Ab initio phase stability at high temperatures and pressures in the V-Cr system

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The phase stability of vanadium metal and vanadium-chromium alloys at high temperatures and pressures is explored by means of first-principles electronic-structure calculations. Utilizing the self-consistent *ab initio* lattice dynamics approach in conjunction with density-functional theory, we show that pressure-induced mechanical instability of body-centered cubic vanadium metal, which results in formation of a rhombohedral phase at around 60–70 GPa at room temperature, will survive significant heating and compression. Furthermore, alloying with chromium decreases the temperature at which stabilization of the body-centered cubic phase occurs at elevated pressure.

I. INTRODUCTION

Vanadium metal has seen a surge in research, both experimental and theoretical, driven mainly by its importance in applications but also because of its surprising destabilization of the body-centered cubic (bcc) ground-state phase close to 60 GPa.

On the experimental side, synchrotron x-ray diffraction measurements [1] reported a novel rhombohedral (rh) phase that is a relatively small distortion of bcc in vanadium metal around 63–69 GPa. Also, Jenei *et al.* [2] found a dependence of the transition pressure from bcc to rh as a function of the hydrostatic condition of the pressure media. Nonhydrostatic conditions (no pressure medium) lead to lower transition pressures (∼30 GPa) while for quasihydrostatic compression in Ne pressure medium the bcc → rh phase transition occurs at much higher pressure (∼60 GPa).

Theoretically, the bcc → rh transition has been confirmed by numerous electronic-structure studies [3–6] that also predict the bcc phase to reenter above 300 GPa. It has been proposed that intraband Fermi-surface (FS) nesting is responsible for the instability of the cubic phase of vanadium metal under compression [7,8] that appears to be associated with a substantial pressure-induced softening of the shear elastic constant, C_{44}. Even though the existence of the intraband FS nesting in vanadium metal is widely acknowledged, it has repeatedly been argued in the literature [3,8] that the softening of C_{44} will disappear at higher temperatures because the rhombohedral distortion is very small. In other words, elevated temperatures would wash out the destabilization of the bcc phase, thus removing the bcc → rh transformation.

This claim has never been challenged by rigorous theory or modeling and it is the principal purpose of our study to clarify if indeed high temperatures expand the bcc stability field in the vanadium phase diagram [3,8].

We also address the influence of alloying on the stability of the bcc phase of vanadium metal at elevated pressures and finite temperatures. Previous calculations [8–10] show that a small (∼3–5 at. %) amount of 4*d*- (Zr, Nb, Mo) or 5*d*- (Hf, Ta, W) metal stabilizes the bcc phase of vanadium metal at all pressures. Addition of about 10 at. % of chromium (the nearest 3*d*-metal neighbor to the right of vanadium) also stabilizes the bcc crystal at all pressures [3,9]. However,

these calculations [3,8–10] were performed at $T = 0$ K and temperature effects (lattice vibration) were not accounted for. Therefore, in this Rapid Communication, we include thermal effects and calculate compositional dependence of the stability field of the bcc phase (rh phase → bcc phase transition temperature) for a set of vanadium-chromium disordered alloys: $V_{95}Cr_{05}$, $V_{90}Cr_{10}$, $V_{85}Cr_{15}$, and $V_{80}Cr_{20}$. Notice that vanadium metal is the only element in the Periodic Table that forms a complete solid solution with chromium metal [11] and similar computations can be extended, if desired, to the whole compositional range of V-Cr alloys.

For the select V-Cr alloys we apply a scheme to take phonon-phonon interactions into account at elevated temperatures, namely, the self-consistent *ab initio* lattice dynamics (SCAILD) method [12] that we will describe briefly in the next section. Section II also deals with computational parameters and methods for the density-functional-theory model that is used for the force calculations required for SCAILD. In Sec. III we present and discuss our results for the V-Cr alloy system, and conclude with a discussion in Sec. IV.

II. COMPUTATIONAL DETAILS

The bcc stability for the V-Cr alloy system is studied for two atomic volumes (10.41 and 8.58 Å³) that correspond to zero-temperature pressures (p) of 74 and 182 GPa, respectively. These volumes are chosen because one represents the early onset of the rhombohedral phase and the other the maximum rh stability in terms of the bcc–rh energy difference. For these volumes, the bcc stability is determined by computing the phonon dispersions as functions of temperature using the SCAILD method. This approach is described in great detail [13] and not repeated here, but the general idea is to account for thermal vibrations of the atoms and their interactions. This is accomplished by (i) calculating the forces on atoms, displaced from the ideal bcc positions according to the temperature, and (ii) computing the phonon dispersions. Because the forces, displacements, and the phonons depend on each other the scheme is set up to self-consistently determine the temperature dependence of the lattice dynamics. If the procedure converges and the bcc entropy is large enough at the studied temperature bcc stabilization will occur due to the phonon-phonon interaction.

