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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 body-centred cubic (bcc) V and Nb. A mechanical instability in C_{44} is found for V at pressures of ∼2 Mbar which also shows a softening in Nb at pressures of ∼0.5 Mbar. We argue that the pressure-induced shear instability (softening) of V (Nb) is due to the intra-band nesting of the Fermi surface.

1. Introduction

The group-VB transition metals V and Nb have recently been the subject of numerous experimental and theoretical studies [1–5] due to the high superconducting transition temperatures of its components (for example, Nb 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 Nb in the pressure range up to 1.32 Mbar. They observed anomalies in $T_c(p)$ at 50–60 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 Nb and identified changes in the Fermi surface (FS) topology that are responsible for these anomalies.

Ishizuka *et al* [3] performed experiments similar to [1] on V in the pressure range up to 1.2 Mbar. They discovered that $T_c = 5.3$ K at ambient pressure and increases linearly

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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 Nb, these measurements did not find any indications of anomalies in T_c for V within this pressure range. Takemura [4] performed high-pressure diamond-anvil cell (DAC) powder x-ray diffraction experiments on V and Nb 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 the lattice dynamics of V in the pressure range up to 1.5 Mbar. They found that the transverse acoustic phonon mode TA [ξ00] around $\xi = 1/4$ shows a dramatic softening under pressure and becomes imaginary at pressures higher than $\sim$1.3 Mbar, indicating the possibility of such a structural phase transition. Because, in the limit of long-wave lengths ($q \rightarrow 0$), this mode is directly related to the trigonal shear elastic constant (C_{44}), a clear understanding of the anomaly in the TA curve is principally important in the problem of the shear lattice stability of bcc V. 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 bcc V and Nb in the pressure range up to 4 Mbar. It is widely believed that particular features of the Fermi surface (FS), e.g. 'nesting', could cause a pre-martensitic phonon softening and lead to martensitic transformations [6]. For example, the pre-martensitic softening of the acoustic phonon mode in the β-Ni–Al alloys was attributed to the existence of the parallel pieces of the FS which cause a strong electronic response at the nesting wavevector that translates these pieces one onto the other [7, 8]. Recent Compton scattering measurements [9] have been able to image the nested FS in the shape memory $Ni_{62}Al_{38}$ alloy with the translation (nesting) vector associated with the pre-martensitic phonon softening in this system. In the present paper, we discuss the physical nature of the anomaly in the trigonal shear elastic constant of V and Nb in terms of the FS nesting.

This paper is organized as follows. Our computational approach is discussed in section 2, followed by results and discussion in section 3.

2. Theoretical background

The calculations that we have referred to as exact muffin-tin orbitals (EMTO) are performed using a scalar-relativistic Green's function technique based on an improved screened Korringa–Kohn–Rostoker method [10, 11]. For the exchange/correlation approximation, we use the generalized gradient approximation (GGA) [12]. The calculations are performed for a basis set including valence spd orbitals, whereas the core states are recalculated at each iteration. Integration over the irreducible wedge of the Brillouin zone (IBZ) is performed using the special k-points method [13] with 819 k-points for the bcc lattice. The Green's function has been calculated for 60 complex energy points distributed exponentially on a semicircle with a 3.5 Ryd diameter enclosing the occupied states. The equilibrium density and EOS are obtained from a Murnaghan fit [14] to about ten total energies calculated as a function of the lattice constant. For the determination of the trigonal shear elastic constant, we apply a volume-conserving monoclinic distortion [15] and calculate the internal energy response. This setup requires 17 457 k-points to perform integration over the IBZ.

