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FERMI SURFACE NESTING AND PRE-MARTENSITIC SOFTENING IN V AND Nb AT HIGH PRESSURES

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Fermi surface nesting and pre-martensitic softening in V and Nb at high pressures

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Abstract

First-principles total-energy calculations were performed for the trigonal shear elastic constant (C_{44}) of vanadium and niobium. A mechanical instability in C_{44} is found for vanadium at pressures ~ 2 Mbar which also shows softening in niobium at pressures ~ 0.5 Mbar. We argue that the pressure-induced shear instability (softening) of vanadium (niobium) is due to the intra-band nesting of the Fermi surface.

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1. Introduction

The group-VB transition metals vanadium and niobium have been recent subject of numerous experimental and theoretical studies [1-5] due to the high superconducting transition temperatures of its components (for example, niobium has the highest superconducting transition temperature T_c = 9.25 K among the elemental metals at ambient pressure). Struzhkin *et al.* [1] measured the superconducting transition temperature of niobium in the pressure range up to 1.32 Mbar. They observed anomalies in $T_c(p)$ at 50-60 kbar and 600-700 kbar and suggested that these anomalies arise from an electronic topological transition (ETT). Later, Tse *et al.* [2] performed a theoretical investigation of the electron-phonon coupling in high-pressure niobium and identified changes in the Fermi surface (FS) topology that are responsible for these anomalies.

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Ishizuka *et al.* [3] performed similar to [1] experiments on vanadium in the pressure range up to 1.2 Mbar. They discovered that T_c = 5.3 K at ambient pressure and increases linearly with pressure and reaches 17.2 K (the highest T_c among the elemental metals reported so far) at 1.2 Mbar. However, in contrast to niobium, these measurements did not find any indications of anomalies in T_c for vanadium within this pressure range. Takemura [4] performed high-pressure DAC powder X-ray diffraction experiments on vanadium and niobium and found no anomalies in the equations of state (EOS), which could be connected with the ETT, up to the maximum pressure of 1.54 Mbar. In order to explore the possibility of a structural phase transition from bcc to another phase, Suzuki and Otani [5] performed first-principles calculations of lattice dynamics of vanadium in the pressure range up to 1.5 Mbar. They found that the transverse acoustic phonon mode TA [ξ00] around ξ =1/4 shows a dramatic softening under pressure and becomes imaginary at pressures higher than ~ 1.3 Mbar, indicating a possibility of such structural phase transition. Because in the limit of long–wave lengths ($q \rightarrow 0$) this mode is directly related to the trigonal shear elastic constant (C_{44}), clear understanding of the anomaly in the TA curve is principally important in the problem of the shear lattice stability of bcc vanadium. The authors [5], however, did not discuss the physical reasons behind the dip in the TA curve.

This paper is devoted to an *ab initio* study of the trigonal shear elastic constant of vanadium and niobium in the pressure range up to 4 Mbar. We apply two complementary computational techniques, exact muffin-tin orbitals (EMTO) [6, 7] and full-potential linear muffin-tin orbitals (FPLMTO) [8, 9] for calculating the electronic band structure of vanadium and niobium in order to obtain the EOS and then calculate C_{44} within the pressure range under consideration. For the exchange/correlation approximation we use the generalized gradient approximation (GGA) [10]. We discuss the physical nature of the anomaly in the trigonal shear elastic constant of vanadium and niobium in terms of the FS nesting that was detected by construction of the generalized susceptibility of non-interacting electrons using the highly precise analytic tetrahedron method [11].

2. Results and discussion

Figure 1 and Figure 2 show pressure dependence of the trigonal shear elastic constant of vanadium and niobium, respectively. EMTO calculations reveal a mechanical instability in C_{44} at pressures ~ 2 Mbar for vanadium (similar tendency is observed from FPLMTO calculations, but at lower pressure). According to the EMTO calculations, the trigonal shear elastic constant of niobium shows the softening at pressures ~ 0.5 Mbar (similar tendency is observed from FPLMTO calculations, but at slightly higher pressure). One should also mention that similar

softening for C_{44}, although less pronounced, was predicted from FPLMTO calculations for tantalum [12], the remaining member of the group-VB.

