Pressure-induced structural phase transition of vanadium:  
A revisit from the perspective of ensemble theory

Bo-Yuan Ning¹,²,³ and Xi-Jing Ning¹,²

¹Institute of Modern Physics, Fudan University, Shanghai, 200033, China  
²Applied Ion Beam Physics Laboratory, Fudan University, Shanghai, 200033, China  
³Department of Materials Science and Engineering,  
Southern University of Science and Technology, Shenzhen 518055, China  
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For realistic crystals, the free energy strictly formulated in ensemble theory can hardly be obtained because of the difficulty in solving the high-dimension integral of the partition function, the dilemma of which makes it even a doubt if the rigorous ensemble theory is applicable to phase transitions of condensed matters. In the present work, the partition function of crystal vanadium under compression up to 320 GPa at room temperature is solved by an approach developed very recently, and the derived equation of state is in a good agreement with all the experimental measurements, especially the latest one covering the widest pressure range up to 300 GPa. Furthermore, the derived Gibbs free energy proves the very argument to understand most of the experiments reported in the past decade on the pressure-induced phase transition, and, especially, a novel phase transition sequence concerning three different phases observed very recently and the measured angles of two phases agree with our theoretical results excellently.

The structural phase transition of crystal vanadium (V) under high pressure at room temperature attracts a long-time interests. Although it had been already a consensus that the BCC phase is highly stable [1] and early experiments affirmed this stability up to 220 GPa [2], theoretical works based on calculations of phonon mode softening and trigonal shear elastic instability predicted a likely structural transformation within a range from 130 GPa [3] to 200 GPa [4, 5], which inspired an experiment [6] in year 2007 showing that a phase transition does take place at about 63 GPa. Specifically, the BCC phase transits into a rhombohedral (RH) structure with the RH angle $\alpha > \alpha_{\text{BCC}} (109.47^\circ)$ denoted as RH$_1$ to distinguish from a similar structure RH$_2$ with $\alpha < \alpha_{\text{BCC}}$.

The above mentioned phase transition was further confirmed by later experiments [7-11], and the relevant theoretical works, based on either approximate calculations of free energy [12-14] or ab initio lattice dynamics [14-18], reached a qualitative agreement that the transition pressure ($P_t$) would be $60 \sim 90$ GPa for BCC$\rightarrow$RH$_1$, and predicted that $P_t$ for RH$_1 \rightarrow$ RH$_2$ and RH$_2 \rightarrow$ BCC are around 120 and 250 GPa respectively. Nevertheless, two experiments reported in year 2021 [19, 20] exhibited different results. Akahama et al. [19] compressed foil V up to 300 GPa at room temperature and found that BCC lattice is a stable phase until the RH$_2$ and BCC phase coexisting at pressure ($P$) larger than 242 GPa, while the RH$_1$ phase is a metastable phase caused by nonhydrostatic pressure effects. Stevenson et al. [20], on the other hand, observed that the BCC lattice transform into RH$_2$ when $P > 40$ GPa and then turns back to BCC until RH$_1$ emerges for $P > 100$ GPa. It is noticeable that the measured $\alpha$ by Stevenson et al. for RH$_1$ (or RH$_2$) is $109.54^\circ$ (or $109.35^\circ$), which is significantly different from the theoretical result, $110.5^\circ$ (or $108.5^\circ$) for RH$_1$ (or RH$_2$).

In the viewpoint of statistical mechanics, all the discrepancies stated above as well as others mentioned in literatures [21, 22] should be settled down as long as the partition function (PF) can be obtained to produce the free energy (FE). Unfortunately, the exact solution to the PF of condensed matters is almost impossible because of the $3N$-fold configurational integral, and various approximations [23], such as the one in Ref. [13], were developed to calculate the FE without knowledge of the PF. As expected, those approximated methods provided lots of interesting information on the phase transitions of condensed matters, while may not address all the issues substantially.

Very recently, we put forward a direct integral approach (DIA) to the PF of condensed state systems with ultrahigh efficiency and precision [24-28], and has been successfully applied to reproduce the equation of state (EOS) for solid copper [25], argon [27] and 2-D materials [26] obtained from experiments or molecular dynamics simulations. Compared with phonon model based on harmonic or quasi-harmonic approximations, which is currently applied to produce EOS, DIA is applicable to much wider realm with much higher precision [28]. In the present work, DIA is used to compute the PF of crystal V with various phases and the derived Gibbs FE is applied to investigate the phase transitions induced by pressure at room temperature.

