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B. Lee, R. E. Rudd, J. E. Klepeis, R. Becker

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Elastic constants and volume changes associated with two high-pressure rhombohedral phase transformations in vanadium

Byeongchan Lee, Robert E. Rudd,[*] John E. Klepeis, and Richard Becker

Lawrence Livermore National Laboratory, Livermore, California 94551

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We present results from ab-initio electronic-structure calculations of mechanical properties of the rhombohedral phase of vanadium reported in recent experiments (R Ia), and other predicted high-pressure phases (R Ib and bcc), focusing on properties relevant to dynamic experiments. We find that of the three transitions the largest volume collapse (1.3%) is for the R Ia to R Ib transition. Calculations of the single crystal and polycrystal elastic constants reveal a remarkably small discontinuity across the phase transitions even at zero temperature where the transitions are first order.

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The existence of a high-pressure rhombohedral (R I) phase of pure crystalline vanadium has been the focus of an intense research effort recently. The first indication of a phase transition came from the theoretical observation that the C_{44} shear modulus of bcc vanadium diminishes under pressure,[1,2] becoming negative at pressures of greater than $\sim$1.3 Mbar, pressures that are experimentally accessible.[1,2] A negative shear modulus means the material is mechanically unstable under monoclinic (prismatic) shear, suggesting a phase transition. At that time the experimental evidence showed no phase transition up to 1.54 Mbar.[3] Then recently, Mao and coworkers[4] conducted x-ray diffraction experiments in the diamond anvil cell (DAC) up to 1.5 Mbar and found features in the diffraction peaks that were consistent with a second-order phase transformation to a rhombohedral structure with an $R\bar{3}m$ point group symmetry at pressures above 0.69 Mbar. It was soon confirmed that density functional theory (DFT) finds the rhombohedral phase to be the ground state at zero temperature and pressures above 0.8 Mbar, in reasonably good agreement with experiment.[5] In fact, it was shown that DFT predicts additional phase transformations that had not been found in experiment, i.e. a first-order transformation to a different rhombohedral structure at 1.2 Mbar and a third transformation back to the bcc structure at 2.8 Mbar.[5] These pressures have not been reached in the recent DAC experiments.

Alternative techniques may provide the pressures needed to observe the second rhombohedral phase and the reentrant bcc phase. Dynamic experiments do not rely on the mechanical integrity of anvils and are able to reach multi-megabar pressures. They have been used to study similar transformations such as the diffusionless alpha-epsilon transition in iron.[6] There are several challenges specific to vanadium, however. The softening of the shear modulus and the rhombohedral phase transition are related to a subtle electronic effect,[2] which is likely to be weakened by increased temperature. Dynamic experiments that generate shocks cause substantial temperature rises. Recent ramp wave techniques based on Z,[7] laser[8,9] and graded-density impactor[10]

drives are able to generate high pressure without the entropy generation of a shock, and are therefore preferable. Another challenge is that the lattice distortion at the phase transition is subtle (less than half a degree). It was detected by x-ray diffraction in the DAC, but it is probably too small for in-situ x-ray diffraction in dynamic experiments.[11] Indirect techniques are more promising to detect the transition. For example, VISAR free-surface velocity measurements can detect changes in the density due to a volume collapse, and they can be used to infer the longitudinal stress, and hence the strength if the equation of state is known.[9,12] Rayleigh-Taylor growth rate is another way to probe strength.[8]

In this article we use DFT to make predictions about the properties of high-pressure vanadium relevant to dynamic experiments. We compute the magnitude of the volume change associated with the three phase transitions related to the rhombohedral structure. We also compute the elastic constants and calculate bounds on, and an explicit estimate of, the polycrystalline shear modulus. Since the strength is roughly proportional to the shear modulus,[13] any anomalies in the shear modulus are likely to provide a signature in the VISAR trace. Indeed, an important motivation for the present work is to assess whether the bcc shear modulus C_{44} going to zero is likely to produce a strong signature. The shear modulus also affects defect energetics, and may have a measurable effect on transition kinetics. We consider the implications of our results for dynamic experiments to detect the high-pressure phases.