The FS nesting is detected by construction of the generalized susceptibility of non-interacting electrons ($\chi(q)$) using the highly precise analytic tetrahedron method [16]. This computational procedure yields simple analytical expressions for the susceptibility integral inside a tetrahedral micro-zone of the BZ: the contribution to the susceptibility from a given tetrahedron is determined *solely* from a knowledge of the difference of the energy-band eigenvalue at the corners of the tetrahedron and the volume of the tetrahedron. In order to

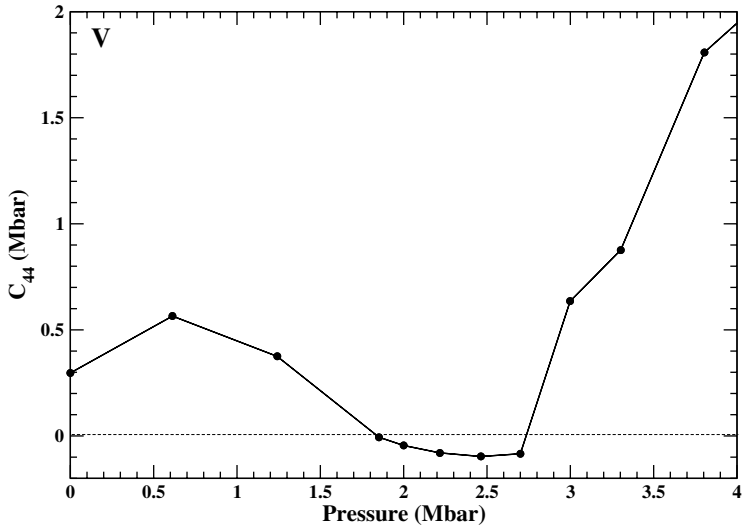

Figure 1. Pressure dependence of the trigonal shear elastic constant of V.

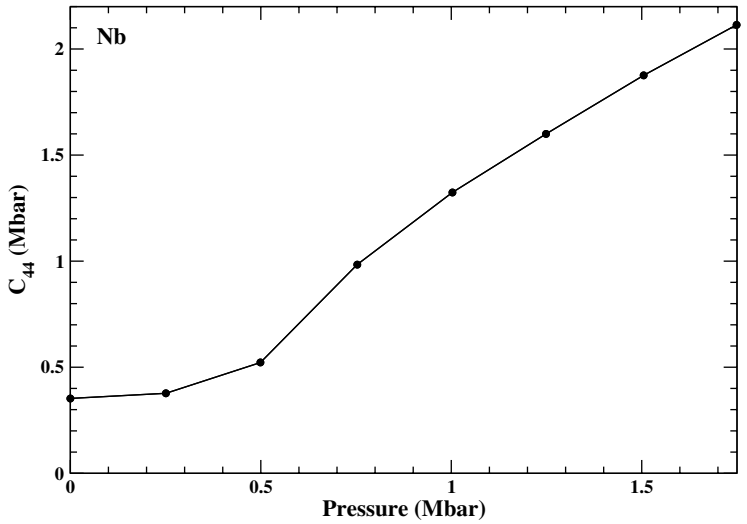

Figure 2. Pressure dependence of the trigonal shear elastic constant of Nb.

reach high precision in the $\chi(q)$ calculation, the IBZ of the bcc lattice is divided into 16 000 tetrahedra.

3. Results and discussion

Figures 1 and 2 show the pressure dependence of the trigonal shear elastic constant of V and Nb, respectively. EMTO calculations reveal a mechanical instability in C_{44} at pressures of $\sim$2 Mbar for V, and the trigonal shear elastic constant of Nb shows softening at pressures of $\sim$0.5 Mbar. One should also mention that a similar softening for C_{44} was predicted from calculations for Ta [17, 18], the remaining member of the group-VB.

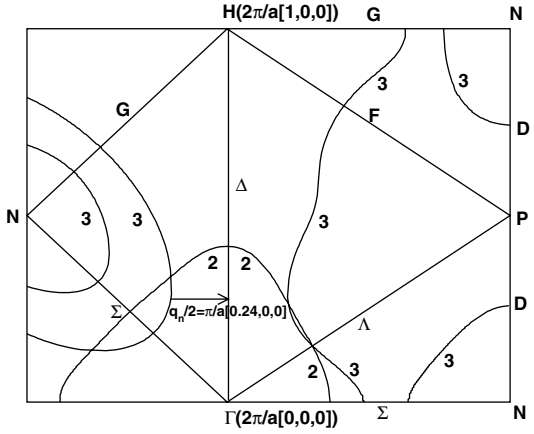

Figure 3. Central {100} and {110} cross sections of the FS of V at ambient pressure.

