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.*[1] 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 approximation[9] (GGA) was applied to obtain the one-electron Hamiltonian and the ion-electron interaction was described by projector augmented waves[10] (PAW). An energy convergence of 0.1 meV/atom was reached with a $30\times30\times30$ Monkhorst–Pack **k**-point grid. A Methfessel–Paxton[11] 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.

	Reference	V_0	B'	B_0
V	GGA and PAW (this study)	13.49	3.75	182
	Experiments in Ref. 2	13.905	3.5(2)	195(3)
	Experiments in Ref. 4		3.5(5)	162(5)
Nb	GGA and PAW (this study)	18.32	3.85	174
	Experiments in Ref. 25	17.98		
	Experiments in Ref. 5	17.98	3.4(3)	168(4)
Ta	(this study)	18.11	3.67	211
	Experiments in Ref. 27	18.04	3.52	194
Mo	(this study)	16.01	4.22	254
	Experiments in Refs. 25 and 26	15.58	4.5	261
W	(this study)	16.13	3.89	329
	Experiments in Ref. 27	15.86	4.3	296

TABLE II. The elastic constants c_{11}, c_{12}, and c_{44} (in GPa) at 0 GPa for bcc V, Nb, Ta, Mo, and W.

	Reference	c_{11}	c_{12}	c_{44}
V	GGA and PAW (this study)	260	135	17.1
	Theory (Ref. 17)	…	…	30
	Experiments in Refs. 26 and 28–33	227 ± 4	118 ± 4	42.5 ± 1.3
Nb	GGA and PAW (this study)	247	138	10.3
	Theory in Ref. 17	…	…	35
	Experiments in Ref. 12	284	164	30.9
Ta	(this study)	265	159	74
	Experiments in Refs. 34 and 35	266	158–161	83–87
Mo	(this study)	463	163	103
	Experiments in Ref. 26	463	158	107
W	(this study)	513	199	140
	Experiments in Ref. 34	532	205	163

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 ~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 ~−30 and ~−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,

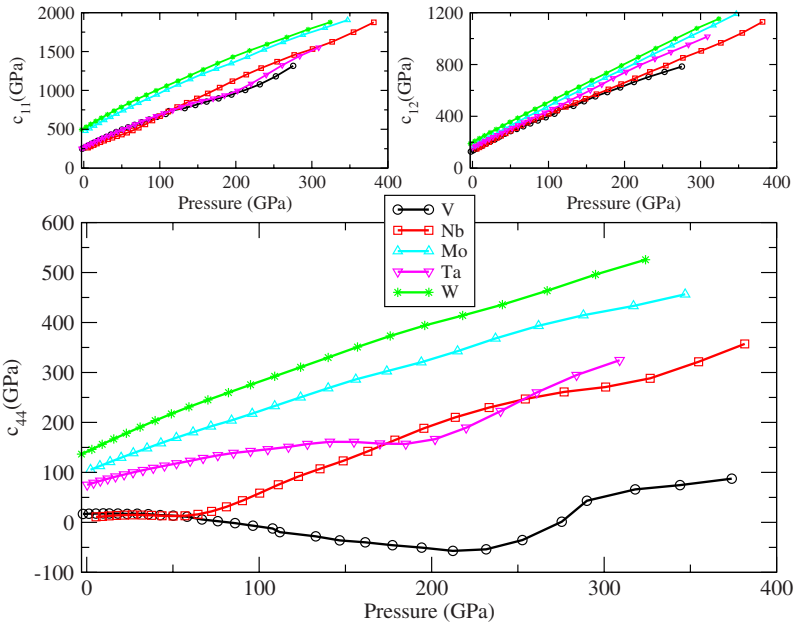

FIG. 1. (Color online) The elastic constants c_{11}, c_{12}, and c_{44} for V, Nb, Mo, Ta, and W. For all metals but V, the cubic crystal stability criteria ($c_{44}>0$, $c_{11}-c_{12}>0$, and $c_{11}+2c_{12}>0$) are fulfilled.