The rhombohedral crystal structure of vanadium results from a slight distortion of the bcc structure. Consider an atom in the bcc structure and three of its nearest neighbors arrayed symmetrically about a three-fold crystal axis ($\langle 111 \rangle$ in the bcc crystal). The angle formed between any two of these neighbors is $\alpha_0 = \arccos(-1/3) = 109.47°$. Now imagine the crystal strained uniaxially in the direction of this three-fold axis such that these vectors are pushed symmetrically in (out) so that the angles between the pairs decrease (increase) remaining equal. The resulting crystal retains the three-fold symmetry axis. It is the rhombohedral structure (R I). It still
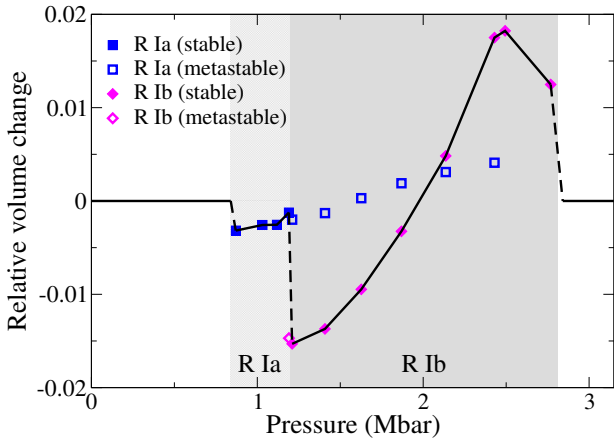
FIG. 1: The volumetric strain $\Delta V/V$ of the ground state of single-crystal vanadium at zero temperature with respect to that of the bcc structure.

has a single atom per unit cell, so the bcc - R I transition may be expected to be diffusionless (martensitic) and likely rapid despite the small energy difference. There are four independent three-fold axes $\langle 111 \rangle$, so there are four variants of the rhombohedral crystal that are degenerate in energy (unless a shear stress is applied).

The ground state of the single-crystal rhombohedral phase has been determined in DFT using this rhombohedral shear path.[5] The specific approach here as in our previous calculations is to use DFT in combination with a gradient-corrected exchange and correlation energy functional[15] as implemented in the Vienna Ab-initio Simulation Package (VASP) code along with the projector augmented-wave (PAW) method[16] and standard computational parameters.[17] In Ref. 5, we calculated the enthalpy and pressure as functions of strain along the rhombohedral deformation path, and used the enthalpy to find any stable or metastable crystal structures. We noted that the equation of state in the bcc and rhombohedral phases is almost identical, so their bulk moduli are essentially equal (differing by no more than 3%). We now use those data to determine the volume change associated with the corresponding phase transformations. Suppose the pressure change in going from phase 1 to phase 2 at constant volume is $\Delta P_{12} = P_2 - P_1$ and the bulk modulus of phase 2 is K. Then the volumetric strain induced by changing the pressure in phase 2 to P_1 is

$$\frac{\Delta V}{V} = \Delta P_{12}/K. \qquad (1)$$

This relative volume change is plotted in Fig. 1.

In principle, there is a single volume change during the transformation from bcc to the first rhombohedral phase (R Ia), and a second volume change associated with the transformation to the second rhombohedral phase (R Ib), and a third volume change associated with the transformation back to bcc at high pressure. In practice, the kinetics of the transformation may cause the transformation to be overdriven so that the initial phase is retained

in a metastable state past the phase boundary until the new phase has a chance to nucleate and grow. For this reason it is interesting to examine the entire curve in Fig. 1, and not just the values at the equilibrium phase boundary.

