Structural phase transitions in vanadium under high pressure

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Abstract – Results of structural phase stability under high pressure using first-principles electronic-structure calculations are presented for vanadium up to few-megabar pressures. A unique structural phase transition sequence BCC $\sim 60 \text{ GPa} \rightarrow \text{Rhom} 1 (\alpha = 110.50^\circ) \sim 160 \text{ GPa} \rightarrow \text{Rhom} 2 (\alpha = 108.50^\circ) \sim 240 \text{ GPa}$, BCC is predicted for the first time in V. Our detailed electronic-structure analysis shows that it is an example of a band Jahn-Teller-induced structural phase transition.

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Introduction. – The elemental solids are the most fundamental materials and their structural evolution under pressure is a major area of research in condensed matter. The majority of the elemental solids, particularly the transition metals, crystallize in very high symmetric structures many of which are close-packed hexagonal (HCP), face-centered cubic (FCC) or body-centered cubic (BCC) structures. It might be expected that these would merely compress under compression and those elements whose structure was not close packed or BCC would become close packed under pressure. But in reality this is not always the case; the pressure dependence of electronic energy levels can change the nature of bonding in such a way that it results in a structural transition to a phase with lower symmetry and less packing than found at ambient pressure (see [1], and references therein).

Vanadium crystallizes in a BCC structure at ambient pressure and its ambient pressure behavior is considered to be well understood theoretically. But its high-pressure behavior has been the subject of many experimental and theoretical studies in the past [2–7]. In fact, the development of new techniques for electric and magnetic measurements in a diamond-anvil cell (DAC) has made it possible to perform measurements at megabar pressures where the electronic states of substances change substantially with respect to those at ambient pressure as a result of a significant decrease in volume or structural changes. Ishizuka et al. [3] measured the superconducting transition temperature of vanadium in DAC experiments up to 120 GPa of pressure using a superconducting quantum interference device. They observed a linear increase in $T_c$ from 5.3 K at ambient pressure to 17.2 K (the highest $T_c$ among the elemental metals reported so far) at 120 GPa pressure. In addition, they also found a small step-like increase in $T_c$ near 60 GPa pressure but because of its smallness, its existence could not be confirmed. To explore the possibility of a structural phase transition from BCC to another phase and to gain an insight into the origin of the observed characteristic pressure dependence of $T_c$, first-principles lattice dynamic calculations were performed by Suzuki and Otani [6] in a pressure range up to 150 GPa. They found that the frequencies of the transverse acoustic (TA) phonon mode get softened near a quarter of the $\Gamma$-H line with increasing pressure and eventually become imaginary at pressures higher than 130 GPa. To understand this, Landa et al. [7] carried out ab initio elastic constant calculations with pressure and reported an anomalous pressure behavior of the $C_{44}$ elastic constant. Though these are signatures of the development of some kind of structural instability in BCC lattice under pressure, the authors corroborated this behavior to the combined Fermi surface nesting, ETT and band Jahn-Teller (J-T) effect without exploring the possibility of any structural phase transition [7]. However, recently Ding et al. [8] reported a phase transition to a rhombohedral structure corresponding to an increase in the angle between the primitive unit cell vectors spanning the BCC crystal in the 60–70 GPa pressure range. The rhombohedral phase was stable up to the highest pressure, 155 GPa, of their study, although an earlier DAC study under hydrostatic conditions by Takemura claimed a BCC structural stability at least up to 150 GPa pressure [4].

In this paper we explored the possibility of structural phase transition in V under high pressure using
Table 1: The experimental data shown in brackets is of Takemura [4].

| Lattice constant \((a_0)\) (in Å) | Bulk modulus \((B_0)\) (in GPa) | Pressure derivative of \(B_0\) \((B'_0)\) |
|-----------------------------------|-------------------------------|-------------------------------|
| 2.998 \(\pm\) 3.00              | 182 \(\pm\) 165, 188         | 3.70 \(\pm\) 3.5, 4.04       |

density-functional-theory–based calculations. The total energies were calculated at various pressures for a rhombohedral unit cell as a function of its angle ranging between 50 and 120 degrees, covering FCC-SC-BCC structures in one go, apart from the usual rhombohedral structures. Our calculations show a unique (BCC → rhombohedral → rhombohedral2 → BCC) sequence of structural changes under pressure for V. From our detailed electronic structure and lattice dynamics results we predict that a band Jahn-Teller (J-T) effect is responsible for the BCC-to-rhombohedral phase transition [9].