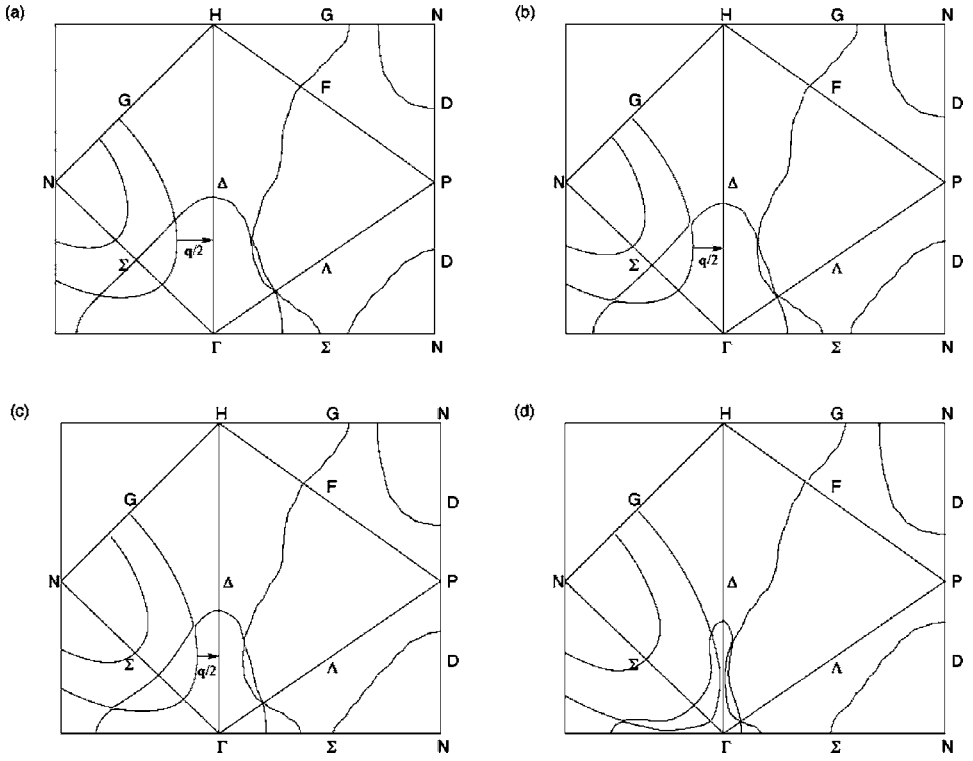

FIG. 2. Fermi surface cross sections for V for the lattice parameters $1a_0$, $0.95a_0$, $0.90a_0$, and $0.85a_0$ corresponding to the pressures 0, 37, 104, and 217 GPa.

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,[18] 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 {100} and {110} planes were studied for the lattice parameters $1a_0$, $0.95a_0$, $0.90a_0$, and $0.85a_0$, respectively, as shown in Fig. 2. We have found that the hole-pocket-shaped second band around the Γ point shrinks with pressure, indicating that the motion of this point is toward the Fermi level. The nesting vector $\mathbf{q}$, from the third energy band to the Γ-H line, clearly decreases with pressure. The vector relation to the elastic constant in the long wavelength limit is

$$c_{44} = \omega^2(q)\rho/q^2, \tag{1}$$

where ω is the phonon frequency and ρ the density. Kohn anomalies, showing infinities in $\delta\omega/\delta\mathbf{q}$ for the transverse acoustic modes, have been found on the vanadium group metals.[19,20] More recently, Suzuki and Otani,[21] and Luo *et al.*[6] found this anomalous behavior of phonon frequency softening at higher pressure for V, and at $P \sim 130$ GPa, the frequencies became imaginary.

Figure 3 shows that the length of the inserted nesting vector $\mathbf{q}$ for V, Nb, and Ta decreases with pressure, and disappears at 247, 74, and 275 GPa, respectively. The shrinking nesting vectors are therefore a possible reason for the c_{44} 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 $\mathbf{q}=0$, the c_{44}:s 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 $\epsilon(\mathbf{k}) = E_F > E_c$. 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 Γ 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.[22,23] As the $\Gamma - N$ neck forms an hourglass shape, the model band structure can be written as

$$\epsilon(\mathbf{k}) = E_c + E^* c^2 k_z^2 - E^* a^2 (k_x^2 + k_y^2), \tag{2}$$

describing a saddle point as E is decreased toward E_c. Here, $E^* > 0$, 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

$$N(E) = \frac{V}{4\pi^3} \int_{S(E)} \frac{dS}{|\nabla \epsilon|} = \frac{1}{4\pi^2 |E^*|} \left[\pi - \sqrt{\frac{E - E_c}{E^*}} \Theta\left(\frac{E - E_c}{E^*} \right) \right], \tag{3}$$

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

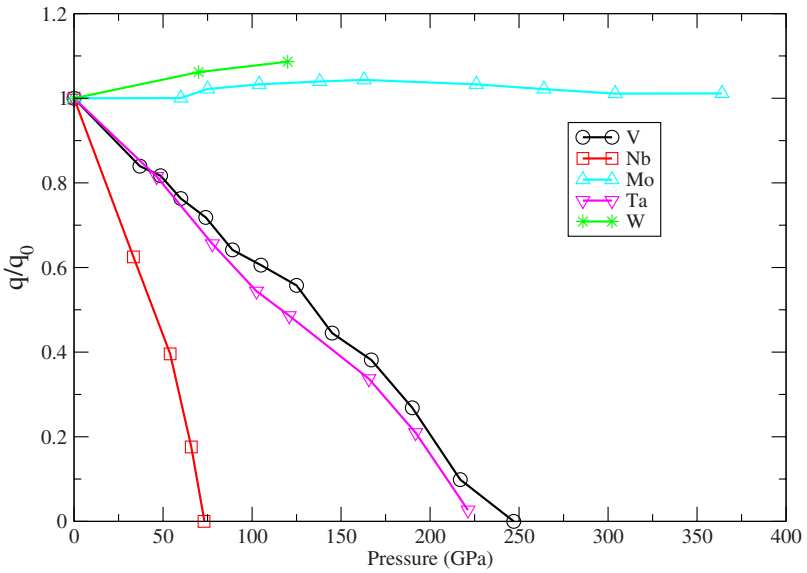

FIG. 3. (Color online) The decreasing nesting vector q for V, Nb, Mo, Ta, and W as a function of pressure.

