78] explored the phase stability of vanadium at high temperatures and pressures by using the self-consistent ab initio lattice dynamics (SCAILD) approach combined with DFT. In this study, the phonon-phonon interactions at elevated temperatures were considered. In Figure 3 (taken from [78]), Landa et al. showed the calculated phonon frequencies for vanadium under different temperatures at 182 GPa. The maximum stability of RH phase was measured by analyzing the variation in phonon dispersion of BCC phase. Their results showed that temperature promoting the phonon frequencies from being imaginary to being real along the $\Gamma \rightarrow H$ and $\Gamma \rightarrow N$ lines. When the temperature is above 8000 K, BCC phase becomes stable again. Since this temperature is significantly higher than the shock melting temperature of 6800 ± 800 K at 182 GPa [79], Landa et al. [78] concluded that the BCC phase is actually never stable at this density. Namely, high-pressure RH phases of compressed vanadium should have a very broad pressure-temperature stability region.

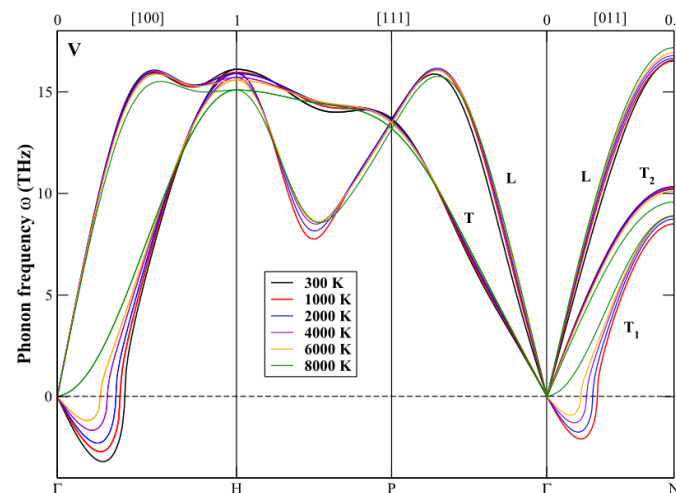


Figure 3. Calculated phonon dispersions for vanadium under different temperatures at a pressure of 182 GPa. (By the courtesy of Ref. [78]).

Nonetheless, lattice dynamics stability is not the unequivocal criterion for the thermodynamic stability of a phase. For the latter purpose, one should resort to free energy difference. To this end, based on Landa et al.'s initial results [78], Wang et al. further investigated the effect of thermo-electrons on the structure stability of vanadium by calculating the free energy using finite temperature DFT method [54]. Since the phase transitions of vanadium are closely related to the changes in the electronic structure, Wang et al. estimated that the contribution of thermo-electrons may be greater than that of lattice dynamics. As shown in Figure 4 (taken from [54]), the electronic temperature significantly reduces the stability of RH phases, and RH1 and RH2 transform back to BCC at around 1440 K (at 140 GPa) and 1915 K (at 211 GPa), respectively. Compared with the results of Landa et al. [78], this new transition temperature is much lower. It clearly demonstrated that compressed vanadium should transition back to BCC structure in the solid state; and the transition temperature is much lower than the melting temperature. Wang et al. analyzed the impact of lattice dynamics by including both thermo-electronic and phonon corrections in their assessment. It revealed that phonon correction will further reduce the transition temperature by about 260 K at 200 GPa [54], comparable to the usual expectation. Further study by Wang et al. indicated that this heating-induced reentrant transition in vanadium was mainly driven by electronic entropy.

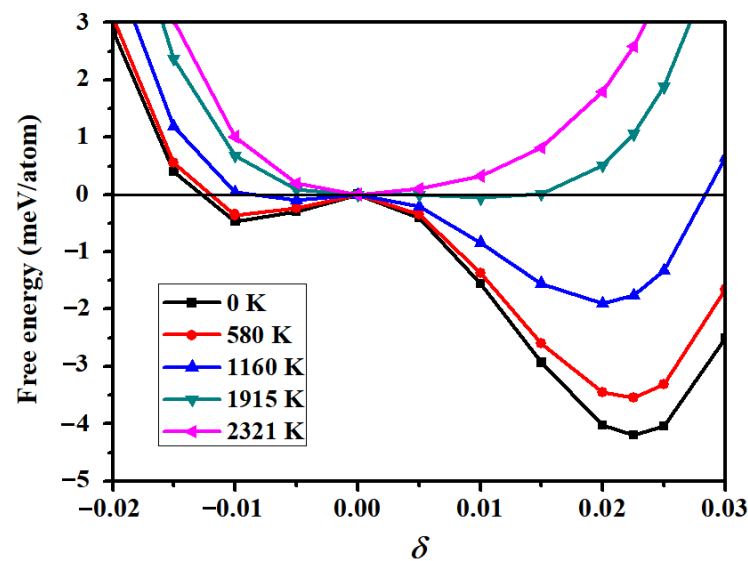


Figure 4. Effect of thermo-electrons on the phase stability of vanadium at 211 GPa. (By the courtesy of Ref. [54]).