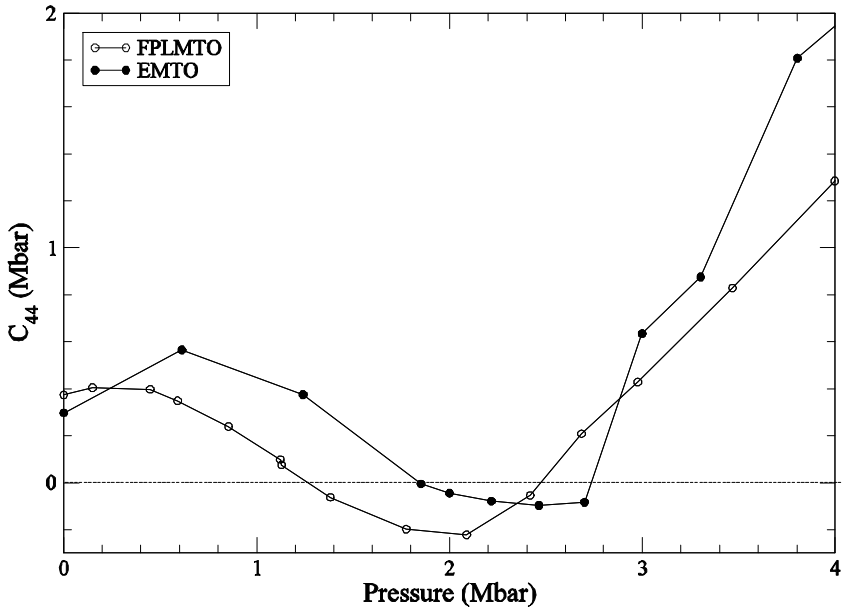

Figure 1. Pressure dependence of the trigonal shear elastic constant of vanadium.

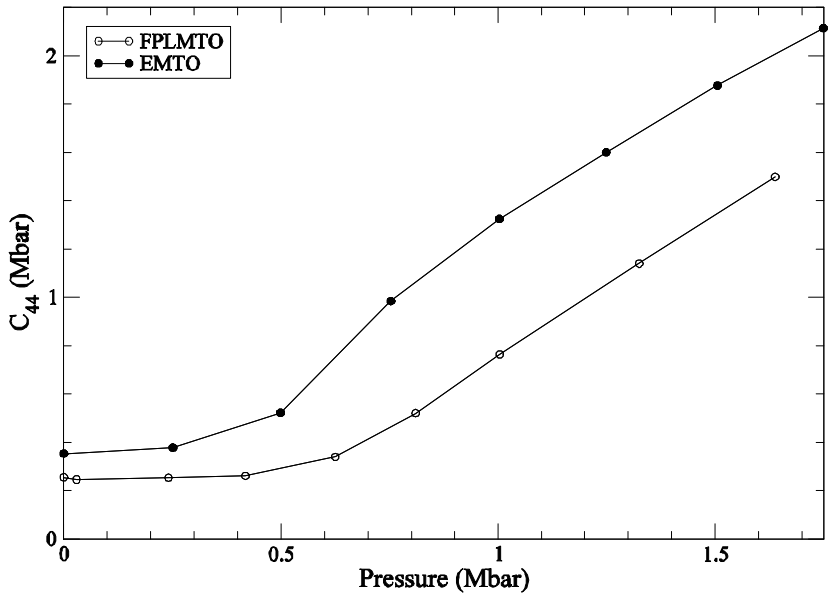

Figure 2. Pressure dependence of the trigonal shear elastic constant of niobium.

The pressure evolution of the FS of vanadium can be understood from its cross sections in the central {100} (triangular (*ΓHN*)) and {110} (rectangular (*ΓHNPN*)) planes shown in Figures 3-5 (the notations are borrowed from Mackintosh and Andersen [13]). Since vanadium

contains 5 valence electrons per atom, they fill entirely the first, most of the second, and a significant part of the third conduction band. In this figure, the first filled band is not shown, the second band (2) has a closed hole-surface centered at the point Γ and has the shape of a distorted octahedron. The third band (3) has closed distorted hole-ellipsoids centered at points *N* and multiple connected opened hole-tubes, so called 'jungle-gym' (J-G), which extend from Γ to *H* in the [100] (Δ) directions. We found that as pressure increases, the distorted octahedron hole-pocket around the Γ point shrinks, indicating a movement of this point towards the Fermi level (Figure 4), as well as the J-G hole-tube becomes narrower and finally terminates at the [100] direction (Figure 5).

