Elasticity of the superconducting metals V, Nb, Ta, Mo, and W at high pressure

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First-principles calculations have been performed for V, Nb, Ta, Mo, and W. The recently discovered bcc→rhombohedral transition for vanadium [Phys. Rev. Lett. 98, 085502 (2007)] was confirmed as the mechanical instability of \( c_{44} \) was found at \( P=80 \) GPa. Furthermore, the \( c_{11}, c_{12}, \) and \( c_{44} \) constants for the group-V elements showed erratic behaviors whereas the constants for the group-VI elements were monotonically increasing with pressure. The metals were analyzed with Fermi surface calculations, showing shrinking nesting vectors with pressure for V, Nb, and Ta but were not seen for Mo and W. From electronic topological transition contributions, a critical energy closely situated to the Fermi level for vanadium could be the reason why the elastic constants of V and Nb were difficult to reproduce at ambient pressure.

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Transition metals such as vanadium (V), niobium (Nb), and tantalum (Ta) are of fundamental interest due to their superconducting properties. With an increasing pressure-temperature coefficient of \( \Delta T_c/\Delta P=0.1 \) K/GPa, Ishizuka et al. have reported a superconducting transition temperature (\( T_c \)) of 17.2 K at 120 GPa for V. At ambient pressure, Nb has the highest \( T_c = 9.25 \) K.

A recent experimental study based on synchrotron x-ray diffraction by Ding et al.2 has shown a transition from the body-centered-cubic (bcc) structure to a rhombohedral phase in vanadium at 69 GPa. The transition was also found from the theoretical calculations by Lee et al.3 at the somewhat higher pressure of 84 GPa. For the vanadium group metals V, Nb, and Ta, the stability of the bcc has long been predicted to be very high as no transition was found for pressures up to 154 GPa for V and Nb,4 and up to 145 GPa for Nb.5 Therefore, the findings of a phase transition for pressures below 70 GPa is quite remarkable.

Molybdenum (Mo) and tungsten (W), neighbors of Nb and Ta in the Periodic Table, are often used as pressure calibrant materials at high pressure and/or at high temperature. The metals have very high melting points at ambient pressure and a bcc stability up to high pressures. However, the newly discovered rhombohedral phase in V has intensified the search of this type of phase in other elements in the Periodic Table both from experiments and theory. Moreover, very recently, the theoretical study by Luo et al.6 has shown that the lattice dynamics under high pressure is related to a very drastic change in the electronic structure. In this work, the properties of V, Nb, Ta, Mo, and W have been examined by means of first-principles (ab initio) calculations, based on the density functional theory.7 The calculations were performed by using the Vienna Ab Initio Simulation Package.8 As implemented in the code, the generalized gradient approximation9 (GGA) was applied to obtain the one-electron Hamiltonian and the ion-electron interaction was described by projector augmented waves10 (PAW).

An energy convergence of 0.1 meV/atom was reached with a \( 30 \times 30 \times 30 \) Monkhorst–Pack \( k \)-point grid. A Methfessel–Paxton11 smearing was used with a width of 0.2 eV and the cutoff energy was set to 500 eV.

The results of ambient pressure calculations are shown in Table I. For V, there is a slight underestimation of 3% for the equilibrium volume \( V_0 \). For the other studied metals Nb, Ta, Mo, and W, \( V_0 \) is consequently somewhat overestimated compared to the experiment although the difference is at most 3%. The bulk properties \( B_0 \) and \( B'_0 \) agree reasonably well with the experimental data. The elastic constants \( c_{11}, c_{12}, \) and \( c_{44} \) at ambient pressure are shown in Table II. For V, both \( c_{11} \) and \( c_{12} \) show an overestimation of ~14%. However, by using the experimental equilibrium volume,2 the \( c_{11} \) and \( c_{12} \) constants could be reproduced perfectly. For \( c_{44} \), there is a significant underestimation as the calculated constant is

TABLE I. Properties of bcc V, Nb, Ta, Mo, and W compared to the experiments.2,4,5,25,26 Volumes are in Å\(^3\)/atom and bulk moduli in GPa.