Based on these new theoretical data, Wang et al. [54] constructed a comprehensive phase diagram for vanadium under high pressure and temperature for the first time. According to their diagram (see Figure 5 taken from [54]), RH1 phase stabilizes at 100–126 GPa with a maximum transition temperature of 1440 K at 140 GPa, while RH2 phase stabilizes at 126–280 GPa with a maximum transition temperature of 1915 K at 211 GPa. In addition, the stability of RH1 and RH2 phases decreases with increasing temperature, and both transform back to BCC before melting. This picture completely changes our understanding about vanadium which insisted that RH phases could stand up to the melting temperature [79,80]. Meanwhile, Wang et al. identified a triple point at about 1440 K and 140 GPa [54], where there may be spectacular physical properties due to the structural frustration.

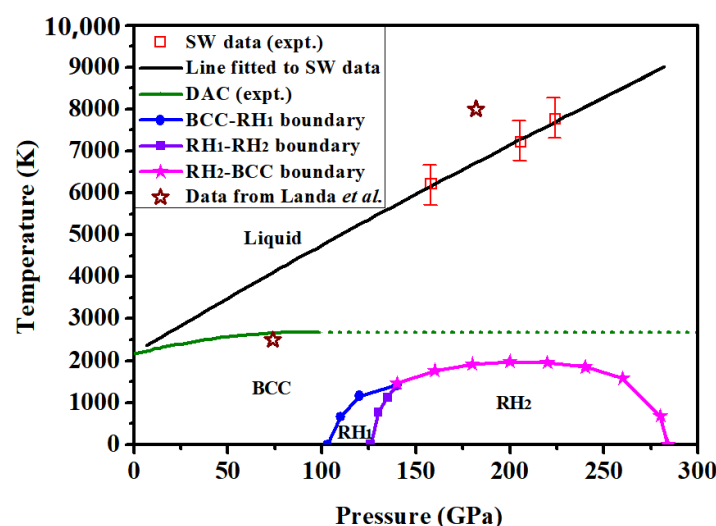


Figure 5. High-pressure and high-temperature phase diagram of vanadium. (By the courtesy of Ref. [54]).

Following Wang et al.'s prediction, Errandonea et al. [62] performed powder XRD experiments on vanadium up to 120 GPa and 4000 K. Under compression, the BCC vanadium was observed up to 53 GPa at room temperature. At higher pressure of 64 GPa, the measured XRD spectra at room temperature belonged to the RH structure of the $R\bar{3}m$ space group. This observation supports the previous report by Ding et al. [20]. According

to Errandonea et al. [62], the RH phase could be observed at temperatures up to 1560 K at 64 GPa and up to 1700 K at 120 GPa. Under the higher temperature of 1840 K at 64 GPa, the existence of BCC phase can be seen through the measured XRD pattern. This result is in accordance with the prediction of Wang et al. [54] but is less than one quarter of the initial estimate of Landa et al. [78]. Moreover, Errandonea et al. [62] interpreted their observations as the RH lattice distortion in vanadium that is triggered by phonon anomalies at high pressure and can be eliminated by phonon-phonon scattering effects at high temperatures.

According to the experimental results, Errandonea et al. further presented a phase diagram for vanadium under HPHT, as shown in Figure 6 (taken from [62]). The phase boundary of BCC→RH (dashed blue line) is tentatively drawn, which is qualitatively similar to the phase boundary given by Wang et al. [54] and consistent with other available results [19–21,47,78,81]. In addition, Wang et al. [54] also predicted the reentrance of the BCC phase at room temperature around 280 GPa, but this exceeded the pressure limit in Errandonea et al.'s experiments. This ultra-high pressure prediction still requires experimental verification.