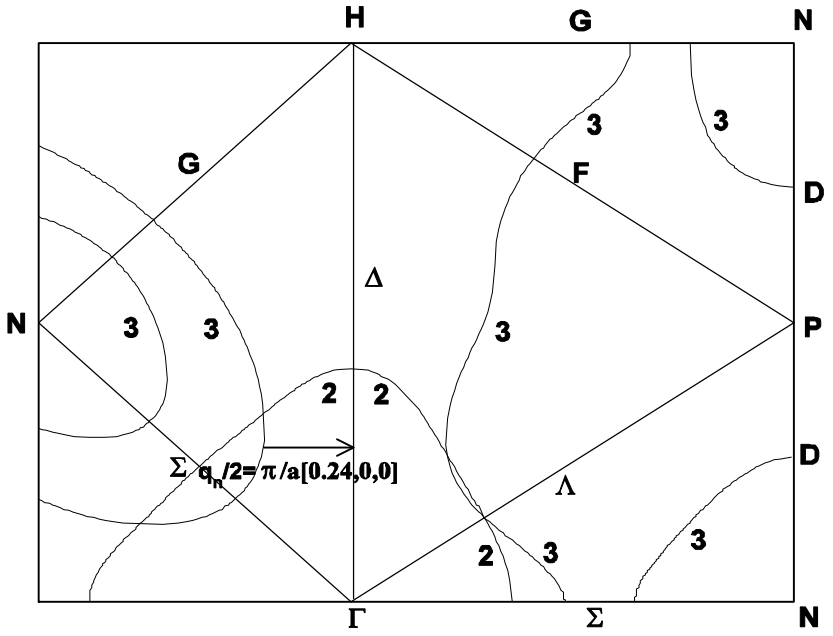

Figure 3. Central {100} and {110} cross sections of the FS of vanadium at ambient pressure.

Figure 6 shows the partial (due to the $3^{rd} \rightarrow 3^{rd}$ electron band transitions) contribution to the generalized susceptibility, $\chi(q)$, of vanadium calculated along the Γ-*H* direction. As can be seen from this plot, at ambient pressure this function shows a pronounced peak at $\xi \approx 0.24$, due to the nesting properties of the FS in the 3^{rd} band (intra-band nesting). As pressure increases, this peak shifts swiftly towards the smaller ξ (lower wave vector *q*), for example, at 1.8 Mbar the peak is located at $\xi \approx 0.06$. The half of the nesting vector ($|\boldsymbol{q}_n|/2 \approx \pi/a[0.24, 0, 0]$) can be clearly seen in Figure 3. It corresponds to the position of the anomaly in the TA found by Suzuki and

Otani [5]. As pressure increases, $|q_n|$ decreases (Figure 4) and finally becomes equal to zero at pressure of the above mentioned termination of the J-G hole-tube (Figure 5).

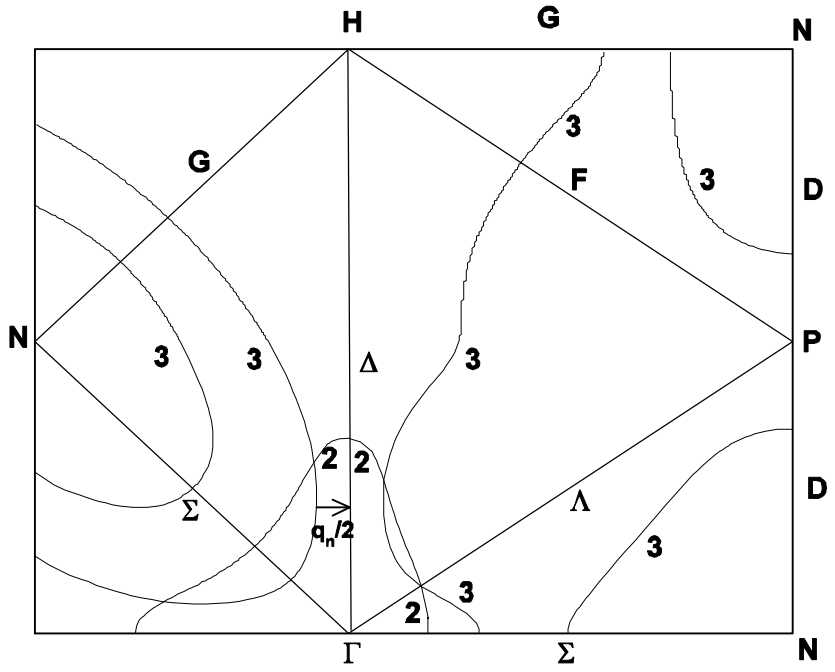

Figure 4. Central {100} and {110} cross sections of the FS of vanadium at 2.216 Mbar.

