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Theoretical study on the lattice dynamics and electron–phonon interaction of vanadium under high pressures

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Abstract

First-principles calculations are performed for the lattice dynamics and electron–phonon interaction of the body-centred-cubic (bcc) phase of solid vanadium.

A remarkable phonon anomaly is found, i.e. frequencies of the transverse mode around a quarter of the Γ–H line show softening with increasing pressure and become imaginary at pressures higher than ∼130 GPa.

The superconducting transition temperatures T_c of bcc vanadium estimated as a function of pressure increases at first linearly with pressure, and then the rate of increase of T_c is abated around 80 GPa.

This calculated pressure dependence of T_c shows qualitatively the same behaviour as the experimental result.

1. Introduction

Superconductivity of the vanadium group (V, Nb, Ta) has been well studied because these three metals have a relatively high transition temperature T_c. In particular, Nb has the highest T_c among the elemental metals ($T_c = 9.25$ K) at ambient pressure, and the pressure dependence of its T_c has been investigated [1, 2]. Struzhkin *et al* reported that Nb has two discontinuities in the pressure dependence of T_c, which can be explained by changes in topology of the Fermi surface.

For V the pressure dependence of T_c has been investigated in several works [3–5]. Recently Ishizuka *et al* observed a characteristic behaviour of T_c. The value of T_c is 5.3 K at atmospheric pressure, increases linearly with pressure, and reaches 17.2 K at 120 GPa (the rate of increase is 0.096 K GPa^{-1}) [6]. With further increase in pressure from 120 to 150 GPa, T_c stops increasing and has a constant value [7]. The crystal structure of V is reported to be bcc from ambient pressure up to 150 GPa [8].

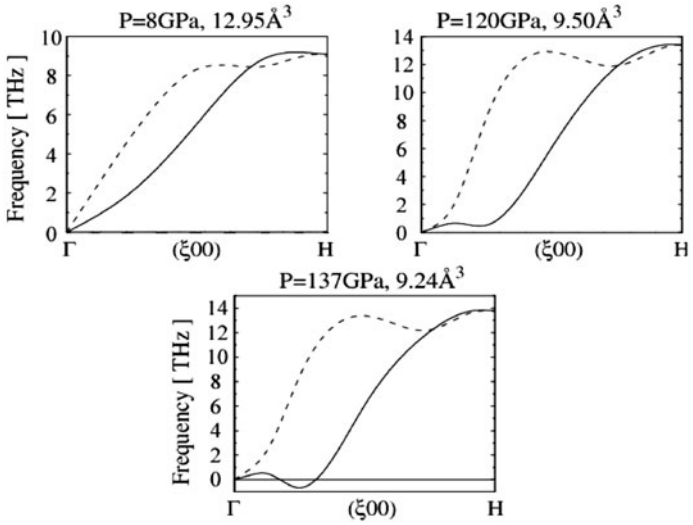

Figure 1. The phonon dispersion along the Γ–H line for three different pressures for bcc V. The dashed and solid curves denote longitudinal and transverse modes, respectively.

Theoretically, Vaitheeswaran *et al* [9] calculated T_c as a function of pressure by using a semi-empirical calculational method. They have pointed out that the increase in T_c is attributable to the continuous $s \rightarrow d$ electron transfer under pressure. However, they give no consideration to the behaviour of T_c from 120 to 150 GPa.

In this paper we apply first the full-potential LMTO (FPLMTO) method [10] for calculating the electronic band structure of V in order to estimate the equation of state, and secondly the linear-response FPLMTO (LR-FPLMTO) method [11] for calculating lattice dynamics and electron–phonon interaction of V to explore the possibility of a structural phase transition from bcc to another phase and to give insight into the origin of the characteristic pressure dependence of T_c observed by Ishizuka *et al*.

2. Results of the calculation and discussion

In order to estimate the equation of state for bcc V we have calculated the electronic band structure and the total energy as a function of volume. Then, to evaluate the pressure as a function of volume we fitted the calculated total energies to Murnaghan's equation [12]. We obtained the bulk modulus and its pressure derivative as $B_0 = 194.6$ GPa and $B_0' = 3.0$, which are in reasonable agreement with the experimental values [8] ($B_0 = 188.0$ GPa and $B_0' = 2.4$), and the pressure dependence of the volume is in excellent agreement with the experimental results [8]. The density of states (DOS) at the Fermi level ($N(\varepsilon_F)$) decreases monotonically from 26.4 (states Ryd^{-1}/atom) at 8.3 GPa to 16.6 (states Ryd^{-1}/atom) at 120 GPa.