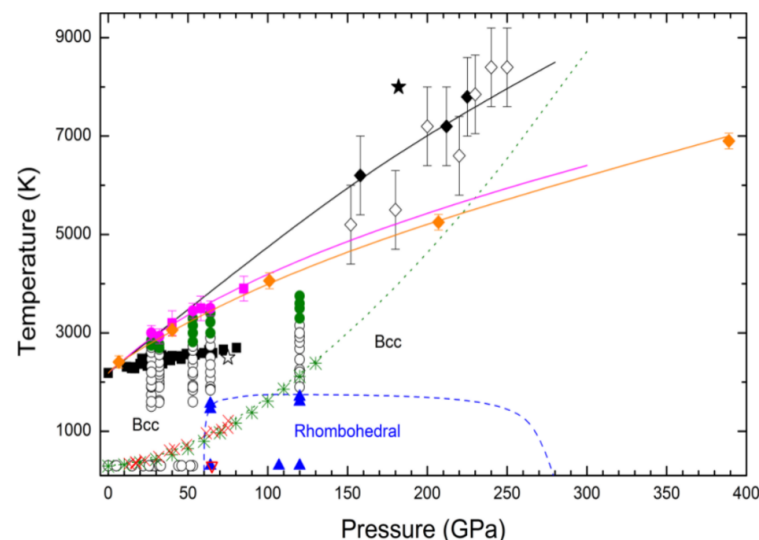


Figure 6. Pressure–temperature phase diagram of vanadium. (By the courtesy of Ref. [62]).

Most recently, Zhang et al. [69] also determined the phase stability of vanadium at 0–4400 K and 20–100 GPa by using synchrotron XRD independently. The results showed that BCC vanadium stabilized below 44 GPa at room temperature. With increasing the pressure above 52 GPa, a BCC→RH phase transition occurs, which is consistent with the observations of Errandonea et al. using NaCl as the pressure medium at 53 GPa [62]. Moreover, Zhang et al.'s experimental results showed that the RH vanadium stabilized between 50 and 100 GPa at room temperature [69]. At the pressure of 52 GPa, the RH phase transformed back to BCC when increasing the temperature to 1881 K. This supports the prediction by Wang et al. [54] that electronic temperatures will reduce the stability of RH phase in vanadium, as well as the experiment of Errandonea et al. [62].

In contrast to vanadium, only few studies [65,82] on the structure stability of niobium and tantalum have been carried out in the literature. In 2018, Haskins et al. [82] examined possible HPHT polymorphism in tantalum with complementary DFT-based model generalized pseudopotential theory (MGPT) multi-ion interatomic potentials. Their results showed that four orthorhombic structures of Pnma, Fddd, Pmma, and α -U are similarly energetically favorable. Moreover, the MGPT-MD simulations of them further revealed possible spontaneous heating-induced Pnma→BCC and Fddd→BCC transitions at modest temperatures. Nevertheless, neither unequivocal experimental (DAC or shock wave) nor direct DFT calculation evidence exists for these proposed phase transitions in tantalum by far.

As for niobium, Errandonea et al. [65] recently reported a result of static laser-heated DAC experiments up to 120 GPa, as well as *ab initio* quantum molecular dynamics simulations. They found that niobium undergoes a BCC→Pnma phase transition at high temperatures, which can be seen from their experimental XRD data. Errandonea et al.'s finding could provide evidence for the topological similarity of the phase diagrams of niobium and tantalum. All of them may undergo orthogonal phase transitions, and the HPHT phase is Pnma. However, this phase transition in niobium is the only report available so far; and no other relevant studies have been reported. Errandonea et al.'s experiments and theoretical calculations seem to be self-consistent, suggesting that such a type of phase transition may exist. However, more accurate experimental and theoretical studies are still needed for final confirmation.

2.3. Elastic Anomalies in V, Nb, Ta

In addition to the investigations on structural stability, the anomaly in the elastic constants of the group VB transition elements also attracts a lot of attention. Early theoretical and experimental studies [17,21] have shown that the transverse acoustic phonon mode of vanadium and niobium all exhibit softening. Since the shear elastic constant C_{44} is directly related to the transverse acoustic mode in the limit of short q -vector lengths, anomalous softening in this phonon mode implies that vanadium and niobium should have extraordinary elastic moduli. Landa et al. [18,19] confirmed this anomaly in the elastic constants of vanadium and niobium through first-principles calculations. The results show that vanadium is mechanical instability in C_{44} at pressures between 120 and 245 GPa. The results also show a softening in niobium at around 50 GPa. Their further study suggested that the pressure-induced shear instability (softening) in vanadium (niobium) is mainly due to the electronic structure with FSN.

Later, Koči et al. [22] confirmed the mechanical instability of C_{44} in vanadium through first-principles calculations. Meanwhile, they found that the elastic constants of group VB elements (V, Nb, Ta) exhibit anomalous behaviors, while those of group VIB elements (Mo, W) increase monotonically with pressure. According to Koči et al. [22], the calculated C_{44} of both vanadium and niobium is significantly underestimated by comparing to experimental data, while C_{11} and C_{12} are consistent with the experimental results. They further analyzed these metals by Fermi surface calculations and found that the nesting vectors of vanadium, niobium, and tantalum contracted with increasing pressure. This phenomenon, however, was not observed in molybdenum and tungsten. To explore the reason why C_{44} was underestimated in theoretical calculation, Liu et al. [48] further calculated the Fermi surface of these metals. The results suggested that the underestimation of C_{44} is mainly caused by the FSN.