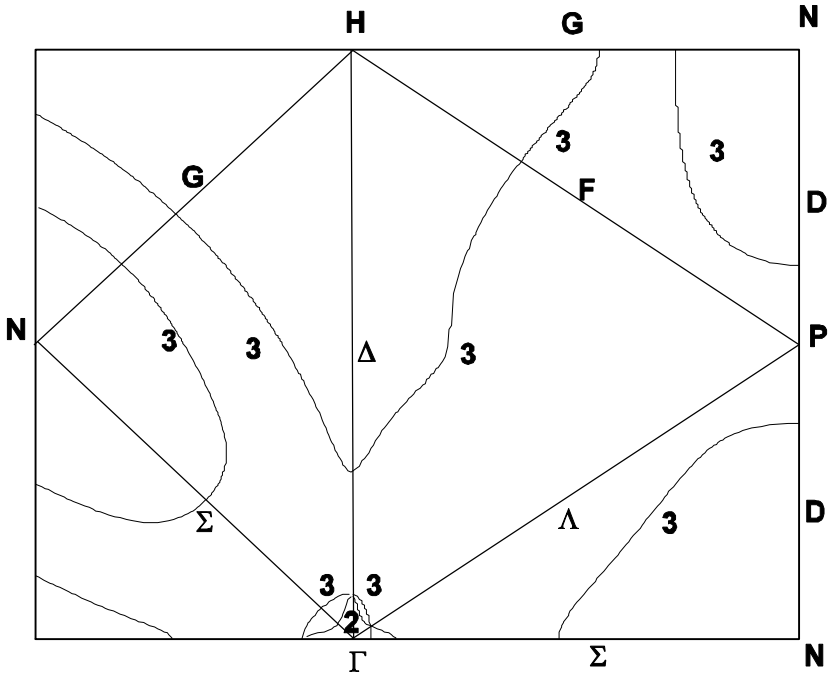

Figure 5. Central {100} and {110} cross sections of the FS of vanadium at 3.302 Mbar.

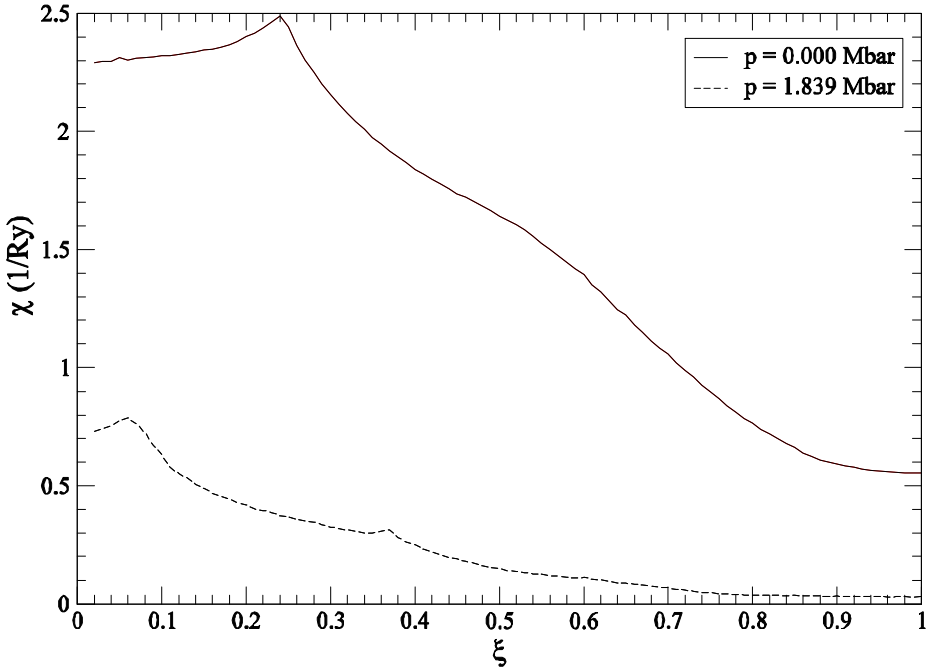

Figure 6. Partial ($3^{rd} \rightarrow 3^{rd}$ intra-band transition) electron susceptibility of vanadium along the Γ-H ([100]) direction.