<table>
<thead>
<tr>
<th>Reference</th>
<th>( V_0 )</th>
<th>( B' )</th>
<th>( B_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>V GGA and PAW (this study)</td>
<td>13.49</td>
<td>3.75</td>
<td>182</td>
</tr>
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<td>Experiments in Ref. 2</td>
<td>13.905</td>
<td>3.5(2)</td>
<td>195(3)</td>
</tr>
<tr>
<td>Experiments in Ref. 4</td>
<td>3.5(5)</td>
<td>162(5)</td>
<td></td>
</tr>
<tr>
<td>Nb GGA and PAW (this study)</td>
<td>18.32</td>
<td>3.85</td>
<td>174</td>
</tr>
<tr>
<td>Experiments in Ref. 5</td>
<td>17.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta (this study)</td>
<td>17.98</td>
<td>3.4(3)</td>
<td>168(4)</td>
</tr>
<tr>
<td>Experiments in Ref. 27</td>
<td>18.04</td>
<td>3.52</td>
<td>194</td>
</tr>
<tr>
<td>Mo (this study)</td>
<td>16.01</td>
<td>4.22</td>
<td>254</td>
</tr>
<tr>
<td>Experiments in Refs. 25 and 26</td>
<td>15.58</td>
<td>4.5</td>
<td>261</td>
</tr>
<tr>
<td>W (this study)</td>
<td>16.13</td>
<td>3.89</td>
<td>329</td>
</tr>
<tr>
<td>Experiments in Ref. 27</td>
<td>15.86</td>
<td>4.3</td>
<td>296</td>
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less than half of the reported experimental findings. In contrast to \(c_{11}\) and \(c_{12}\), the \(c_{44}\) was found to be relatively insensitive to variations in volume. Although several PAW potentials were tried with different numbers of valence electrons included in combination with different smearing widths, the monoclinic strain was consistently low. The large discrepancy compared to the experiment is also present for Nb, as all constants are underestimated. Although \(c_{11}\) and \(c_{12}\) are reasonable compared to the results of Trivisonno et al.,\(^{12}\) the \(c_{44}\) from this work shows exactly one third of the experimental results. Therefore, there is a need to investigate why the calculations in this work show such low \(c_{44}\) for V and Nb.

The difficulty of reproducing experimental elastic constants for vanadium was also stated by Söderlind et al.\(^{13}\) From full potential linear muffin-tin orbital (FP-LMTO) calculations, the authors reported an extremely low \(c_{44}\) of 5 GPa, i.e., just above 10% of the experimental results \(\sim 42.5\) GPa shown in Table II. Furthermore, a similar study\(^ {14}\) to this, using GGA PW91 (Perdew-Wang 91),\(^ {15}\) showed a very good match to the diamond-anvil cell data with \(B_0=185\) and \(c'=\frac{1}{2}(c_{11}-c_{12})=65\) GPa. However, the shear constant \(c_{44}=20\) GPa, showed an underestimation, just as in this work. For Nb, GGA and LDA calculations have shown the instability of the bcc phase at ambient conditions, as the \(c_{44}\) was found at \(\sim 30\) and \(\sim 50\) GPa, respectively.\(^ {16}\) Thus, the above examples imply a big theoretical uncertainty regarding the elasticity of vanadium and niobium. At this stage, the elastic constant calculations as a function of pressure for V and Nb can only be used to see the trends, and the specific data should be treated with caution. To resolve this discrepancy, more accurate experiments are also required. On the other hand, the elastic constants for Ta and the group-VI elements Mo and W in Table II show good agreement with the experiment. The constants \(c_{11}\), \(c_{12}\), and \(c_{44}\) as a function of pressure, are shown in Fig. 1. The \(c_{44}\) for V shows a similar behavior, as shown by Landa et al.\(^ {17}\) More interestingly, the authors present a pressure range with a negative constant between 180 and 275 GPa. In this study,