To verify the theoretically predicted shear modulus anomalies, Jing et al. conducted XRD experiments on niobium powders under pressures up to 61 GPa at room temperature using DAC technique [60]. They observed an obvious softening in the yield strength of niobium between 42 and 47 GPa, which unexpectedly follows the trend of abnormal softening in the shear modulus predicted by recent theoretical studies [56]. Therefore, Jing et al. predicted that there should be a close relationship between the abnormal strength softening of niobium and the abnormal shear modulus softening [60]; however, this needs to be confirmed by further experimental evidence.

Furthermore, Li et al. [75] experimentally investigated the sound velocities of niobium up to 69 GPa and 1100 K under shock compression. It was found that both the compressional and shear sound velocities soften significantly between 50 and 60 GPa. Li et al. [75] suggested this anomalous behavior might be due to a pressure-induced ETT at 50–60 GPa. However, their data deviate significantly from all theoretical calculations [18,19,22,48]. Especially, by extrapolating their sound velocity to an impact pressure above 100 GPa, the longitudinal sound velocity of niobium would be much higher than that of vanadium; that is unphysical. In this regard, it is still an open question, and more experimental data with much higher precision are needed to pin down the predicted elastic anomalous softening in niobium.

It should also be mentioned that a similar softening in C_{44} was predicted by calculations for tantalum [83,84]. According to Gülseren et al. [84], the C_{44} of tantalum shows softening at pressures of 100–200 GPa. They also found that the C_{44} softens with temperature at low pressures, but then it becomes rather flat at higher pressures. Soon after, Landa et al. [41] further predicted a similar softening of C_{44} in tantalum between 50 and 80 GPa through first-principles calculations. Later, Antonangeli et al. [43] studied the elasticity of tantalum under pressures over 100 GPa. Their experiments showed that the shear velocity softened between 90 and 100 GPa, and with a pressure dependence above 120 GPa. They suggested that this abnormal behavior may be due to the intraband FSN that causes an ETT and a concomitant transverse acoustic phonon mode softening, which is consistent with the other theoretical predictions [22,48].

Jing et al. thought that there was a potential physical relationship between yield strength and shear modulus, so they further measured the yield strength of tantalum up to 101 GPa at room temperature by XRD-DAC experiment [53]. They detected a yield strength softening at 52–84 GPa, which is in accordance with one of the previous calculations [41] that suggested a significant softening in the shear modulus of tantalum between 50 and 80 GPa, but not others [43,84]. In addition, their measurements showed that the softening trend of the yield stress is roughly the same as that of the shear modulus given by the first-principles calculations [41]. To verify this result, Zhang et al. [85] re-studied the elastic properties of tantalum at high pressures through first-principles calculations. Their calculations showed elastic softening for both the C_{11} and C_{44} at pressures above 100 GPa, rather than at 50 GPa. The softening in C_{44} overall agrees with previous powder tantalum IXS data by Antonangeli et al. [43], but is different from Jing et al.'s results of 52–84 GPa [53].

In order to have a comprehensive understanding about the elastic anomalies of compression-induced softening, Wang et al. [54,56] revisited the elastic properties of the group VB transition metals, by noticing that DFT already correctly predicted many metals that also having Fermi surface nesting or Van Hove singularities. They first calculated the C_{44} and C' of BCC vanadium under different pressures [54], as shown in Figure 7 (taken from [54]). The obtained C_{44} is negative between 125 and 260 GPa, which is in agreement with that of Landa et al.'s full-potential linear muffin-tin orbitals (FP-LMTO) [18]. However, the calculated C_{44} from first-principles by Qiu et al. [39] shows that the first mechanical instability pressure for vanadium occurs at about 60 GPa, which is markedly different from the results of Landa et al. [18,19]. Qiu et al. suggested that this difference is mainly due to the fact that Landa et al.'s work ignored the pressure correction. However, Wang et al. [54] explicitly included the same pressure correction as Qiu et al. [39] when calculating the elastic modulus C_{44} . The obtained results perfectly match with that of Landa et al. [19], demonstrating that the pressure correction is not the reason for the difference between them. By using DFT, Wang et al. [56] further studied the elastic properties of niobium under pressure through first-principles calculations. The results demonstrated that the C_{44} and C' of niobium soften significantly in the range of 20–150 GPa. In addition, a new softening range for C_{44} at 275–400 GPa was also discovered. They suggested that the first anomaly was directly related to the underlying RH distortion, whereas the latter originated in an ETT.