SCAILD has been applied for elemental metals in the past [12,13] showing that bcc stability takes place from excited phonons that are commensurate with the supercell and provide the necessary entropy. However, only recently this approach has been expanded to deal with phase stability in an alloy system (Ti-V) [14].

The forces needed for the SCAILD methodology are obtained from electronic-structure calculations performed within the framework of DFT and the necessary assumption for the unknown electron exchange and correlation functional is that of the local-density approximation (LDA) [15]. Although newer varieties of this approximation have been proposed, our experience is that the calculated forces are easier to numerically converge with LDA compared to other formulations. For elemental vanadium we pursued the generalized gradient approximation (GGA) [16] and found only minor numerical differences in the calculated forces ($\sim$10%) with very little effect on the overall phonon dispersions.

Our particular DFT implementation is founded on the full-potential linear muffin-tin orbitals (FPLMTO) method that has been outlined in Ref. [17]. The basis functions are well converged; specifically, we associate a set of semi–core states $3s$ and $3p$ and valence states $4s$, $4p$, and $3d$ to two kinetic energy parameters for a so-called double basis set. For the SCAILD simulation a bcc super cell is required and similar to previous investigations [12] we apply a $4 \times 4 \times 4$ (64 atom) cell size.

In all present calculations the sampling of k points in the Brillouin zone (BZ) for the appropriate summations are carefully checked for convergence and 64 k points are sampled in the irreducible part of the BZ.

In order to study the V-Cr alloy system we conveniently apply the virtual crystal approximation (VCA) that is usually applicable and appropriate when alloying metals that are neighbors in the Periodic Table. The concept of the VCA is to replace the true alloy with an artificial metal that consists of a weighted average between the two components. For example, the VCA $V_{80}Cr_{20}$ alloy is simply a monoatomic metal with a nuclear charge of 23.2 and a total of 23.2 electrons. The VCA has been shown to effectively model the behavior of the elastic constants for the d-transition alloys [18] and this lends credence to its utilization here for the V-Cr alloy system.

III. STABILITY OF VANADIUM METAL AND V-Cr ALLOYS

In Fig. 1 we show the FPLMTO total energy as a function of the rhombohedral distortion for vanadium metal at volumes of 10.41 and 8.58 Å^3 (74 and 182 GPa). Our model predicts the bcc $\rightarrow$ rh transition at 60 GPa (not shown) while Fig. 1 (74 GPa) shows a small rhombohedral distortion ($\delta = -2\%$) of the bcc structure. At 182 GPa the rhombohedral phase ($\delta = 2.5\%$) reaches its maximum stability in terms of the depth of the energy minimum. Hence, we have two configurations of the rhombohedral structure, one relatively weakly stable (10.41 Å^3) and one strongly stable (8.58 Å^3) over the bcc phase. These two volumes are chosen as representatives of the entire rhombohedral phase field to investigate the influence of temperature and alloying with Cr.
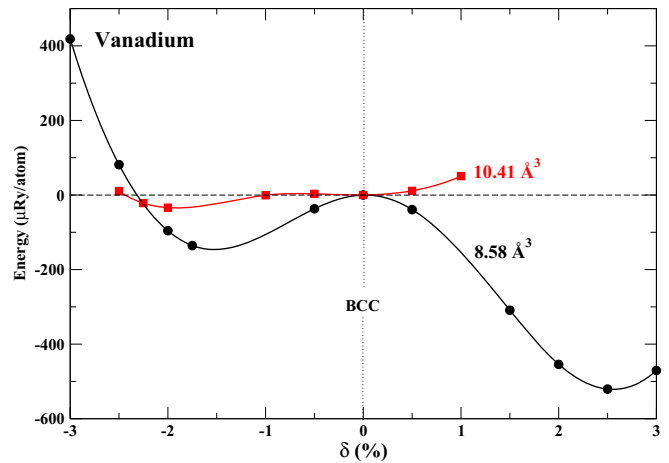

FIG. 1. (Color online) Calculated (FPLMTO) total energy of vanadium metal as a function of the rhombohedral deformation parameter δ (see Ref. [3] for explanation). The undistorted ($\delta = 0$) crystal corresponds to the bcc phase (vertical dashed line).