<table>
<thead>
<tr>
<th>Reference</th>
<th>(c_{11}) (GPa)</th>
<th>(c_{12}) (GPa)</th>
<th>(c_{44}) (GPa)</th>
</tr>
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<tbody>
<tr>
<td>V</td>
<td>GGA and PAW (this study)</td>
<td>260</td>
<td>135</td>
</tr>
<tr>
<td>Theory (Ref. 17)</td>
<td>...</td>
<td>...</td>
<td>30</td>
</tr>
<tr>
<td>Experiments in Refs. 26 and 28–33</td>
<td>227 ± 4</td>
<td>118 ± 4</td>
<td>42.5 ± 1.3</td>
</tr>
<tr>
<td>Nb</td>
<td>GGA and PAW (this study)</td>
<td>247</td>
<td>138</td>
</tr>
<tr>
<td>Theory in Ref. 17</td>
<td>...</td>
<td>...</td>
<td>35</td>
</tr>
<tr>
<td>Experiments in Ref. 12</td>
<td>284</td>
<td>164</td>
<td>30.9</td>
</tr>
<tr>
<td>Ta</td>
<td>(this study)</td>
<td>265</td>
<td>159</td>
</tr>
<tr>
<td>Experiments in Refs. 34 and 35</td>
<td>266</td>
<td>158–161</td>
<td>83–87</td>
</tr>
<tr>
<td>Mo</td>
<td>(this study)</td>
<td>463</td>
<td>163</td>
</tr>
<tr>
<td>Experiments in Ref. 26</td>
<td>463</td>
<td>158</td>
<td>107</td>
</tr>
<tr>
<td>W</td>
<td>(this study)</td>
<td>513</td>
<td>199</td>
</tr>
<tr>
<td>Experiments in Ref. 34</td>
<td>532</td>
<td>205</td>
<td>163</td>
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</tbody>
</table>

FIG. 1. (Color online) The elastic constants \(c_{11}\), \(c_{12}\), and \(c_{44}\) for V, Nb, Mo, Ta, and W. For all metals but V, the cubic crystal stability criteria \((c_{44}>0,\ c_{11}-c_{12}>0,\ \text{and}\ c_{11}+2c_{12}>0)\) are fulfilled.
the higher pressure limit is reproduced accurately whereas the lower limit is found already at 80 GPa. Therefore, as this pressure shows a mechanical instability, the comparison to the bcc-rhombohedral transformation pressure for vanadium at 62 (Ref. 6) and 63–69 GPa (Ref. 2) is indeed remarkable.

An obvious difference in Fig. 1 is that the group-VI elements Mo and W show a steady, increasing behavior as a function of pressure, whereas the results from the elastic constant calculations for the group-V elements V, Nb, and Ta are much more irregular. Therefore, we have analyzed cuts of the Fermi surfaces. The Brillouin zone cross sections of the surfaces of V in the central point are shown for the group-V elements V, Nb, and Ta. Mo and W show a steady, increasing behavior as a function of pressure, whereas the results from the elastic constant calculations for the group-V elements V, Nb, and Ta decreases with pressure, and disappear at 247, 74, and 275 GPa, respectively. The shrinking nesting vectors are therefore a possible reason for the irregularities seen for V, Nb, and Ta. Mo and W, on the other hand, show vector magnitudes close to the ambient one throughout the entire studied pressure range. Furthermore, at the pressures where $q = 0$, the $c_{44}$, for the group-V elements start to show a more steady behavior and increase monotonically ($\Delta c_{44}/\Delta P > 0$), as shown in Fig. 1.

From the Fermi surface calculations performed in this study for V, the energy $E_F$ is close to a critical point $E_c$, showing a peak in the electronic density of states. At this energy, the Fermi surface undergoes a topological transition shaped as a saddle point. In Fig. 4(a), the Fermi surface and its cut are shown for $E(k) = E_F > E_c$. As the Fermi energy is shifted past the critical point $E_c = E_F - 46$ meV, a neck is developed along the $\Gamma$–$N$ symmetry direction connecting the inner sheet around the $\Gamma$ point with the disk shaped sheet around the $N$ point. This neck is shown in Fig. 4(b), where the Fermi level has been shifted to 60 meV.

Now, we study the effect that the electronic topological transition (ETT) could have on the elastic constants. As the $\Gamma$–$N$ neck forms an hourglass shape, the model band structure can be written as

$$e(k) = E_c + E^0 c^2 k_x^2 - E^0 a^2 (k_y^2 + k_z^2),$$

(2)

describing a saddle point as $E$ is decreased toward $E_c$. Here, $E^0 > 0$, and $a$, $b$, and $c$ are real parameters. From Eq. (2), the contribution of the ETT to the density of states $N(E)$ can be calculated as

$$N(E) = \frac{V}{4\pi^3} \int_{S(E)} \frac{dS}{|\nabla e|}$$

$$= \frac{1}{4\pi^2 |E^0|} \left[ \pi - \sqrt{\frac{E - E_c}{E^0}} \Theta \left( \frac{E - E_c}{E^0} \right) \Theta \left( \frac{E - E_c}{E^0} \right) \right],$$

where $S(E) = \{ k \in \mathbb{R}^3 | e(k) = E \}$ and $\Theta(x) = 1$ for $x > 0$, and $\Theta(x) = 0$ for $x < 0$. 

