High temperature equation of state of vanadium

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Abstract

The unit cell dimensions of vanadium, NaCl and Au have been collected to 11. 5 GPa and 1000 K by powder x-ray diffraction and are used to constrain a practical high temperature EoS for *bcc* vanadium. The resulting 3rd-order Birch-Murnaghan EoS is described with parameters $K_{T0,300}$ = 150.4 +/-6.2 GPa, K_T' = 5.5 +/-1.0, α_0 = 4.8(6)$\cdot10^{-5}$, α_1 = -2.4(9)$\cdot10^{-8}$ and $\delta K_T/\delta T$ = -0.0446(7) GPa/K. The parameter $\alpha.K_{0,300}$ is 616$\cdot10^{-5}$ K$^{-1}\cdot$GPa and reduces to zero at an estimated 60 GPa at RT. This EoS description is entirely consistent with the majority of x-ray, ultrasonic, shock wave and calculated datasets in this *p*, *T* range. These measurements facilitate the estimation of in situ temperatures under high pressures when vanadium is used inside sample assemblies and is useful, when used with *h*-BN, to estimate *p*, *T* over the full range of *h*-BN stability.

Keywords: vanadium, high pressure, equation of state, diffraction

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Introduction

The estimation of pressures and temperatures of *in situ* data sets can be achieved through the simultaneous numerical solution of the equations of state of materials with contrasting compressibilities and thermal expansivities when they are included within the sample assembly and their densities determined by, for instance, x-ray diffraction; *e.g.* Crichton and Mezouar (2002). Constraints on the selection of materials that form the couple could include the lack of phase transitions, low absorption, simple diffraction pattern, etc. They would typically be a ceramic and metal couple such as NaCl or MgO mixed with Au or Pt. In the search for more refractory materials that are easily worked and relatively cheap we have identified that vanadium can be advantageously used as a furnace and capsule material due to its high melting temperature, low x-ray absorption and very simple, small-lattice *bcc* structure that contributes little to the diffraction pattern. It also sees considerable use in neutron experiments due to its low contribution to any elastic scattering and by being non-magnetic. However, one handicap for extending its use as a higher temperature *p*, *T* couple (e.g. with *h*-BN) for pressure and temperature estimation is the absence of a description of its lattice dimension in the high temperature, pressure domain.

Vanadium had been relatively little studied under high pressures compared to other transition metals until a phase transition was recently proposed as being due to the onset of a mechanical instability in its elastic constants (c_{44}) at unexpectedly low pressures (Landa *et al*, 2006*a*, 2006*b*; Suzuki and Otani, 2007). This was investigated experimentally and a rhombohedral lattice was identified from x-ray diffraction measurements at 69 GPa (Ding *et al.*, 2007). First-principles calculations established this transition (Lee *et al.*, 2007; 2008; Veerma and Modak, 2008), and a reentrant *bcc* phase at 280 GPa has been proposed (Luo *et al.*, 2007). These have been supplemented by phonon dispersion and electronic structure calculations that highlight several anomalies linked to instabilities and superconducting behavior (Bosak *et al.,* 2008). The transition pressures to rhombohedral and *bcc* structures have been further refined as 60 GPa and 310 GPa

(Landa, 2006b). Other x-ray diffraction studies have investigated the effect of non-hydrostaticity on the transition pressure (Ding *et al.*, 2007; Jenei *et al.*, 2011). The elastic properties and bulk moduli have been experimentally determined by numerous methods (McQueen and Marsh, 1960; Bolef *et al.*, 1971; Ming and Manghnani, 1978; Gathers, 1986; Takemura, 2002; Nakamoto *et al.*, 2005; Ding *et al.*, 2007; Jenei *et al.*, 2011; Yu *et al.* 2014). The thermal expansivity (Westlake, 1967; Bolef *et al.*, 1971; Touloukian *et al*, 1975; Wang and Reeber, 1998) is well-documented and discussed. Theoretical investigations into its thermodynamic properties have been illustrated by the work of Sha and Cohen (2007), Koci *et al.* (2008), Karbasi *et al.* (2011) and references therein.