In each case it is a volume collapse, so the volume is reduced following the transition. The volume collapse associated with the bcc to R Ia transformation is small, 0.3% or less in magnitude. It would not be easy to detect such a small change in a dynamic experiment. The magnitude of the volume collapse associated with the second transformation is larger: about 1.5% for the R Ia to R Ib transformation at 1.2 Mbar. The volume change would be about the same if bcc were retained to a pressure of $\sim$1.2 Mbar and then transformed directly to R Ib. This change is not as great as in the alpha-epsilon transition in iron, but it may be large enough to detect. The final transition back to bcc again has a change of over 1% in magnitude. So the R Ia to R Ib transformation has the strongest signature in terms of volume change, and it is large enough that it may be detectable.

We next consider how the single crystal elastic constants change with pressure. The elastic constants of the bcc structure as a function of pressure have been calculated previously,[2] but those of the rhombohedral structure have not. Specifically, we calculate $B_{ijkl}(P)$, the elastic constants with respect to the reference state at pressure P and zero shear stress. They are equal to C_{ijkl} when the pressure vanishes; for $P \neq 0$, the relation is[20]

$$B_{ijkl} = -P(\delta_{jl}\delta_{ik} + \delta_{il}\delta_{jk} - \delta_{ij}\delta_{kl}) + C_{ijkl} . \qquad (2)$$

The details of the calculation of the elements B_{ijkl} will be given elsewhere.[21] The six independent elastic constants, B_{11}, B_{33}, B_{12}, B_{13}, B_{44}, and B_{66} (here given in the usual Voight notation in the rhombohedral frame with the three-fold axis in direction 3), are discontinuous at the first-order phase transitions; however, within each domain of stable phases (bcc, R Ia, R Ib, and reentrant bcc), most of the elastic constants increase monotonically. The exception is B_{33} in the R Ib phase (roughly 1.1 – 2.8 Mbar). Since B_{33} is associated with uniaxial deformation in the direction of the three-fold axis, its anomalous behavior is suggestive, but a better presentation is needed to separate the effects of shear and compression. We turn to it now.

Indeed, there is a remarkable approximate continuity of the elastic properties across the phase transitions that is not readily apparent from the elements of B_{ijkl}. The bulk modulus of the rhombohedral phases is within 3% of that of the bcc structure, as we already discussed. The eigenvalues of the 9×9 matrix $B_{(ij)(kl)}$ provide a description of the elasticity that is less coordinate dependent, but there is a technical issue. In the rhombohedral phase, shear and compression are mixed in the sense that a non-equiaxed strain is required to produce purely hydrostatic pressure, and the tetragonal strains to produce hydrostatic pressure and pure shear are not orthogonal. To eliminate any ambiguity, we restrict to the space of con-
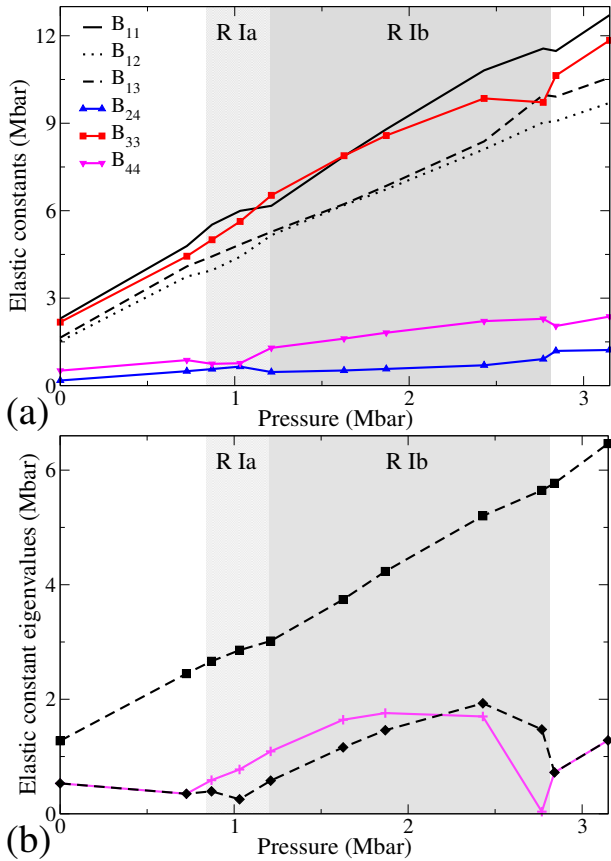
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FIG. 2: The elastic constants of the ground state single-crystal structure–bcc, R Ia, R Ib, and reentrant bcc–as a function of pressure; (a) B_{ijkl} written in the Voight notation in the frame of the primitive rhombohedral cell, and (b) the corresponding eigenvalues of the 9×9 elastic constant matrix B_{ijkl}. In the rhombohedral phase there are six independent elastic constants (vs. 3 for bcc),[20] and four independent eigenvalues for vanadium metal (dashed curves represent 2 degenerate eigenvalues). Remarkably, both the ground-state bulk modulus (the top curve) and the B' (the second curve from the top) are fairly smooth through the rhombohedral phase.