We perform SCAILD simulation for bcc V and four bcc V-Cr alloys ($V_{95}Cr_{05}$, $V_{90}Cr_{10}$, $V_{85}Cr_{15}$, and $V_{80}Cr_{20}$) as a function of temperatures paying attention to the lowest temperature that stabilizes all phonons. In Fig. 2 we show these phonon frequencies for V, $V_{90}Cr_{10}$, $V_{85}Cr_{15}$, and $V_{80}Cr_{20}$ calculated at the atomic volume $\Omega = 8.58$ Å^3. The finite temperature calculations predict the stability of the bcc phase at some temperature, e.g., $\sim$8000 K for elemental V, by promoting the frequencies of the phonons along Γ to H and Γ to N symmetry lines from imaginary to real. Similar calculations are performed for vanadium and the same four V-Cr alloys at the atomic volume $\Omega = 10.41$ Å^3 resulting in a bcc stabilization of vanadium at $\sim$2500 K.

In Fig. 3 we display the mechanical-stability temperatures of bcc V and the four V-Cr alloys mentioned above. Calculations are performed, as mentioned, at $\Omega = 10.41$ Å^3 (the early onset of the rhombohedral phase) and $\Omega = 8.58$ Å^3 (the maximum stability of the rhombohedral phase). One realizes that addition of Cr to V decreases the temperature of stabilization of the bcc phase, although in the case of the larger atomic volume this effect is less pronounced.

Another way of checking the mechanical stability is to evaluate the elastic constants and their stability criteria [19]. The elastic moduli are obtained from the slopes of the calculated phonon dispersions approaching the Γ point. For example, C_{44} is associated with the transverse mode of the Γ-H branch.

There are two simplifications in the SCAILD treatment. First of all, we do not adjust the volume of the system due to alloying. Secondly, no effects related to thermal expansion are accounted for. Assuming the first approximation, we follow the methodology of our recent papers [9,10], where the equation of state at $T = 0$ K (cold curve) did not account for the effect of the alloying. This is reasonable because the main purpose of this Rapid Communication is to study how lattice vibrations influence the FS nesting that is responsible for the bcc destabilization at low temperatures. Secondly, we ignore thermal expansion because the volume change due to alloying,
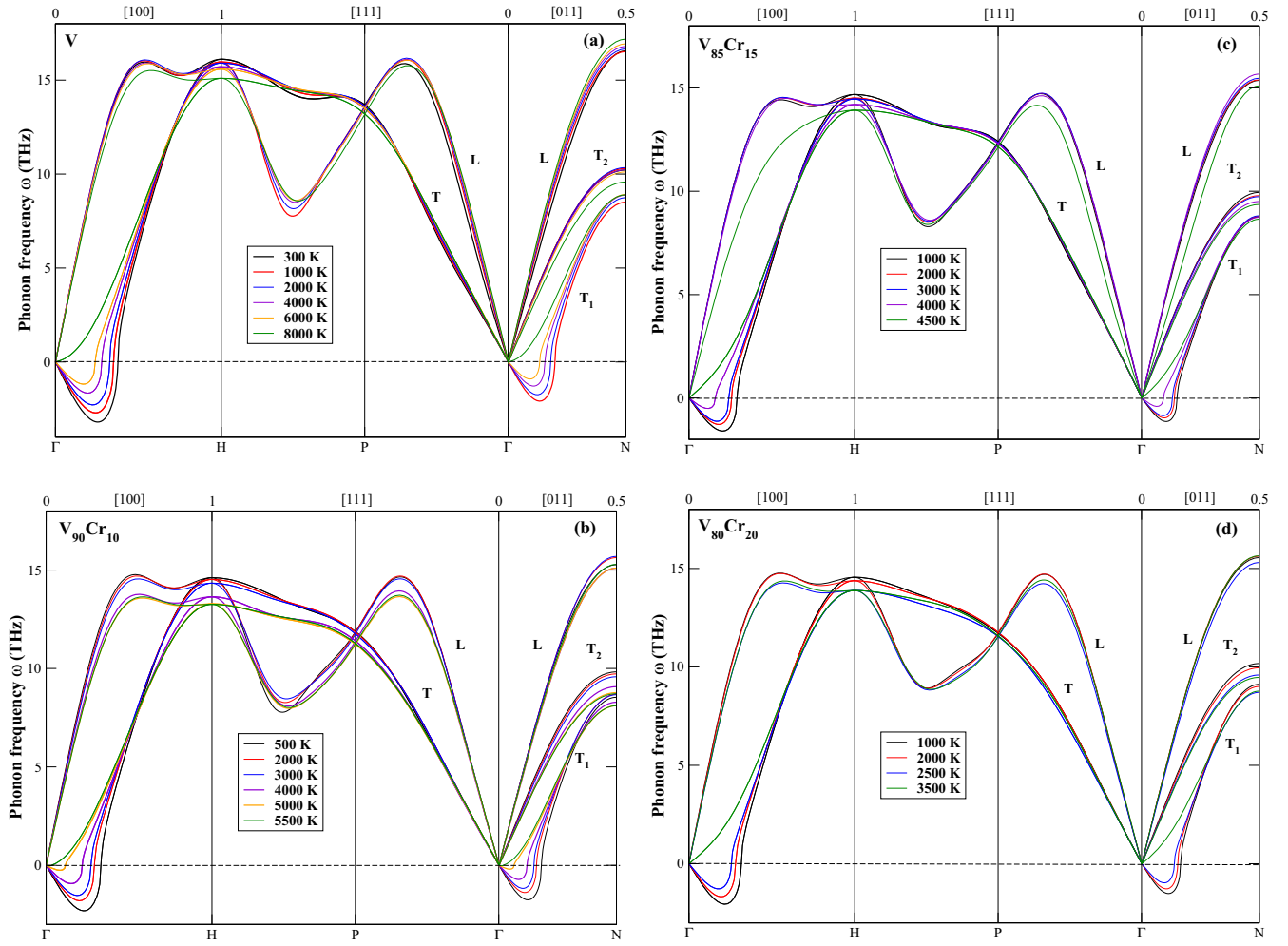
FIG. 2. (Color online) Calculated phonon dispersions for (a) V, (b) $V_{90}Cr_{10}$, (c) $V_{85}Cr_{15}$, and (d) $V_{80}Cr_{20}$ bcc alloys at different temperatures at the atomic volume $\Omega = 8.58$ Å^3.