We complement this database with the measurement of the lattice volumes of vanadium together with the NaCl:Au couple, and from these data determine a practical EoS description that can be used to estimate lattice parameters, pressures or temperatures at non-ambient conditions. Using a description of $(\alpha.K)_{p,T}$ *i.e.* the product of the thermal expansion and the bulk modulus, which is equivalent to $(\delta p/\delta T)_V$, we can also demonstrate a contrast in values for that between V and *h*-BN the fitted *p*, *T* range. This contrast will affect how unique a solution for cross-calibrated EoS in *p*, *T* space will be.

Experimental

Vanadium foil, with 0.020 mm thickness was obtained and used as delivered, from Advent. This was cut into rough 0.3 mm strips (Figure 1), crumpled and pressed with NaCl:Au (Goodfellow) oven-dried powder mix into an *h*-BN (Goodfellow) capsule (1.9 mm OD, 1.2 mm ID). This was loaded in a 10 mm sintered Cr-doped MgO octahedron (Ceramic Substrates) with a 2.5 mm external diameter cylindrical graphite furnace (Mersen). The furnace included the 2.5 mm-long capsule, a ZrO_2 rod (Ceramic Substrates) at each end and was capped with a 0.25 mm thick Mo disk, which served as the furnace contact with the anvils. The assembly was windowed with a low-*Z* amorphous compound

(TU Freiberg) and gasketed with pyrophyllite and B:epoxy along the beam direction. These assemblies were compressed with 25 mm carbide cubes (Hawedia), with a 5.0 mm edge-length truncation and 7 mm spacer plates inside the 60 mm edge-length primaries of the 20 MN large-volume modified cubic press at ID06 of the ESRF.

The data collection was in angle-dispersive mode using x-rays with an energy of 55 keV (λ = 0.2254 Å) selected by Cinel double-crystal Si111 monochromator from the emission of a u18 undulator at 6.05 mm gap. Diffraction data were collected through the horizontal anvil gap on a Detection Technology GOS linear detector with 0.2 mm pixels located at approximately 2052 mm from the sample, in a similar manner to Guinard and Crichton (2015). Precise calibration of the detector was ensured using SRM660a and Fit2D (v17; A. Hammersley, ESRF), written for polar data collection, and the raw pixel data were treated using the same to produce regular 2θ-intensity diffraction patterns. Sequential data were fitted using the M-FIT routine, within Fit2D, which produced arrays of 2θ positions for selected NaCl, Au and V peaks. The sample pressures and temperatures were estimated by the PTX-Cal code (Crichton and Mezouar, 2002), using 2θ-derived lattices for the couple, by searching for a numerical solution of quasi-unique pressures, within a $|(P_{NaCl}-P_{Au})_T|$ = $<10^{-6}$ GPa tolerance, while scanning T-space. This effectively limits acceptable solutions for $P(V_{NaCl},V_{Au})_T$ to a range of roughly 0.5 K, which is safely less than propagating errors in fit through lattice determination and the coupled EoSs. For ambient temperature, pressure data solution temperatures are returned within this range at T_{ref} = 300 K. The average of returned values for solved p and T were used together with lattice volumes for vanadium at each datum to fit parameters of a Birch-Murnaghan equation, using a linear expression for the variation of $\alpha(T)$ with T, with EOS-FIT5 (Angel, 2002).

The p, V, T set was collected after first increasing pressure with individual collections at 50 W increments until recrystallisation of the NaCl:Au couple became significant. After heating, the furnace power was ramped to 0 in about 15 seconds. This was repeated with increasing load-steps

to a maximum of about 11.5 GPa. The sample was then decompressed to minimum overpressure to retain furnace contact and a last cycle was completed, at which point the sample had relaxed to ambient. In each case the total exposure time was 3.2 sec per datum, corresponding to 32x bin of 0.1 second individual exposures. Data in the first compression, to about 600 K, were evidently not in the trend of the remainder of the p, V, T dataset. This was assumed due to inherited stress from foil fabrication which was subsequently removed during the first-cycle of annealing. It is therefore recommended to anneal foils before use.