The nesting vector $\boldsymbol{q}_n$, spanning two flat pieces of the FS in the 3rd band, *already exists* at zero pressure and leads to the Kohn anomaly in the transverse acoustic phonon mode TA [ξ00] of vanadium for small $|\boldsymbol{q}_n|/2 \approx 0.24\pi/a$ [5]. This anomaly also softens the elastic constant C_{44} because in the limit of long waves ($q \rightarrow 0$) $\rho\omega^2(q)/q^2 \rightarrow C_{44}$. It is remarkable that under pressure $\boldsymbol{q}_n$ shrinks at a fast rate and the effect of the Kohn anomaly on C_{44} increases. As soon as $\boldsymbol{q}_n$ turns to zero, the ETT, when the neck between two electronic sheets of the FS appears (the J-G hole-tube terminates at the [100] direction), takes place. Qualitatively, it is analogous to the event when the FS touches the Brillouin zone boundary and is always accompanied by a sharp minimum in the shear elastic constants [14]. So as $\boldsymbol{q}_n \rightarrow 0$, the softening in C_{44} develops up to the point when $\boldsymbol{q}_n$ turns to zero.

Figure 7 shows the partial (due to the $3^{rd} \rightarrow 3^{rd}$ electron band transitions) contribution to the generalized susceptibility, $\chi(q)$, of niobium calculated along the Γ-H direction. At ambient pressure this function also shows a pronounced peak but at the smaller value ($\xi \approx 0.16$) than for vanadium. However in the case of niobium, the termination of the J-G hole-tube occurs at significantly lower pressures (~ 0.75 Mbar) that in the case of vanadium (~ 2.75 Mbar). In other words, the intra-band FS nesting occurs within a significantly smaller pressure range for niobium

than for vanadium causing only a slight softening of C_{44} in the former metal in contrast with instability in the later.

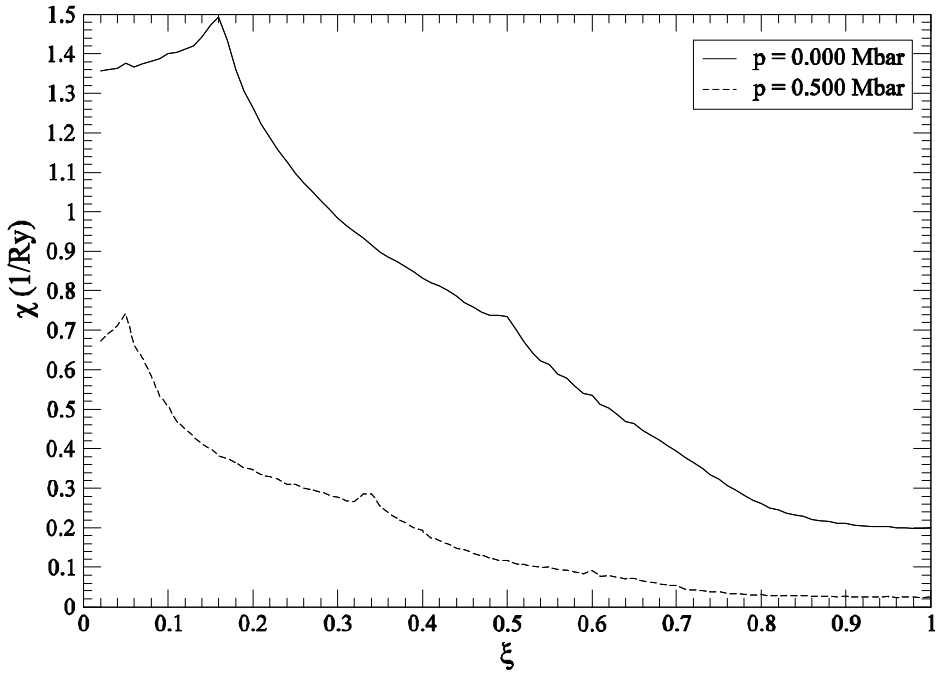

Figure 7. Partial ($3^{rd} \rightarrow 3^{rd}$ intra-band transition) electron susceptibility of niobium along the *Γ-H* ([100]) direction.

We have recently established [15] that the Madelung (electrostatic) contribution to the C_{44} elastic constant always stabilizes the bcc lattice under compression. Here we emphasize again that the softening of the trigonal shear elastic constant of vanadium and niobium is entirely due to the band-structure features.

Finally, one should mention the well-known fact that the interaction that leads to superconductivity may also cause anomalies in the phonon spectrum (Fröhlich [16]). The Fröhlich Hamiltonian is the fundamental in both BCS theory of superconductivity and the charge density wave (CDW) formation theory (CDW causes a pre-martensitic phonon mode softening in materials [14, 17]). However, as vanadium shows a tendency to increase its superconducting transition temperature and electron-phonon coupling, under compression [3, 5], niobium shows an opposite behavior [1, 2]. This difference between vanadium and niobium is also reflected in the degree of the softening of the trigonal shear elastic constant of these metals under compression.

Acknowledgements

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