which we have already neglected, is far greater than that of the thermal expansion. The choice of keeping the volume constant is certainly practical from a computational point of view, but fundamentally has the advantage of not introducing

FIG. 3. (Color online) Calculated temperature of mechanical stability of bcc V-Cr alloys at $\Omega = 10.41$ Å^3 and $\Omega = 8.58$ Å^3.

uncertainties related to assumptions of volume expansions or contractions.

IV. DISCUSSION

By applying DFT calculations for the V-Cr alloy system, combined with the self-consistent lattice dynamics scheme, we find that the rhombohedral phase remains stable under heating up to ~2500 K at the early onset of the room-temperature bcc to rh phase transition ($\Omega = 10.41$ Å^3). This result contradicts the reported argument [3,8] that the FS nesting in vanadium metal has a "subtle" character that is easily destroyed by a moderate temperature increase. The aforementioned temperature (~2500 K) of destabilization (stabilization) of the rh (bcc) phase is significantly below the shock melting temperature of the bcc vanadium, $T_m \sim 4000$ K, reported in Ref. [20] at ~75 GPa. Thus, we conclude that the transition to the rhombohedral phase in vanadium metal shall be exposed by diamond-anvil cell (DAC) experiments at high temperatures (up to the upper temperature limit, ~2500 K that can be achieved by laser heating). However, above 2500 K our calculations predict recovery of bcc vanadium up to its melting point of ~4000 K at ~75 GPa.
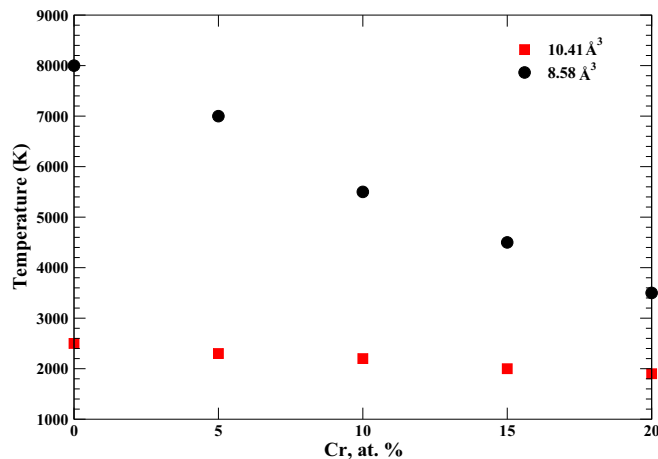
At the smaller volume ($\Omega = 8.58 \text{ Å}^3$, $p = 182$ GPa at room temperature), our model establishes 8000 K as an upper bound of stability of the vanadium rhombohedral phase with bcc taking over beyond that. This temperature, however, is clearly above the shock melting temperature, $T_m \sim 6800 \pm 800$ K at 182 GPa [20], which then implies that the bcc phase is actually never stable at this volume.

Finally, our calculations also reflect compositional dependence of the mechanical-stability temperature of the bcc V-Cr alloys up to 20 at.% of Cr. Addition of Cr to V lowers the temperature of the rh $\rightarrow$ bcc transition, which is consistent with our previous statement in Ref. [9]: For a transition metal from group VB (V, Nb, and Ta) alloying with its nearest neighbor to the right from the same d-transition series (e.g., V with Cr) causes stabilization of the bcc phase.

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