For a crystal containing $N$ atoms confined within volume $V$ at temperature $T$, the atoms are regarded as $N$ point particles of the atomic mass $m$ with Cartesian coordinate $\mathbf{q}^N = \{ \mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N \}$, and the total potential energy, $U(\mathbf{q}^N)$, as the function of $\mathbf{q}^N$ is computed by quantum mechanics, i.e., for a given set of $\mathbf{q}^N$, the total potential energy $U(\mathbf{q}^N)$ concerned with the motions of electrons in the field of the nucleus fixed at the lattice
sites is calculated by quantum mechanics. With knowledge of $U(q^N)$, the PF of the system reads

$$Z = \frac{1}{N!} \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3N}{2}} \int dq^N \exp[-\beta U(q^N)]$$

$$= \frac{1}{N!} \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3N}{2}} Q,$$

where $h$ is the Planck constant and $\beta = 1/k_B T$ with $k_B$ the Boltzmann constant. If the configurational integral $Q = \int dq^N \exp[-\beta U(q^N)]$ is solved, then the pressure $P$ and the Gibbs FE $G$ can be computed by

$$P = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Q,$$

$$G = \frac{1}{\beta} \ln \left[ \frac{1}{N!} \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3N}{2}} \right] - \frac{1}{\beta} \ln Q + PV.$$

In this way, the contributions from both the electrons and nucleus are included in the calculations.

According to our proposed DIA, for a single-component crystal with $N$ atoms placed in their lattice sites $Q^N$ and with the total potential energy $U_0(Q^N)$, we firstly introduce a transformation,

$$q'^N = q^N - Q^N, \quad U'(q^N) = U(q^N) - U_0(Q^N),$$

where $q^N$ represents the displacements of atoms away from their lattice positions, and then the configurational integral can be expressed in a one-fold integral,

$$Q = e^{-\beta U_0} \left[ \int e^{-\beta U'(q'_{i,x,y,z})} dq'_{i,x,y,z} \right]^{3N} = e^{-\beta U_0} L^{3N},$$

where $q'_{i,x,y,z}$ denotes the distance of the $i$th atom moving along the $x$ (or $y$, $z$) direction relative to its lattice site while the other two degrees of freedom of the atom and all the other atoms are kept fixed. As shown in Fig.1, we take BCC structure of V placed in a $3 \times 3 \times 3$ RH supercell as an example to illustrate the implementation of the DIA. The basis vectors of the primitive cell are set as $a_1 = a_{rh} \cdot (1,0,0)$, $a_2 = a_{rh} \cdot (\cos \alpha, \sin \alpha, 0)$, $a_3 = a_{rh} \cdot (\cos \alpha, -\cos \alpha, \sin \alpha)$, and the volume of the cell equals to $a_{rh}^3 \sqrt{1 - 3 \cos^2 \alpha + 2 \cos^2 \alpha}$ and the lattice constant of a cubic primitive cell. According to Eq. (5), an arbitrary atom is selected and moved 0.5 Å by a step of 0.05 Å along the direction of $a_1$ as shown in Fig.1(a) with the initial and final positions of the atom colored in blue. During the movement, the total potential energy is computed by the density functional theory (DFT) at every steps and the spline interpolation algorithm is used to smooth the $U'(x')$ curves, which are shown in Fig.1(b).

The DFT calculations is performed in Vienna Ab initio Simulation Package with the projector-augmented wave formalism, and the general gradient approximation of the Perdew-Burke-Ernzerhof parametrizations is adopted for the exchange-correlation functional with 13 valence electrons (3$s^2$3$p^6$4$s^2$) considered. A $\Gamma$-centered $9 \times 9 \times 9$ uniform $k$-mesh grid is set to sample the Brillouin zone by the Monkhorst-Pack scheme and the tetrahedron method with Blöchl corrections is used to determine the electron orbital partial occupancy, together with 342.7749 eV set as the cut-off energy of the plane-wave basis, $1 \times 10^{-6}$ eV as the convergence energy criterion of the electron self-consistent computations.