$\Theta(x)=0$ for $x<0$. With the above $N(E)$, the band contribution from the ETT to the total energy is given by

$$E_{\text{band}} = \int_0^{EF} N(E)EdE = \frac{1}{4\pi^2|E^*|^{3/2}}\left[\frac{\pi E_F^2\sqrt{|E^*|}}{2} - \frac{2E_F}{3}\tilde{E}^{3/2} + \frac{4}{15}\tilde{E}^{5/2}\right] \quad (4)$$

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}^* can, to the leading order in $\tilde{E}$, be calculated from Eqs. (3) and (4) as

$$c_{ij}^* = \frac{1}{V}\frac{\partial^2 E_{\text{band}}}{\partial\epsilon_i\,\partial\,\epsilon_j} \approx \frac{1}{4\pi^2 V|E^*|^{3/2}}\left[-\frac{E_F}{2}\tilde{E}^{-1/2}\right]\frac{\partial\tilde{E}}{\partial\epsilon_i}\frac{\partial\tilde{E}}{\partial\epsilon_j}, \quad (5)$$

where ϵ_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: $\tilde{E}^{-1/2}$ increases rapidly, which means that the first term in the bracketed expression decreases due to the minus sign, lowering the c_{ij}^*. 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

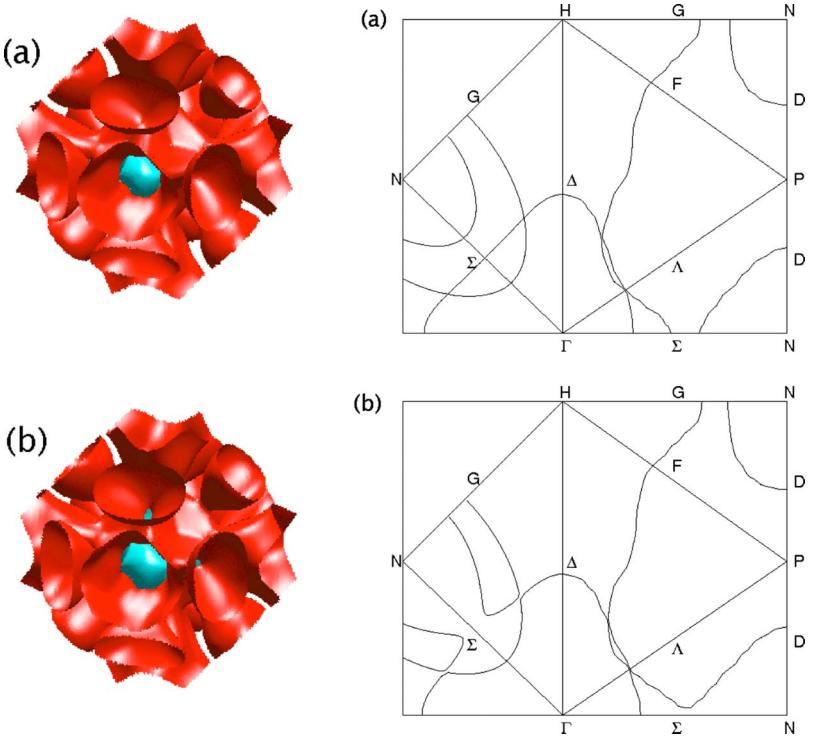

FIG. 4. (Color online) In (a), the Fermi surface (top left) and its cut (top right) are shown for $\epsilon(\mathbf{k})=E_F>E_c$. In (b), the Fermi surface (bottom left) and its cut (bottom right) is shown for $\epsilon(\mathbf{k})=E_F-0.06$ eV$<E_c$. Here, E_c is the critical energy of an electronic 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.

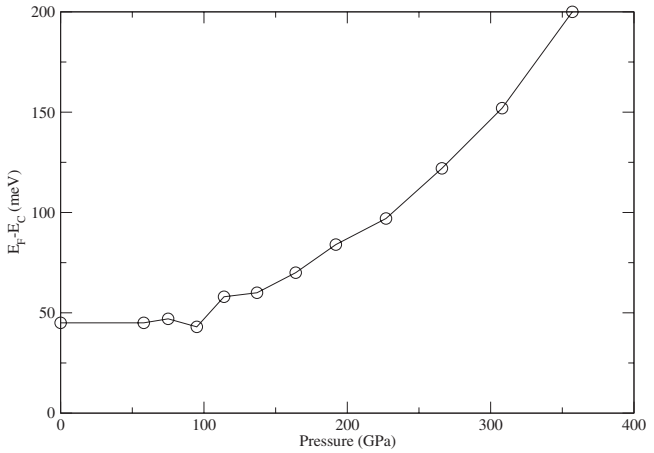

FIG. 5. The energy difference between the Fermi level E_F and the critical point E_c for V.

moves away monotonically from the critical point E_c with pressure. As the ETT effect could be significant at lower pressures, the contribution should, on the other hand, not get 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.*[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 *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.

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