**Computational method.** – The rhombohedral structure with varying values of its angle \(\alpha_{\text{rhom}}\) results in different structures, namely simple cubic (SC, \(\alpha_{\text{rhom}} = 90^\circ\)), body-centered cubic (BCC, \(\alpha_{\text{rhom}} = 109.47^\circ\)) and face-centered cubic (FCC, \(\alpha_{\text{rhom}} = 60^\circ\)) [10]. Thus, we generated all these cubic structures from a rhombohedral cell with atoms at \((0, 0, 0)\) by varying the values of the angle \(\alpha_{\text{rhom}}\). We performed total-energy calculations taking a rhombohedral unit cell for V as a function of \(\alpha_{\text{rhom}}\) in the range of 54°–112° at several volumes. All the calculations were done using the pseudopotential-based PWSCF computer code [11]. The total energy calculations were based on the density functional theory and the phonon dispersions calculations on the density functional perturbation theory [12]. An ultrasoft pseudopotential with \(1s^22s^22p^6\) states as core was used with 40 Ry plane-wave energy cut-off and a 400 Ry cut-off in the expansion of the augmentation charges. Phonon dynamical matrices were computed on a uniform \(6 \times 6 \times 6\) grid of \(q\)-points in the Brillouin zone (BZ) of the BCC structure, leading to a total of 16 \(q\)-points in the irreducible BZ wedge. Using Fourier interpolation, we then constructed and diagonalized the dynamical matrices on a denser grid \((24 \times 24 \times 24)\). For the exchange correlation term the generalized gradient correction approximation of Perdew-Buke-Ernzerof (GGA-PBE) [13] was used. The Brillouin zone integration has been performed using an \(18 \times 18 \times 18\) \(k\)-point Monkhorst-pack mesh with a smearing parameter of 0.03 Ry. Convergence with respect to the smearing parameter was checked. The energy convergence with respect to other computational parameters \((e.g. 28 \times 28 \times 28\) BZ mesh, and 65 Ry energy cut-off with 650 Ry cut-off for the expansion of the augmentation charges) was carefully examined. All the calculations for pressures higher than 200 GPa were checked with the Vienna \textit{ab initio} simulation package (VASP) using a projector-augmented-wave (PAW) pseudopotential with nonlinear core corrections which take care of the effect of the core-core and valence-core overlap at higher pressures [14–16].

**Results and discussion.** – The calculated equilibrium properties for vanadium metal are presented in table 1 along with their available experimental values and are found to be in very good agreement. The pressure-volume equation of states also matches well with existing experimental data (fig. 1), thus justifying the use of pseudopotential and other computational parameters.

Figure 2 depicts our calculated total energy as a function of the angle \(\alpha_{\text{rhom}}\) for V at the equilibrium volume.
The SC structure is at the absolute maximum and the FCC structure is at a local maximum, indicating the unstable nature of these structures for a given rhombohedral distortion. The BCC structure is at the absolute minimum of the total-energy curve as per expectation. However, there are two other local minima located at around the 56° and 68° angle (see the inset of fig. 2). The energy variation in the angle range 106°–111° is about 4.0 mRy per atom. Similar calculations were performed at many volumes which cover a pressure range up to 434 GPa. Figures 3a, b show the total-energy variation as a function of the angles $\alpha_{\text{rhom}}$ in the range 106°–112° at the several pressures of our study. The reason for showing the total-energy variation in this range of angles only is twofold. First, the BCC structure has the lowest energy among all structures and, second, no extra feature appears around the FCC structure except that the local minima become more pronounced with a few degree shifts in $\alpha_{\text{rhom}}$. Particularly at a pressure of 112 GPa the minimum around 68° is shifted to 70° and the minimum around 56° is shifted to 57°. At this pressure the minimum at 70° is lower in energy by 7 mRy per atom relative to that at 57°, and around 12 mRy per atom relative to the FCC structure. However, the SC structure remains at the absolute maximum of the rhombohedral energy surface up to pressures higher than 400 GPa. Thus, we completely ruled out the possibility of the BCC-to-SC transition as predicted by earlier calculations using the tight-binding linear-muffin-tin method within the atomic-sphere approximation [5].

Below a pressure of 60 GPa the behavior of the rhombohedral total-energy curve remains unchanged under compression. However, at around a pressure of 60 GPa a new minimum appears at a rhombohedral angle of 110°50’ (say, Min1) leading to a structural phase transition. Now, the BCC energy is higher by 0.05 mRy per atom relative to Min1. A further increase in pressure leads to the development of another minimum at an angle of 108.50° (say, Min2) and the BCC structure lies at a local maximum. At a pressure of 112 GPa the energy difference between Min1 and Min2 is about −0.057 mRy per atom and that between Min1 and the BCC structure is −0.10 mRy per atom. Thus, now the BCC V becomes mechanically unstable toward a rhombohedral distortion which can lead to $C_{44}$ softening as it is related to trigonal shear. In fact, in Landau’s [7] calculations $C_{44}$ starts to soften above a pressure of 50 GPa and drops to zero at around 180 GPa. These energy changes in our calculations are found to exist even with denser (e.g. $28 \times 28 \times 28$ k-point) meshes for the BZ integration and
Fig. 4: Energy band structure of V for BCC and rhombohedral structures along hexagonal high-symmetry points.

with larger plane-wave energy (65 Ry) and augmentation charges cut-offs (650 Ry). Thus, it is confirmed that this feature cannot be an artifact of calculation. As these calculations were performed with the same rhombohedral cell, with sufficiently dense BZ mesh, for all the angle values inaccuracies due to computational parameters will be the same. At a pressure of 112 GPa the calculations were cross-checked with the VASP program using the PAW pseudopotential. For further compressions, the total energy in the range 106°–112° behaves similar to that at 112 GPa except that at 160 GPa Min2 becomes lower in energy relative to Min1 by 0.20 mRy per atom leading to an iso-structural phase transition. Now the Min2 energy is lower by 0.14 mRy per atom relative to the BCC structure. A further increase in pressure leads to the disappearance of Min1 and the reduction of the energy difference between Min1 and the BCC structure. In fact, above a pressure of 240 GPa the BCC structure becomes lower in energy again and at a pressure of 434 GPa the Min2 disappears completely and there is only one minimum located at 109.47° which corresponds to a BCC structure.