As shown in Fig.2, the isothermal $P$-$V$ curve derived from the PF via Eq. (2) coincides very well with the experiments, which can be seen from the relative difference (RD) between the theoretical volume ($V/V_0$)$_{PF}$ and the experimental one ($V/V_0$)$_{exp}$, defined as $\text{RD} = |(V/V_0)_{PF} - (V/V_0)_{exp}|/(V/V_0)_{exp}$, where $V_0_{PF}$ and $V_0_{exp}$ are the theoretical and experimental atomic volumes under ambient conditions (room temperature and one atmospheric pressure). In the low-pressure zone ($P < 20$ GPa), the average RD for all the shown experiments is about 0.25%, which can be seldom achieved in common theoretical work without using empirical data or empirical functionals.
FIG. 2. (Color Online) Isothermal $P$-$V$ curve of the BCC phase at 300K from the PF (red dash line) and the experimental data denoted in different colored symbols. The inset shows the detailed comparisons in the low-pressure zone.

EOS. In the higher-pressure zone ($P > 20$ GPa), the RD for all the experiments except for the one of Ref. [19] get a little larger with the pressure increasing, which may be attributed to the difficulty in precise measurements of higher pressure in considerations of the fact that the results of different experiments diverge larger with increases of the pressure (see the experimental points shown in the inset of Fig. 2). It is worthwhile to see that the RD for one of the latest experiments [19] (grey diamonds shown in Fig.2), covering the widest pressure range, keeps to be smaller than 0.7% except for three pressure points at 135, 176 and 240 GPa. Such an excellent agreement enables us to theoretically determine the lattice constant under exactly given pressure and temperature.

It should be pointed out that the implementation of DIA excludes all the artificial dependence of adjustable parameters, empirical EOS or experimental data, and accordingly, the good agreements between the theory and the experiments for the EOS and the lattice constant strongly indicate that the ensemble theory is the very approach to understand the thermodynamics properties of condensed matters.

To consider the transitions of crystal V from the BCC to RH phases with the angle $\alpha$ different from $\alpha_{\text{BCC}}$, the PF of four RH$_1$ and RH$_2$ phases with the angle deviation, $\Delta = (\alpha_{\text{RH}} - \alpha_{\text{BCC}}) / \alpha_{\text{BCC}}$, $\pm 0.1\%$, $\pm 0.2\%$, $\pm 0.5\%$ and $\pm 1\%$ is solved by the DIA in the same way as described above (see potential-energy curves of the RH phases in supplementary material), and, the derived Gibbs FE differences between the RH and BCC per atom, $G_{\text{RH}} - G_{\text{BCC}}$, are shown in Fig. 3(a). When the amplitude of the angle deviation, $|\Delta|$, equals to 0.1%, the Gibbs FE of both RH$_1$ and RH$_2$ is close to $G_{\text{BCC}}$, and increases abruptly to be larger than $G_{\text{BCC}}$ by more than 120 meV/atom with the $|\Delta|$ increased by only 0.1%, while further increasing the angle deviation leads to a little changes of $G_{\text{BCC}}$. These results show clearly, based on the Gibbs FE criterion, that the phase transition with the angle equal to or larger than 0.2% cannot take place unless the deviation being smaller, and furthermore, Fig. 3(b) indicates that the two phases, RH$_1$ with a deviation of 0.1% and RH$_2$ with a deviation of $\sim$0.1%, would emerge when the pressure is larger than 20 GPa. It is interesting to note that the phase transition was very recently examined by Stevenson et al. [20] who concluded that two kinds of phase transitions, BCC$\rightarrow$RH$_1$ and BCC$\rightarrow$RH$_2$, indeed take place, qualitatively coinciding with the previous experiments or theories, and the determined RH angle for RH$_1$ (or RH$_2$) is 109.5$^\circ$ (or 109.35$^\circ$), corresponding to $|\Delta| \sim 0.1\%$ as our theoretical results, which is a little smaller than the one, 109.65$^\circ$ for RH$_1$, measured in previous experiments [6, 7], where RH$_2$ was not observed, but significantly different from the theoretically predicted 110.5$^\circ$ (or 108.5$^\circ$) [12-14], corresponding to $|\Delta| \sim 1\%$. Since the unique difference between BCC and RH$_1$ (or RH$_2$) phase is the RH angle deviation of about only 0.1%, it should be quite a challenge for experimental observations of the subtle difference, which may be the reason why early literatures reported no phase transitions for V induced by pressure less than 220 GPa [6].