Results

An unconstrained fit of all EoS parameters against the 62 p, V, T unweighted data by EOSfit5 resulted in $K_{0,300}$ = 150.4 +/- 6.2 GPa, K' = 5.5(10), α_0 = 4.8(6)$\cdot 10^{-5}$, α_1 = -2.4(9)$\cdot 10^{-8}$ and $\delta K_T / \delta T$ = -0.0446(7) GPa$\cdot$K^{-1}. The product $(\alpha . K)_{0,300}$ = 616 10^5 K^{-1}·GPa, and reduces with T to zero at 2000 K and, with p, at 61.5 GPa, both through the influence of the estimated $\alpha_{\boxed{\boxed{\boxed{}}}}$ tending to 0. The identity $(\delta \alpha / \delta p)_T$ = $(\delta K / \delta T)_p K^{-2}_T$ and is then estimated at -2.0$\cdot 10^{-6}$ K^{-1}·GPa^{-1}. The unconstrained V/V_0 was 1.005(1), and is fortuitously identical to the relaxed final run value of V/V_0 = 1.005 (or 27.995 Å^3), but which was not included in the fit. These p, V, T data and the selected derived isotherms in p, V/V_0 space are illustrated in figure 1, together with observed p, T data within 20 K of each estimated isotherm. In order to draw closer comparison with other determined values, fits to 3rd-order equations were conducted with K' fixed at appropriate values. Fixing K'= 3.5 results in K_T = 160.5 +/- 3.5 GPa, which is within error equivalent to that obtained by Takemura (2002) at K_T = 162(5) and, at K' set to 4, the K = 157.9 +/- 3.5 GPa is comparable with Ding *et al.* (2007)'s K_T = 158 GPa, K'= 3.9 and with the Nakamoto *et al*. (2005) value of K = 152.1 GPa, K'= 4.1. These values are also compatible to those highlighted and obtained by Ming and Manghnani (1978) of K_S = 155.6 GPa, K' = 4.27 (ultrasonic), K_S = 157.0 GPa, K' = 3.5 (shock) and K_T = 154 GPa (x-ray, also plotted in Figure 2) combined with K' = 4.27 (fixed by ultrasonic), and from the elastic constant data, K_S = 157.12 GPa at 300 K (and 159.81 GPa at 4.2 K, ultrasonic) of Bolef *et al.* (1971). Our value, and these here, are distinct from that of

Jenei *et al.* (2011) at 179 +/- 8 GPa and the purposefully nonhydrostatic values of 195 GPa of Ding *et al.* (2007). The CALPHAD database values collated in Karbasi *et al.* (2011) indicated a preferred K_0 = 162 GPa and K' = 3.5 from available cold compression data and are considerably different from those of Koci *et al.* (2008), at K = 182 GPa, K'= 3.7. An estimate of the bulk modulus of vanadium (Z = 23) from tabulated values of Nb (Z = 41, 170 GPa) and Ta (Z = 73, 200 GPa) would be in the region of 153 GPa. Any value for $\delta K/\delta T$ above ambient temperature is only available from calculation. From Sha and Cohen (2007), which are cited as compatible (at T_{calc} = 250 K) to the cold compression volumes of Takemura (2002) and Ming and Manghnani (1978), we can estimate a linear $\delta K/\delta T$ of -0.037 GPa·K^{-1} for temperatures above ambient conditions. The values here obtained for α_0 and α_1 to derive $\alpha(T)$ are about 50% higher than those expected from the linear thermal expansivity of vanadium of 8.3·10^{-6} m·m^{-1}·K^{-1}. This difference, however, is suppressed within the range of our observations where most, but not all, are above Θ_D. For typical sample assemblies, at pressures of between 8 and 12 GPa the contrast in between the behaviour of BN and V (estimated through the identity $(\delta p/\delta T)_V = \alpha K$, Figure 3) reduces to a factor of 4 (from 6 at ambient). At p > = 10 GPa, at T > 1000 K, αK of *h*-BN is expected to be nil as the thermal expansivity, estimated from the expansion of *h*-BN at ambient (Pease, 1952) other EoS parameters of Le Godec *et al* (2000), tends to 0 and no reliable solution for *p, T* will be found. By this point, though, we may expect *h*-BN to have transformed to *w*-BN. Therefore, V and *h*-BN can be used while *h*-BN remains present at high *p, T*. Extension to higher *p, T* conditions will require changes in capsule materials; to *e.g.* CsCl.