stant pressure strains using a projection matrix $\Pi_{(ij)(kl)}$. Then the 9×9 matrix $\Pi B \Pi$ has 5 nontrivial eigenvalues, corresponding to different shear moduli.

The eigenvalues are plotted in Fig. 2(b). The top curve represents two degenerate eigenvalues that are equal to $2B'$ in the bcc phase, where B' is the usual shear modulus for tetragonal shear in the cubic crystal. The remaining three eigenvalues are degenerate in the bcc phase and equal to $2B_{44}$, where B_{44} is the shear modulus for prismatic shear in the cubic crystal (not to be confused with the B_{44} in the rhombohedral frame). In the rhombohedral phase two of these eigenvalues remain degenerate but one splits off. That single eigenvalue represents a pure shear corresponding to the rhombohedral deformation. Its value is decreasing to zero as the pressure in the rhombohedral phase approaches the bcc phase boundary. This decrease is most pronounced approaching the high-

pressure reentrant bcc phase (2.8 Mbar), but it is present at both. In the energy curves, it is clear that the width of the rhombohedral well is broadening with the change in pressure as it rises above the bcc well and quickly becomes unstable. At the R Ia – R Ib boundary, it is the other B_{44}-like moduli, the paired modui, that are approaching zero, although interestingly the R Ia structure remains metastable with an order parameter that goes smoothly to zero at $\sim$2.7 Mbar.[5]

In polycrystalline vanadium the single-crystal elastic constants are homogenenized into effective elastic constants. In the case of a microstructure without texture, the mechanical behavior is isotropic, and there are only two independent elastic moduli: the bulk modulus K and the shear modulus G. The bulk modulus is very close to that of the bcc phase as mentioned earlier. The shear modulus may be bounded using the Voight and Reuss approximations of constant strain and constant stress, respectively. In the Voight approximation the shear modulus is expressed in terms of the two rotational invariants of the elastic constant tensor, $I_1 = B_{ijij}$ and $I_2 = B_{iijj}$ where the repeated indices are summed. In the Reuss approximation the shear modulus is expressed in terms of the two rotational invariants of the elastic compliance tensor, $I'_1 = S^B_{ijij}$ and $I'_2 = S^B_{iijj}$. In particular, the respective shear moduli are given by[18]

$$G_V = \frac{1}{30}\left(3B_{ijij} - B_{iijj}\right); \quad G_R^{-1} = \frac{1}{15}\left(6S^B_{ijij} - 2S^B_{iijj}\right)$$

where the elastic compliance tensor S^B_{ijkl} is defined as usual[19] except expressed in terms of the B_{ijkl} elastic constants rather than C_{ijkl}. The expression for the shear modulus in the Voight approximation in terms of the independent rhombohedral elastic constants is

$$G_V = \frac{1}{30}\left(7B_{11} + 2B_{33} - 5B_{12} - 4B_{13} + 12B_{44}\right). \quad (3)$$