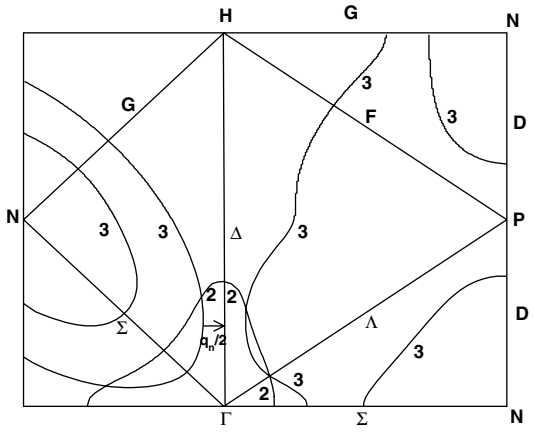

Figure 4. Central {100} and {110} cross sections of the FS of V at 2.216 Mbar.

The pressure evolution of the FS of V 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 [19]). Since V contains five valence electrons per atom, they fill the first conduction band entirely, most of the second conduction band, 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 centred at the point Γ and has the shape of a distorted octahedron. The third band (3) has closed distorted hole-ellipsoids centred at points N and multiple connected opened hole-tubes, a so-called 'jungle-gym' (JG), 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 movement of this point towards the Fermi level (figure 4), and the JG hole-tube becomes narrower and finally terminates at the [100] direction (figure 5).

Figure 6 shows the partial (due to the 3rd → 3rd electron band transitions) contribution to the generalized susceptibility, $\chi(q)$, of V 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

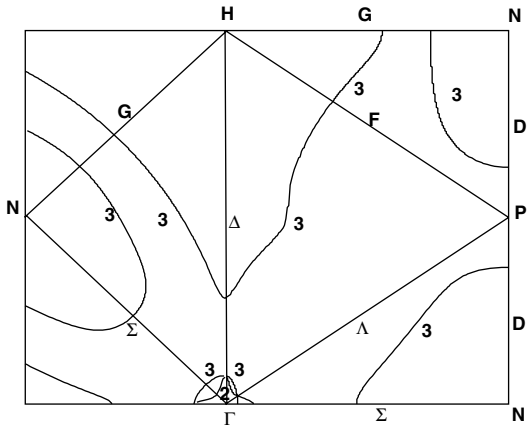

Figure 5. Central {100} and {110} cross sections of the FS of V at 3.302 Mbar.

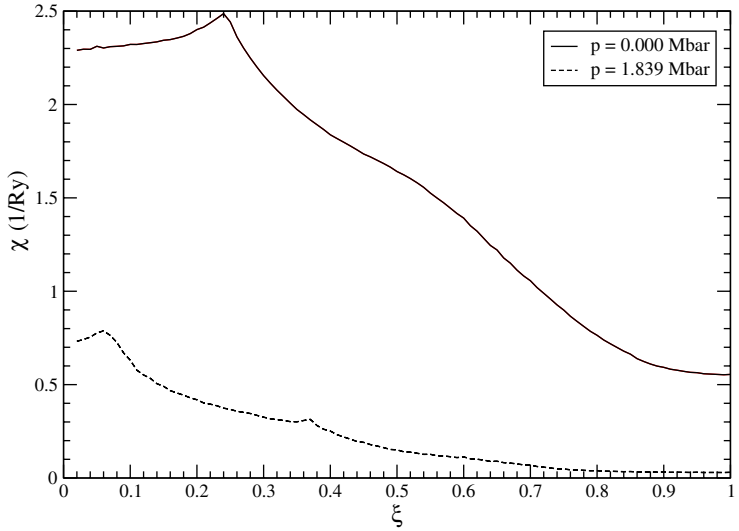

Figure 6. Partial (3rd → 3rd intra-band transition) electron susceptibility of V along the Γ–*H* ([100]) direction.