Conclusion

We have determined here a practical description of the lattice size of vanadium at high temperatures and pressures to ~11 GPa for the purposes of internal calibration of high pressures and temperatures during x-ray-based experiments. The EoS description obtained is consistent with the majority of ambient temperature x-ray, shock and ultrasonic data in the literature. There are clear advantages to using vanadium in neutron-based studies as chambers and sample holders but

its use in x-ray based studies is currently limited. Nonetheless, we have successfully used vanadium as both capsule material and furnace. Vanadium being a first-row transition metal, with a range of valence states possible, it is reactive and will oxidise in air upon heating to produce V_2O_5 (or a range of other oxide forms with more limited supply) and following typical production methods, it will react with Na-sources (such as halides and carbonates) at high temperature to produce $NaVO_3$ under oxidising conditions. It is therefore incompatible, for instance, with syntheses that make use of oxygen sources such as Na_2O_2 and $NaClO_4$. It is not anticipated that these will detract from its more general use in the typically reducing environment of the high-pressure assembly, though some care in material selection and compatibility is warranted. For its use as a p, T couple, any temperature can be estimated at low pressures with the expectation of precision intermediate to that of Au and Pt: V will expand by 2.7% compared to 3.4% and 2.1% for Au and Pt from 300 to 1000 K at pressures close to ambient. At higher pressure, as be seen from Figure 2, the reduction in thermal lattice expansion with pressure increase is an important consideration and vanadium effectively becomes approximately half as effective a marker as Au, and is degraded compared to the significantly stiffer Pt. For instance, $1-(V_{1000K}/V_{300K})_{10\ GPa}$ = 2.3% [Au]; 1.6% [Pt] compared to 1.2% [V], at 10 GPa. However, Au will have recrystallised by 1000 K, and Pt by 1300 K, while cross-calibration using V can be amply extended well-beyond these temperatures.