Now we make a detailed comparison between our theoretical results and the experimental observations. As shown in Fig. 3(b), the Gibbs FE of the RH$_1$ and RH$_2$ differ from that of BCC less than 1 meV, which is much smaller than the average kinetic energy, $\sim 30$ meV, of a thermal atom at room temperature, and it seems that RH$_1$ or RH$_2$ is just the thermal fluctuation from the BCC structure instead of a phase transition. Actually, the very “driving force” accounting for the phase transition under given pressure and temperature is not the thermal kinetic energy (or internal energy), but instead, the Gibbs FE that determines the probability for a given phase existence. According to ensemble theory, the relative probability for RH with respect to BCC equals to $e^{(G_{\text{BCC}}-G_{\text{RH}})/k_B T}$, where $G_{\text{BCC}} = N G_{\text{BCC}}$, $G_{\text{RH}} = N G_{\text{RH}}$, and $N$ the number of the atoms in a piece.

| Ref. | DIA | Ref. [9] | Ref. [11] | Ref. [19] | Ref. [20] |
|------|-----|----------|----------|----------|---------|
| $a_c$ (Å) | 3.008 | 3.029 | 3.03 | 3.027 | 3.023 |
| Deviations | / | 0.693% | 0.726% | 0.627% | 0.496% |
| EOS | / | B-M | no report | Vinet | AP2 |

TABLE I. The lattice constant $a_c$ of BCC phase at ambient conditions calculated by DIA and from experiments fitting empirical EOSs, Birch-Murnaghan (B-M), Vinet and AP2.
The above discussions show that most results of our calculation coincide well with the experiments, especially the EOS, the angle deviations of the RH and some results calculated by previous computations, were observed by Akahama et al. very recently at 242 GPa. The agreements with experimental measurements and observations, such as the theoretical phase transition under ~ 20 GPa, which was not reported in all the experiments, may be settled down by future experiments.

In conclusion, the rigorous ensemble theory is applied, for the first time, to investigate phase transitions of crystalline V via DIA solving the PF without any artificial tunable parameters or empirical EOS, achieving very good agreements with experimental measurements and observations, and showing that the theory is substantial to describe phase transitions of condensed matters. The theoretical approach of this work may find its vast applications in the field to predict parameter-free EOS and phase behaviors of condensed matters under extreme conditions.

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of macro bulk crystal is on an order of 10^{23}. Thus, our calculation results indicate clearly that the phase transition BCC → RH2 must take place at room temperature when the pressure is larger than 18 GPa, and then RH1 emerges at 28 GPa. This RH1 transition was observed by Jenet et al. at 32 GPa and by Daniele et al. at 35 GPa, respectively. As the pressure increasing, our results show that RH2 would emerge at ~ 44 GPa, then transforms back to BCC for the pressure larger than 50 GPa until RH1 emerges at 61 GPa, displaying a transition process, RH2 → BCC → RH1, with the pressure increased. Experimentally, Akahama et al. observed a RH phase comes to existence from 45 GPa, and the BCC → RH1 transition was reported at 63 GPa in Ref. 6, 60.5 GPa in Ref. 8 and 64 GPa in Ref. 9, which are all in a good agreement with our results, in considerations of the deviations among the measured pressures being of ~ 2 GPa. It is noticeable that the RH2 → BCC → RH1 transition sequence, neither observed in earlier experiments nor proposed by previous computations, was observed in the one of the latest experiments [20], and the measured transition pressure of RH2, 40 GPa, coincides with our theoretical one, 44 GPa. When the pressure is increased larger than 132 GPa, our results indicate that RH1 would exist until RH2 transition occurs at 154 GPa and the RH2 phase keeps stable with the pressure up to 254 GPa, over which the BCC may coexist with RH2 until the pressure increases up to 280 GPa when BCC becomes the most stable for higher pressures. It is very interesting to note that this coexistence phase of RH2 and BCC, never reported in previous literatures, was observed by Akahama et al. very recently at 242 GPa.

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In conclusion, the rigorous ensemble theory is applied, for the first time, to investigate phase transitions of crystalline V via DIA solving the PF without any artificial tunable parameters or empirical EOS, achieving very good agreements with experimental measurements and observations, and showing that the theory is substantial to describe phase transitions of condensed matters. The theoretical approach of this work may find its vast applications in the field to predict parameter-free EOS and phase behaviors of condensed matters under extreme conditions.

FIG. 3. (Color Online) (a) Gibbs FE of RH phases relative to BCC phase at room temperature up to 170 GPa and (b) the data for RH phases with ±0.1% · α_{BCC} for clarity.
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