To see the pressure dependence of the phonon frequency, we have calculated phonon dispersion curves along high-symmetry lines for several volumes (pressures). As the pressure increases, an overall tendency of increase of the phonon frequency is seen. At the same time we found a remarkable phonon anomaly, i.e. frequencies of the transverse mode at around a quarter of the Γ–H line show softening with increasing pressure and become imaginary at pressures higher than ∼130 GPa. Figure 1 shows phonon frequencies along the Γ–H line

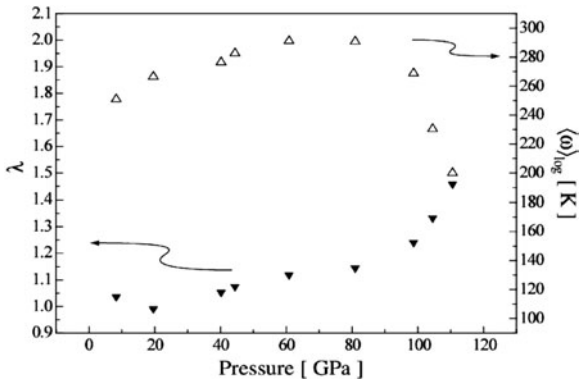

Figure 2. The electron–phonon coupling constant λ and the logarithmically averaged phonon frequency $\langle\omega\rangle_{\log}$ as a function of pressure.

obtained for 8, 120, and 137 GPa. As seen from the figure, the phonon frequencies at around a quarter of the Γ–H line show complete softening at 120–137 GPa, indicating a possibility of structural transition from bcc to another phase. A similar anomaly has been predicted for the phonon frequencies of the transverse mode around the middle of the Γ–N line in bcc Se with decreasing pressure [13].

In order to clarify the origin of the characteristic pressure dependence of the observed T_c, we have calculated the electron–phonon interaction of bcc V at several volumes. Knowledge of the electron–phonon interaction leads us to calculate T_c. Actual calculations of T_c have been performed by using the following Allen–Dynes formula [14]:

$$T_c = \frac{\omega_{\log}}{1.2} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right) \tag{1}$$

where λ is called the dimensionless electron–phonon coupling constant, μ^* represents the screened Coulomb repulsion constant, and $\langle\omega\rangle_{\log}$ is the logarithmic-averaged phonon frequency [14]. For μ^*, the conventional value is ∼0.13. Vaitheeswaran *et al*, however, estimated μ^* as 0.248 by using an empirical relation proposed by Bennemann and Garland [15]. Savrasov [11] has solved the Eliashberg equation and has found the value of μ^* to be 0.30. Since it is difficult to estimate the value of μ^* in an *ab initio* manner, as a first step in estimating the pressure dependence of T_c we adopt $\mu^* = 0.25$ for the whole range of pressure, which reproduces well the value of T_c at 8 GPa.

Figure 2 shows the results of calculations of the pressure dependences of λ and $\langle\omega\rangle_{\log}$. As seen from the figure, the value of λ increases gradually as the pressure is increased from ambient pressure. With further increase in pressure, it increases rapidly at pressures above ∼80 GPa, reflecting a remarkable phonon softening at around a quarter of the Γ–H line. The value of $\langle\omega\rangle_{\log}$ also increases at first with increasing pressure. Above 80 GPa, however, the phonon softening causes an abrupt and significant decrease of $\langle\omega\rangle_{\log}$.

These pressure dependences of λ and $\langle\omega\rangle_{\log}$ give rise to a characteristic pressure dependence for T_c. The values of T_c evaluated as a function of pressure from equation (1) are shown in figure 3 together with the experimental data [7]. In the lower-pressure region the value of T_c increases at first linearly with pressure, since both λ and $\langle\omega\rangle_{\log}$ are increased by applying pressure. At pressures higher than ∼80 GPa, on the other hand, the increase of λ and the decrease of $\langle\omega\rangle_{\log}$ cancel out, and as a result T_c becomes rather independent of pressure. These theoretical results for the pressure dependence of T_c agree fairly well with the observations. As regards the quantitative difference between the theoretical and experimental results in the higher-pressure region, we consider that it may be caused by our overestimation of the phonon softening at around a quarter of the Γ–H line. Finally, we emphasize that our results of lattice

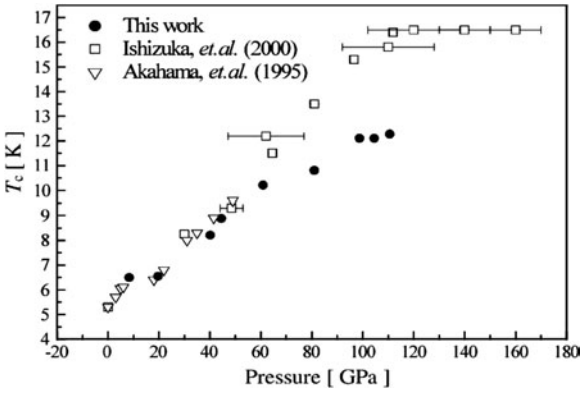

Figure 3. The pressure dependence of T_c. The filled circles represent our work and open squares denote the experimental results [7].

dynamical calculations strongly suggest the possibility of a structural transition from bcc to another phase at higher pressures. Experimental measurements on the crystal structure of V at pressures higher than 150 GPa are desirable.

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