Acknowledgements

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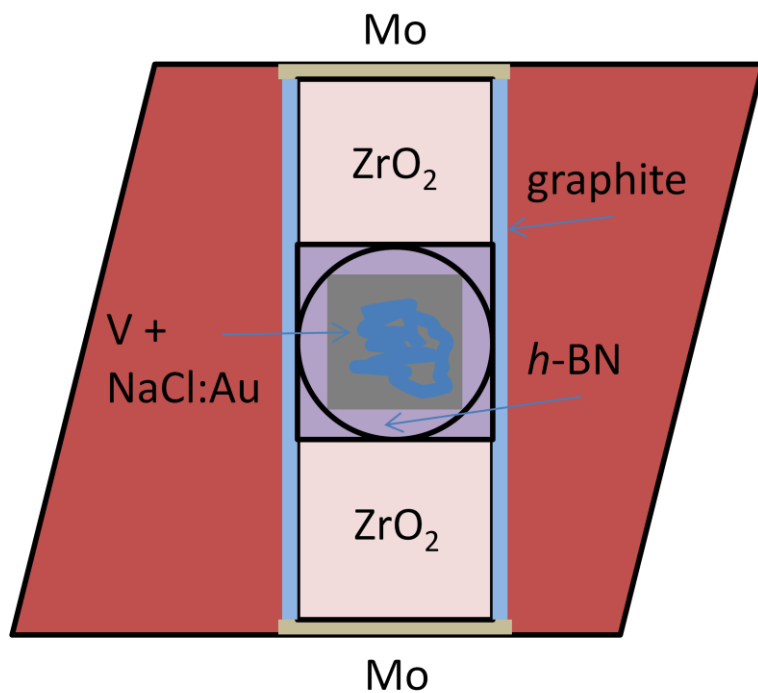
Figure 1. Basic assembly for the measurement of the *p*, *V*, *T* data for NaCl:Au + V foil. The Cr-doped octahedron is drilled to contain the furnace column, which includes a zirconia plug at each end and an h-BN capsule. Inside the capsule is pressed a sample of powder mix of Au and NaCl and crumpled V foil strips. The circle about the sample indicates the position along the beam axis of the amorphous ceramic x-ray window. The furnace is terminated at each end by Mo disks to avoid graphite extrusion to the anvil surface.
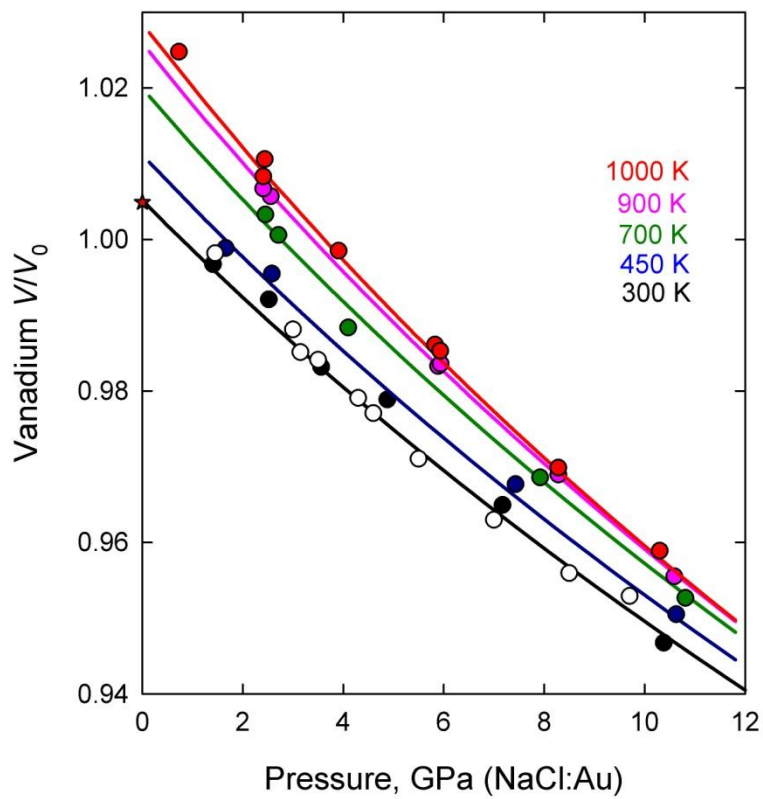
Figure 2. The relative lattice volume of *bcc* vanadium for those data (*filled symbols*) at temperatures estimated at $\pm$ 20 K of the calculated isotherms (*lines*). The calculated V_0 is identical to the return-to-ambient value not included in the fit (*star*). Also shown are ambient temperature data from Ming and Manghnani (*open symbols*), rescaled to the recovered V/V_0 value.
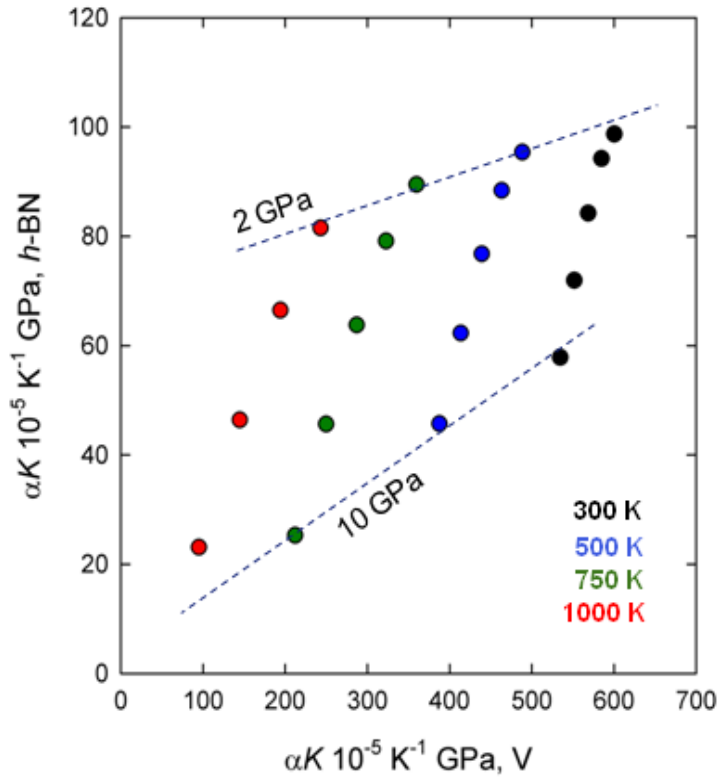
Figure 3. The variation in the estimated products of the thermal expansivity and bulk modulus of V (horizontal scale) and *h*-BN, a typical component in an x-ray assembly (vertical scale). These show distinct contrast at low pressures and temperatures, where there is a factor 6 difference, but this progressively decreases with both increasing temperature and increasing pressure so that at 8 GPa and 1000 K, there is only a factor 4. This reduces the precision likely in estimating combined *p*, *T* from cross-coupled EoS. *h*-BN is no longer stable at high pressure when the point where the product, which is identical to $(\delta p/\delta T)_V$, tends to zero with increasing *T*.