In addition, the shear modulus C_{44} calculated by Wang et al. [66] through GGA (in PBE) is underestimated by about -40% (-30%) for vanadium (niobium) compared with the experimental results [86–89], which is consistent with the evaluation of Liu et al. [48] and Koči et al. [22]. Since the semi-local functional (such as PBE) may not be able to handle strong electron correlations in narrow-band systems, Wang et al. [66] further thoroughly evaluated the accuracy of different XC functionals in describing the C_{44} of vanadium and niobium. The results unexpectedly showed that C_{44} calculated by the common hybrid functionals (PBE0, HSE06, and B3LYP) are negative value at 0 GPa, which means that these functionals incorrectly predict the mechanical stability of these metals. Through systematic analysis, Wang et al. suggested that this unexpected failure is mainly caused by the localization error of these functionals.

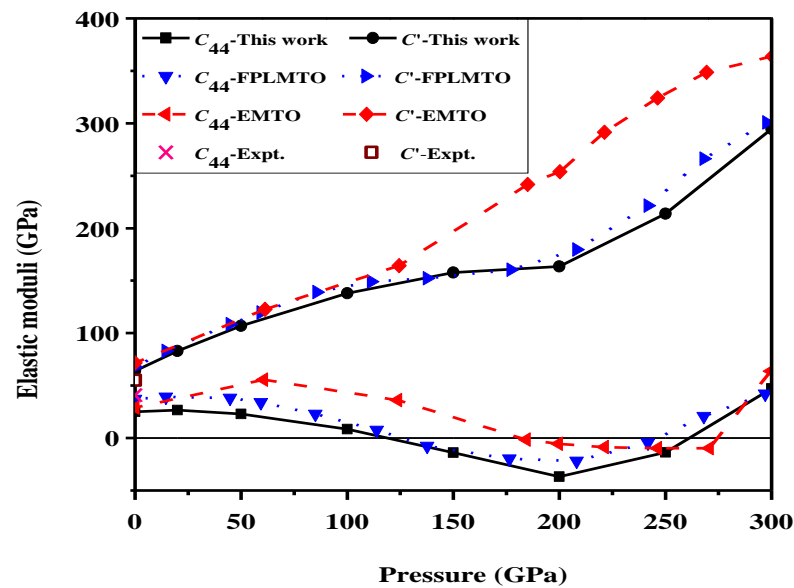


Figure 7. Calculated elastic moduli of BCC vanadium as a function of pressure. (By the courtesy of Ref. [54]).

Subsequently, Wang et al. [66] tentatively proposed a DFT + J method to correct the localization error, which corrected the C_{44} from 25.5 to 37.34 GPa for vanadium, and from 19.77 to 22.07 GPa for niobium at 0 GPa, respectively. To explore the influence of this correction on the high-pressure properties, Wang et al. further used the PBE + J method to study the elastic properties of vanadium under pressure, as shown in Figure 8 (taken from [66]). Obviously, the C_{11} and C_{12} calculated by different methods are consistent with each other, but the C_{44} calculated by different methods as a function of pressure is quite different. Among them, the PBE + J method has the largest correction, especially in the softening pressure range, which means that the correction of localization error could slightly weaken the elastic anomaly of compression-induced softening in group VB transition metals.

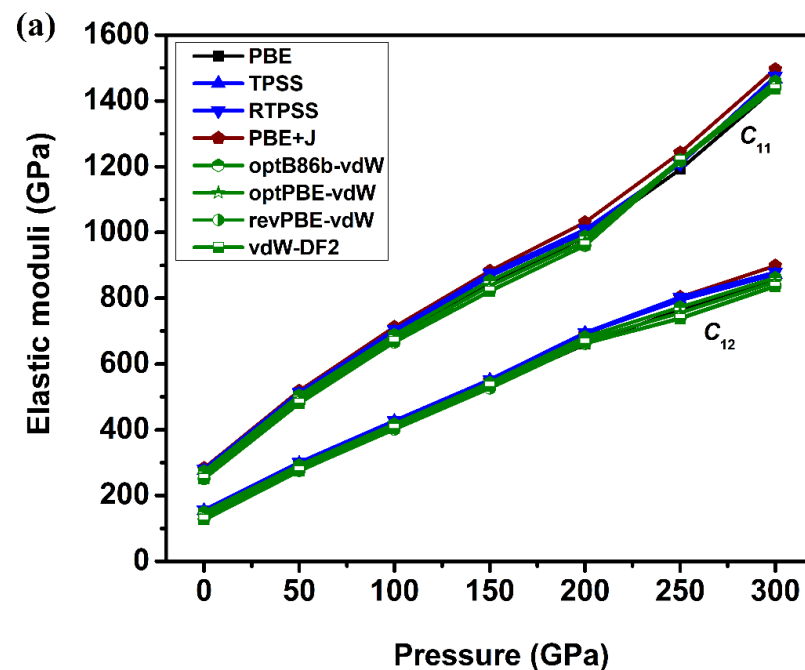


Figure 8. Cont.