the nesting properties of the FS in the 3rd band (intra-band nesting). As pressure increases, this peak shifts swiftly towards the smaller ξ (lower wavevector q), for example, at ∼1.84 Mbar the peak is located at $\xi \approx 0.06$. Half of the nesting vector ($|\boldsymbol{q}_n|/2 \approx \pi/a[0.24, 0, 0]$) can be seen clearly in figure 3. It corresponds to the position of the anomaly in the TA found by Suzuki and Otani [5]. As pressure increases, $|\boldsymbol{q}_n|$ decreases (figure 4) and finally becomes equal to zero at pressure of the above-mentioned termination of the JG hole-tube (figure 5).

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 V 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 ($q \to 0$), $\rho\omega^2(q)/q^2 \to C_{44}$. It is remarkable that, under pressure, q_n shrinks at a fast rate and the effect of the Kohn anomaly on C_{44} increases. As soon as q_n turns to zero, the ETT, when the neck between two electronic sheets of the FS appears

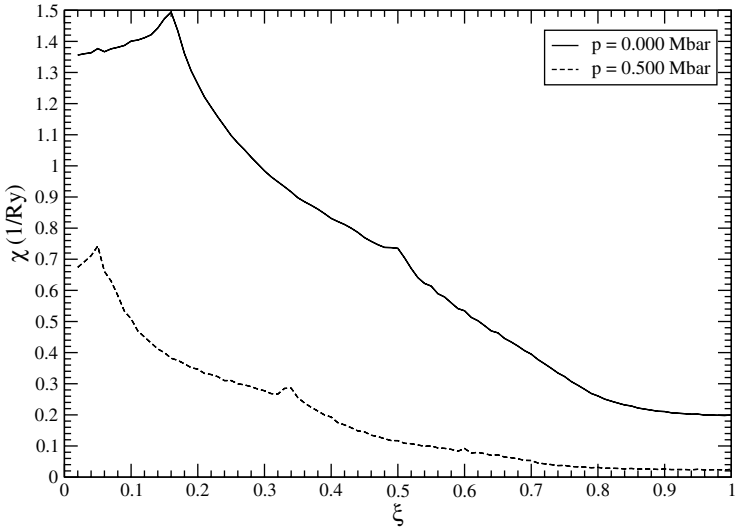

Figure 7. Partial (3rd → 3rd intra-band transition) electron susceptibility of Nb along the Γ–H ([100]) direction.

(the JG hole-tube terminates at the [100] direction), takes place. Qualitatively, it is analogous to the event when the FS touches the BZ boundary and is always accompanied by a sharp minimum in the shear elastic constants [6]. So, as $q_n \to 0$, the softening in C_{44} develops up to the point when q_n turns to zero.

Figure 7 shows the partial (due to the 3rd → 3rd electron band transitions) contribution to the generalized susceptibility, $\chi(q)$, of Nb 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 V.

However, in the case of Nb, the termination of the JG hole-tube occurs at significantly lower pressures (∼0.75 Mbar) than in the case of V (∼2.75 Mbar). In other words, the intra-band FS nesting occurs within a significantly smaller pressure range for Nb than for V, causing only a slight softening of C_{44} in the former metal in contrast with instability in the later.

We have recently established [20] 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 V and Nb is entirely due to the band-structure features. Although we recognize that C_{44} depends on the entire electron distribution and its change under strain, e.g. the initially triple-degenerate $\Gamma_{25'}$ point splits under strain in such way that one of the split level goes up above and another two go down below the Fermi level causing the DOS at the Fermi level to decrease (the so-called band Jahn–Teller (JT) effect), the ETT condition, $q_n = 0$, is reached long before the Fermi level passed the triple-degenerate term $\Gamma_{25'}$ [20]. This observation allows us to conclude that the instability (softening) of C_{44} for V (Nb) is primary due to the intra-band nesting feature of the FS, but not the JT splitting of the $\Gamma_{25'}$ point.