The Reuss expression is too long to be presented here.[21] In calculating the Voight and Reuss approximations (as well as the explicit polycrystalline calculations below), we assume that the deformations are infinitessimal. With the low energy barriers, switching between variants of the rhombohedral phase may contribute to the strain with no cost in stored elastic energy, leading to a reduction in the shear modulus. At larger strains the response to rhombohedral strains stiffens anharmonically. Both of these effects have been neglected. The homogenized shear modulus in the rhombohedral phase is positive (see Fig. 3), indicating mechanical stability. The variation in the difference between the Voight and Reuss bounds is indicative of the changing crystalline anisotropy.

In the case of a microstructure with more equiaxed grains, the polycrystalline shear modulus is homogenized from the single-crystal B_{ijkl} of the ground state structure at each pressure using a virtual test sample (VTS).[22] The finite element VTS is a cube of 1000 grains with random texture, strained in six different modes to get the average
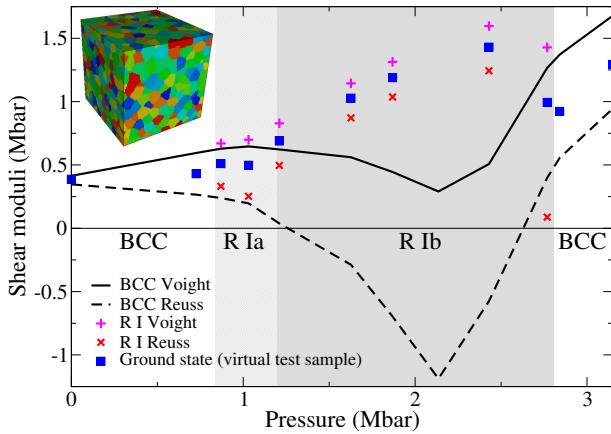
FIG. 3: The polycrystalline shear modulus as a function of pressure, along with the Voight and Reuss bounds for the case of no texture. This shear modulus is based on the elastic constants B_{ijkl} of the ground state single-crystal structure–bcc, R Ia, R Ib, and reentrant bcc (see Fig. 2 (a)). The inset shows the cubic virtual test sample with 1000 grains (100 μm wide in each direction) used in the polycrystalline shear modulus prediction (color indicates grain orientation).

shear modulus plotted in Fig. 3. The overall prediction lies between the Voight and Reuss bounds, but it gives a better value for the shear modulus especially in the region just prior to the R Ib-to-reentrant bcc transition, where the Voight-Reuss difference is as large as 1.34 Mbar. Also around this transition, the predicted polycrystalline shear modulus significantly decreases, and may lead to an anomalous dynamic response.

We have investigated some of the properties relevant to dynamic experiments of two high-pressure rhombohedral phases in vanadium metal. It will be challenging for dynamic experiments to detect the rhombohedral phase unambiguously. The distortion is probably too small for in-situ x-ray diffraction. We have predicted that the volume change of the initial rhombohedral phase (0.3%) is too small to have a clear effect, but the volume change associated with the second transition, rhombohedral to rhombohedral, is larger (1.5%) and may present a signature in the VISAR trace or in wave transit times. We have also predicted values for the single crystal and polycrystalline elastic constants in the rhombohedral phases at zero temperature. The first order transitions between the bcc and rhombohedral phases give remarkably small changes in the elastic constants.

The results here were obtained using DFT at zero temperature for pure vanadium. Since the phase transition is driven by a rather subtle electronic structure effect, the elastic constants may be substantially affected by changes in temperature or impurities.[2,5] It would be interesting to see whether the remarkable continuity of the moduli persists as the phase boundaries and the relative stiffness of the bcc and rhombohedral structures change.

Acknowledgments

[*] Electronic address: robert.rudd@llnl.gov

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