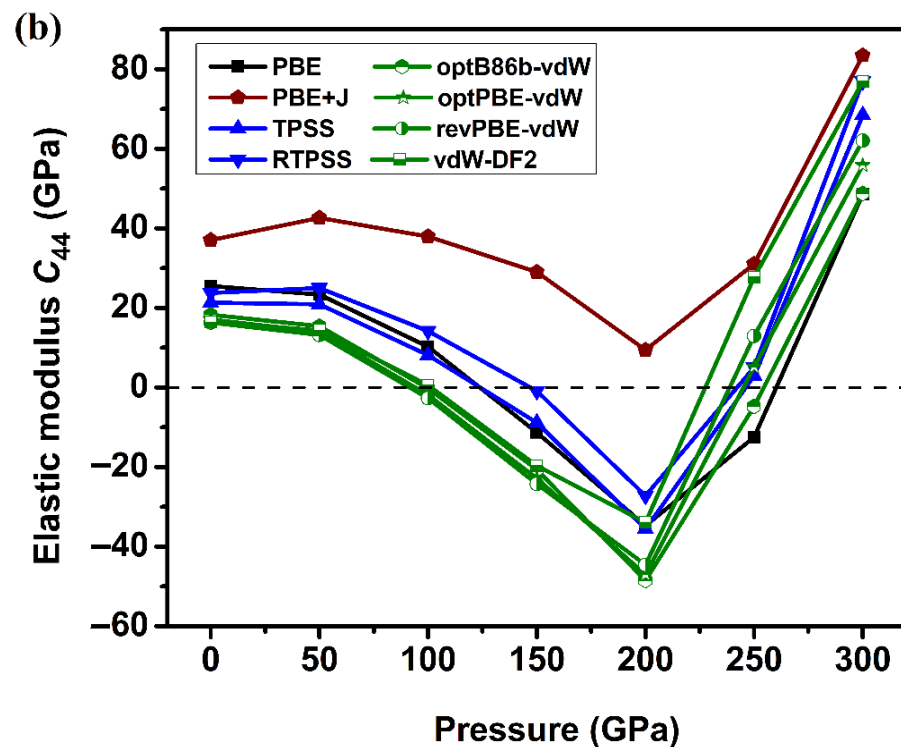


Figure 8. Calculated elastic moduli of BCC vanadium as a function of pressure by using different XC functionals and the PBE + J method (with $J = 2$ eV): (a) C_{11} and C_{12} , and (b) C_{44} . (By the courtesy of Ref. [66]).

Although vanadium, niobium, and tantalum have nearly identical valence electronic configuration, their compression-induced softening ranges of C_{44} are not the same. To explore the potential connection between them, Wang et al. [56] carefully calculated and compared the band structures of these metals under pressure of 0–400 GPa (see Figure 9 taken from [56]). They discovered two electronic topological transitions in the $\Gamma \rightarrow H$ direction for vanadium, niobium, and tantalum. The first ETT occurs around 300, 110, and 280 GPa in vanadium, niobium, and tantalum, respectively. The second ETT occurs at 300 GPa in niobium and at about 600 GPa in both vanadium and tantalum. According to Wang et al. [56], the second pressure-induced ETT should be the cause of the abnormal softening of C_{44} in niobium at 275–400 GPa, thus they predicted that vanadium and tantalum should have the same elastic modulus C_{44} softening at about 600 GPa. This is a quite interesting prediction that needs to be further confirmed by more precise experimental and theoretical studies.

In addition to the elastic anomaly of compression-induced softening, the heating-induced *hardening* in group VB metals was further predicted by Wang et al. [54]. They evaluated the effect of electronic temperature on the C_{44} of BCC vanadium and found that C_{44} increases with the temperature (see Figure 10 taken from [54]). This means that there is a heating-induced *hardening* in this metal, which is against our empirical intuition. In addition, as shown in the inset of Figure 10, at selected pressures of 50 GPa and 300 GPa, when the temperature increases from 0 to 3000 K, C_{44} increases by about 75% and 53%, respectively. At higher temperatures, however, the thermal motion of the nucleus will inevitably soften the metal. Therefore, as the temperature increases, the strength and shear modulus of vanadium will rise to a maximum and then drop to zero.