Finally, one should mention the well-known fact that the interaction that leads to superconductivity may also cause anomalies in the phonon spectrum [21]. The Fröhlich Hamiltonian is the fundamental in both the Bardeen–Cooper–Schrieffer (BCS) theory of superconductivity and the charge density wave (CDW) formation theory (CDW causes the pre-martensitic phonon mode softening in materials [6, 22]). However, as V shows a tendency

to increase its superconducting transition temperature and electron–phonon coupling under compression [3, 5], Nb shows an opposite behaviour [1, 2]. This difference between V and Nb is also reflected in the degree of softening of the trigonal shear elastic constant of these metals under compression.

Acknowledgments

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References

[1] Struzhkin V V, Timofeev Y A, Hemley R J and Mao H-K 1997 *Phys. Rev. Lett.* **79** 4262
[2] Tse J S, Li Z, Uehara K, Ma Y and Ahuja R 2004 *Phys. Rev.* B **69** 132101
[3] Ishizuka M, Iketani M and Endo S 2000 *Phys. Rev.* B **61** R3823
[4] Takemura K 2000 *Proc. Int. Conf. on High Pressure Science and Technology, AIRAPT-17 (Honolulu, July 1999)* (*Sci. Technol. High Pressure* vol 1) ed M H Manghnani, W J Nellis and M F Nicol (India: University Press) p 443
[5] Suzuki N and Otani M 2002 *J. Phys.: Condens. Matter* **14** 10869
[6] Katsnelson M I, Naumov I I and Trefilov A V 1994 *Phase Transit.* **49** 143
[7] Naumov I I and Velikokhatnyi O I 1997 *J. Phys.: Condens. Matter* **9** 10339
[8] Huang X Y, Naumov I I and Rabe K M 2004 *Phys. Rev.* B **70** 064301
[9] Dugdale S B, Watts R J, Laverock J, Major Zs, Alam M A, Samsel-Czekała M, Kontrym-Sznajd G, Sakurai Y, Itou M and Fort D 2006 *Phys. Rev. Lett.* **96** 046406
[10] Vitos L, Skriver H L, Johansson B and Kollár J 2000 *Comput. Mater. Sci.* **18** 24
[11] Vitos L 2001 *Phys. Rev.* B **64** 014107
[12] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[13] Chadi D J and Cohen M L 1973 *Phys. Rev.* B **8** 5747
Froyen S 1989 *Phys. Rev.* B **39** 3168
[14] Murnaghan F D 1944 *Proc. Natl Acad. Sci. USA* **30** 244
[15] Mehl M J, Klein B M and Papaconstantopoulos D A 1995 *Intermetallic Compounds: Principles and Practice* vol 1 *Principles* ed J H Westbrook and R L Fleischer (London: Wiley) chapter 9, pp 195–210
[16] Rath J and Freeman A J 1975 *Phys. Rev.* B **11** 2109
[17] Söderlind P and Moriarty J A 1998 *Phys. Rev.* B **57** 10340
[18] Cohen R E and Gülseren O 2002 *Phys. Rev.* B **65** 064103
[19] Mackintosh A R and Andersen O K 1980 *Electrons at the Fermi Surface* ed M Springford (Cambridge: Cambridge University Press) p 149
[20] Landa A, Klepeis J, Söderlind P, Naumov I, Velikokhatniy O, Vitos L and Ruban A 2006 *J. Phys. Chem. Solids* **67** at press
[21] Fröhlich H 1971 *Phys. Lett.* **35A** 325
[22] Chan S-K and Heine V 1973 *J. Phys. F: Met. Phys.* **3** 795