![Fermi surface cross sections for V for the lattice parameters $1a_0$, $0.95a_0$, $0.90a_0$, and $0.85a_0$ corresponding to the pressures 0, 37, 104, and 217 GPa.](image-url)
\[ \Theta(x) = 0 \] for \( x < 0 \). With the above \( N(E) \), the band contribution from the ETT to the total energy is given by

\[ E_{\text{band}} = \int_{0}^{E_F} N(E) E dE \]

\[ = \frac{1}{4 \pi^2 |E|^{3/2}} \left[ \frac{\pi E_F^2}{2} - \frac{2 E_F}{3} E^{3/2} + \frac{4}{15} E^{5/2} \right] \]  \hspace{1cm} (4)

Here, \( \tilde{E} = E_F - E_c \), and if the distance between the Fermi energy \( E_F \) and the critical point \( E_c \) is small enough, the constants \( c_{ij} \) can be approximated by neglecting all contributions to \( c_{ij} \) except for those emanating from the ETT. Under these conditions, the ETT contribution to the elastic constants \( c_{ij}^{ETT} \) can, to the leading order in \( \tilde{E} \), be calculated from Eqs. (3) and (4) as

\[ c_{ij}^{ETT} \approx \frac{1}{V} \frac{\partial^2 E_{\text{band}}}{\partial e_i \partial e_j} \approx \frac{1}{4 \pi^2 V |E|^{|E_F|^{3/2}}} \left[ -\frac{E_F}{E} \frac{E^{1/2}}{2} \frac{\partial \tilde{E}}{\partial e_i} \frac{\partial \tilde{E}}{\partial e_j} \right] \]  \hspace{1cm} (5)

where \( e_i \) are strain components and \( V \) is the volume. The equation clearly shows the effect when \( \tilde{E} = E_F - E_c \) is very small: \( E^{1/2} \) increases rapidly, which means that the first term in the bracketed expression decreases due to the minus sign, lowering the \( c_{44} \). Therefore, the underestimation of the \( c_{44} \) in this study for V and Nb at ambient conditions might be due to this contribution. Figure 5 shows that the Fermi level \( E_F \) was chosen so that the neck develops along the \( \Gamma - N \) symmetry direction. The 60 meV shift was chosen so that the neck developed would be clearly visible.

FIG. 3. (Color online) The decreasing nesting vector \( q \) for V, Nb, Mo, Ta, and W as a function of pressure.

FIG. 4. (Color online) In (a), the Fermi surface (top left) and its cut (top right) are shown for \( \epsilon(k) = E_F > E_c \). In (b), the Fermi surface (bottom left) and its cut (bottom right) is shown for \( \epsilon(k) = E_F - 0.06 \ eV < E_c \). Here, \( E_c \) is the critical energy of an electronic topological transition in which a neck develops along the \( \Gamma - N \) symmetry direction. The 60 meV shift was chosen so that the neck developed would be clearly visible.
enhanced with increasing pressure but instead grow weaker at high $P$, thus ruling out the ETT as being the phenomenon responsible for the $c_{44} < 0$ mechanical instability of V at finite pressure. Structural changes with pressure in transition metals are often regarded as a consequence of the electronic $s \rightarrow d$ transition. However, Landa et al.\textsuperscript{17} have emphasized that $q$ reaches zero long before the Jahn–Teller effect becomes significant. Furthermore, for the vanadium neighbor chromium with two extra $d$ band electrons compared to V, the $c_{44}$ constant is stiffer at ambient conditions [100 GPa (Ref. 24) for Cr whereas the experimental data for V in Table II show ~43 GPa]. This is also consistent with the finding of this work, where the extra $d$ electron from Nb to Mo and Ta to W manifests in a much higher $c_{44}$, as shown in Fig. 1.

To conclude, we have shown by our \textit{ab initio} calculations that the elastic constant softening in V, Nb, and Ta arises from the Fermi surface nesting, and that the theoretical underestimation of the $c_{44}$ elastic constants of V and Nb at ambient pressure is most probably due to the closeness of the Fermi level $E_F$ to the critical point $E_c$ of a Van Hove singularity.

14. M. Jahnátek (private communication).