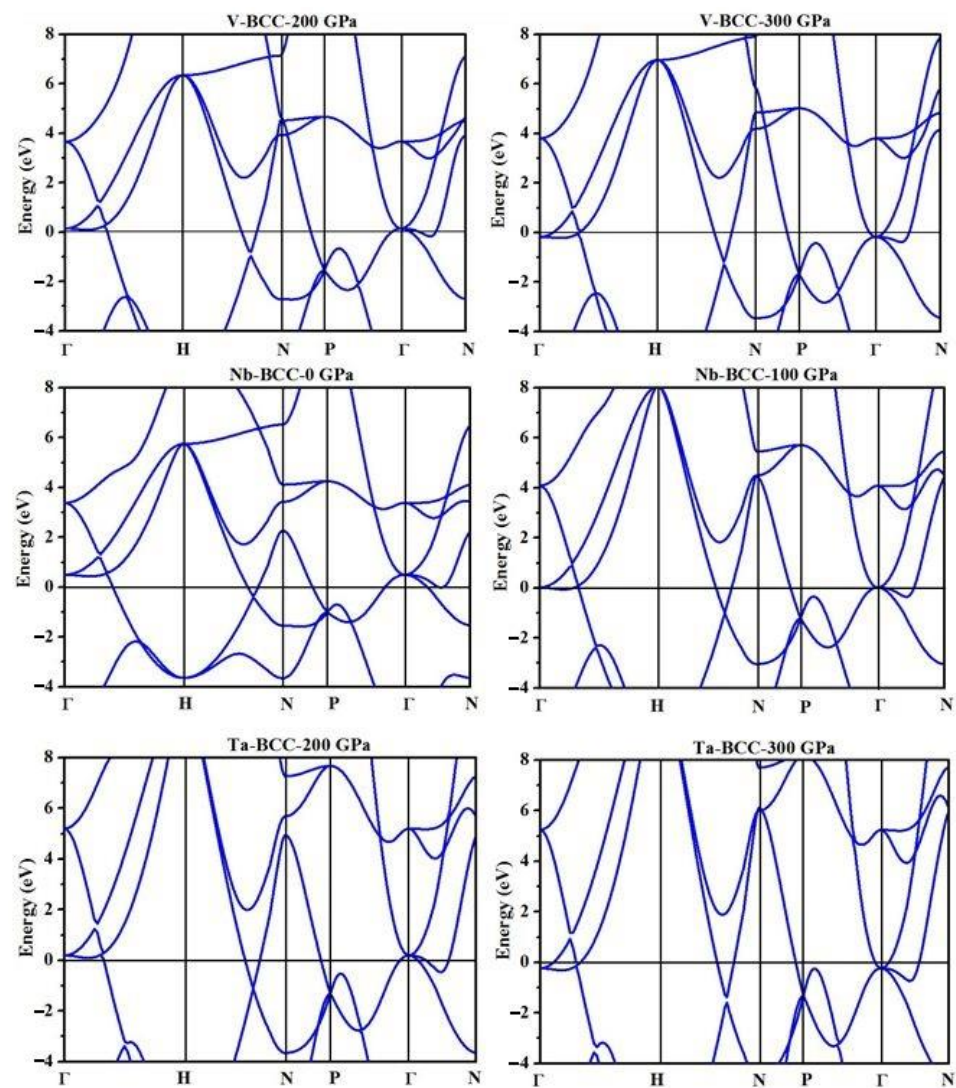


Figure 9. Band structures of vanadium, niobium, and tantalum in BCC phase at various pressures. (By the courtesy of Ref. [56]).

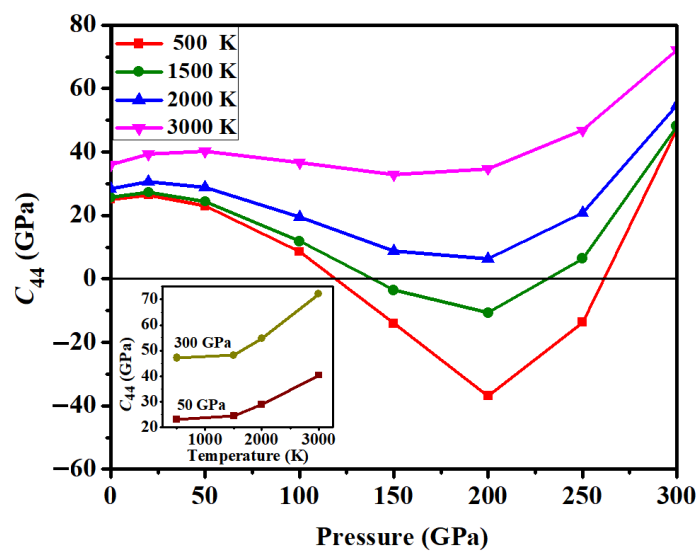


Figure 10. Calculated C_{44} of BCC vanadium as a function of pressure under different electronic temperatures. (By the courtesy of Ref. [54]).