We have also performed total-energy calculations for hexagonal closed-packed (HCP) lattice at optimized c/a axial ratio (1.829) at two pressures; one at ambient and the other at a pressure of 332 GPa and its energy is found always higher compared to the BCC structure. The energy difference (19.6 mRy/atom at ambient pressure) between the BCC and HCP structures increases with pressure (40 mRy/atom at 332 GPa) thus ruling out the BCC-HCP transition. The possibility of body-centered tetragonal structure at high pressures was also explored using Bain-path calculations and we find that the tetragonal structure is not energetically favored.

As it is believed that the high-Z elements of a group in the periodic table follow a structural sequence under pressure [1,17] as that of the low-Z members of that group, we performed similar calculations for the remaining members of the Group-VB (Nb and Ta) under pressure but no structural phase transition is seen (detailed results will be reported elsewhere).

To understand the underlying mechanism of the BCC- to-rhombohedral transition near a pressure of 60 GPa, we critically analyzed the electron energy bands of V in these structures. To make the comparison easier, the band structures for both the phases are plotted along the hexagonal high-symmetry points and are shown in fig. 4. In the BCC structure the 3d band splits into doubly degenerate $e_g$ and triply degenerate $t_{2g}$ (marked in fig. 4)
band at the \( \Gamma \)-point of the BZ. The \( t_{2g} \) band is partially occupied and hence is a J-T sensitive state, which can further split into a singlet (of symmetry \( E \)) and a doublet (of symmetry \( A \)) under rhombohedral distortion as seen in our band structure for the rhombohedral structure. At ambient pressure this mechanism is not favorable because the \( t_{2g} \) band position is such that after splitting the singlet lies just below the Fermi level \( (E_F) \) causing an increase in density of states (DOS) at \( E_F \), denoted as \( (D(E_F)) \), and it may lead to an increase in kinetic energy (not shown). But under pressure as the whole band pertinent to the BCC structure comes closer to \( E_F \), splitting keeps both parts away from it causing a decrease of the kinetic energy as well as of \( D(E_F) \). Near a pressure of 60 GPa we found an 8\% decrease of \( D(E_F) \) in the rhombohedral structure compared to that in the BCC structure and the corresponding reduction in kinetic energy in rhombohedral structure causes a total energy lower than that of the BCC structure. The essential idea of the J-T mechanism is that a lattice deformation partially removes the degeneracy of \( d \) sub-bands which may lie in the vicinity of the Fermi level, causing a repopulation of the various sub-bands and resulting in a lowering of the crystal free energy which is exactly happening here under pressure [9].

Re-appearance of the BCC structure in V at very high pressures prompted us to study its lattice dynamics at high pressures. Similar to Suzuki and Otani [6], our phonon calculations show a decrease in the TA mode frequencies with increasing pressure along the \( \Gamma-H \) line of the BZ (fig. 3c). The atomic displacement pattern related to the TA mode corresponds to rhombohedral distortion of the cubic structure. This mode is doubly degenerate along the \( \Gamma-H \) line of the BZ. The reduction of the frequencies of TA modes under pressure indicates that the rhombohedral distortion is favorable under pressure, which again leads to the splitting of the \( t_{2g} \) electronic states. Hence we infer that a strong coupling exists between the \( t_{2g} \) electron and the TA mode phonon which increases with pressure finally leading to a structural phase transition near a pressure of 60 GPa. Thus, a band J-T mechanism is found responsible for the BCC-to-rhombohedral structural transition. As these modes frequencies become imaginary at around a pressure of 112 GPa, this softening cannot be related to this phase transition as vanadium does not exist in a body-centered cubic structure at this pressure. Above 160 GPa the TA mode frequencies become positive and at further compressions show a normal pressure behavior, establishing the vibrational stability of V in the BCC structure again.

**Conclusion.** – In conclusion, the high-pressure structural behavior of the vanadium metal is investigated using the density functional theory. We find a body-centered-cubic-to-rhombohedral structural phase transition (\( \alpha_{\text{rhom}} = 110.5^\circ \)) at around 60 GPa in agreement with experimental observation. A band Jahn-Teller mechanism is inferred to be responsible for this structural transition. Further, we predict that vanadium exists in a rhombohedral structure at least up to 240 GPa; however its angle is changed to 108.50\(^\circ\) at 160 GPa resulting in an iso-structural phase transition. Finally, the BCC structure re-appears at pressures higher than 240 GPa.

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**Additional remark:** We note that the results of a recent, independent, study of lattice dynamics calculations are consistent with our findings [18].

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