Further investigation by Wang et al. showed that thermo-electrons also have a significant effect on the elastic anomalies of niobium [56]. Like its light neighbor vanadium, the elastic softening in niobium is gradually diminished with increased electronic temperature, effectively causing a heating-induced *hardening* phenomenon. Wang et al. [56] noticed that this thermo-electron effect only presents in the softening pressure ranges for niobium. At the pressure of 75 GPa, the C_{44} of niobium increases by about 135% when the temperature increases from 0 to 2000 K. Further research by Wang et al. [56] showed that the inclusion of phonon contribution could slightly soften the metal; however, it cannot change the conclusion qualitatively.

Subsequently, Keuter et al. [63] studied the anomalous thermoelastic properties of vanadium, niobium, and tantalum based on a DFT model, which could calculate the C_{44} under different temperatures. The results showed that the calculated elastic constants of cuprum and molybdenum decrease monotonically with the increase of temperature, which accords with the general thermoelastic behavior. However, for vanadium and niobium, the C_{44} falls to a minimum at about 500 K and then increases at higher temperatures, which is consistent with the heating-induced *hardening* observed by Wang et al. [56] in these elements.

As a rule of thumb, solids usually harden under compression and soften at high temperatures. Therefore, the theoretical predicted compression-induced softening and heating-induced *hardening* in group VB metals is quite remarkable. Nevertheless, direct experimental evidence has long been lacking. Until recently, Wang et al. [72] measured the HPHT sound velocities at Hugoniot states generated by shock waves and reported the first evidence for the CISHIH counterintuitive phenomenon in group VB metals. They observed that the shock vanadium not only had a significant reduction in sound velocity due to compression, but also had a strong increase in sound velocity due to heating. The former reflects the softening of the shear modulus by compression, while the latter corresponds to the reverse hardening by heat. Their experimental study further highlights the CISHIH dual anomaly behavior in group VB metals and provided inspiration for further theoretical and experimental research on this outstanding problem. The conceptual advancement also might be inspirational in understanding the general exotic behavior of matter, such as electrides [90,91], under extreme conditions.

3. Conclusions

In summary, it is a basic topic in condensed matter physics to reveal and elucidate the trend and mechanism of structural transformation and elastic anomaly of elemental metals. This review covers a large number of theoretical and experimental research on the phase stability and elastic anomalies in group VB transition metals over the last two decades. Two quite different scenarios are emerging from this progress. The first one is focused on phase transition and is represented by the phase diagram shown in Figures 5 and 6. As the basis of this scenario, a tentative theoretical “consensus” has been established on the phase transition sequence of BCC→RH1→RH2→BCC in vanadium under pressure, and RH→BCC under high temperature. Meanwhile, we also showed that some experimental and theoretical facts are incompatible with this scenario. They suggested that the resultant RH is far from being perfect and should be interpreted as lattice distortion rather than a phase transition. The same issue exists for niobium and tantalum. The above discussions cautioned that the phase transition in group VB metals is elusive, and the main problem of this scenario is that it cannot provide a unified and general description for all group VB elements.

The second scenario emphasizes on electronic structure and the resultant elastic anomalies. It viewed the phase transition in vanadium as the natural outcome of the anomaly, rather than the cause of it. In this direction, recent investigations revealed that different from other groups of transition metals, the group VB transition elements exhibit striking anomalous elastic softening under pressure. It is known that vanadium, niobium, and tantalum have nearly identical valence electronic configuration, but the variation of the C_{44} under pressure for them is not the same. According to existing literature reports, the pressure-induced softening of C_{44} in vanadium, niobium, and tantalum originates from the

electronic structure, which is closely related to the FSN and ETT. In addition, the elastic softening in vanadium and niobium are gradually diminished with increased temperature, effectively giving rise to a heating-induced *hardening* phenomenon. The most striking feature of this scenario is that there actually could be *no phase transition* in vanadium at all. We have increasing confidence on this picture, especially after the reported facts that accurate DFT + *J* method completely eliminates RH phases from the thermodynamic equilibrium phase diagram [66], the absence/imperfect RH phase in Stevenson et al.'s experiment [74], the stability of BCC and meta-stability of RH as reported in Akahama et al.'s experiment [73], and the unexpected appearance of RH in shock experiment as reported by Wang et al. [72]. All of them cannot be consistently interpreted in the first scenario. Nonetheless, they can be reconciled in the second scenario, in which the "imperfect" RH as reported in various DAC experiments is viewed as lattice distortions caused by deviatoric stress rather than a new phase. These distortions lead to prominent change in modulus and sound velocity, and are modulated by compression and temperature, leading to CISHIH dual anomaly in both vanadium and niobium. We conclude that it seems the second scenario is more promising, but a lot of investigation is still required to achieve a general consensus.

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