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The role of the phonon anomaly in the superconductivity of vanadium and selenium under high pressures

N Suzuki[1] **and M Otani**[2,3]

[1] Division of Frontier Materials Science, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka 560-8531, Japan
[2] Institute for Solid State Physics, University of Tokyo, 5-1-5 Kahiwanoha, Kashiwa, Chiba 277-8581, Japan

E-mail: otani@issp.u-tokyo.ac.jp

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Abstract

First-principles calculations were performed for the superconductivity of vanadium and selenium under high pressures. The superconducting transition temperature T_c of bcc vanadium, obtained as a function of pressure, shows a considerable increase, at first linearly, with pressure, and then the rate of increase of T_c is abated around 80 GPa. The calculated pressure dependence of T_c shows qualitatively the same behaviour as the experimental result. This characteristic behaviour of T_c as a function of pressure is attributed to a remarkable phonon anomaly, i.e. frequency softening of the transverse mode around a quarter of the Γ–H line with increasing pressure. The superconducting transition temperature T_c, calculated for two high-pressure phases of solid selenium, bcc and β-Po, also shows a characteristic pressure dependence. In bcc Se, T_c increases considerably with decreasing pressure and its maximum exceeds 10 K. In β-Po Se, T_c is less pressure dependent and much lower than that of bcc Se. There is a large jump in T_c at the transition pressure from bcc to β-Po with decreasing pressure. The remarkable increase of T_c with decreasing pressure in bcc Se is attributed also to a phonon anomaly, i.e. a frequency softening of the transverse mode in the middle of the Γ–N line with decreasing pressure.

1. Introduction

The superconductivity of the transition metal vanadium (V) has been investigated in several works [1–5], and quite characteristic pressure dependence of the transition temperature T_c has

[3] Author to whom any correspondence should be addressed.

been observed. According to the experimental results obtained by Ishizuka *et al* [4], the value of T_c is 5.3 K at atmospheric pressure; it increases linearly with pressure, and it reaches 17.2 K at 120 GPa (the rate of increase is 0.096 K GPa^{-1}). With further increasing pressure, from 120 to 150 GPa, T_c stops increasing, and it has a constant value [5]. The crystal structure of V is reported to be bcc from ambient pressure up to 150 GPa [6].

The superconducting transition temperature of tellurium (Te), which is one of the group VIb elements, also shows interesting pressure dependence. The crystal structure of Te transforms from β-Po to bcc phase at 27 GPa [7], and a jump in T_c from 2.5 to 7.4 K has been observed at the structural phase transition [8]. Theoretically, Mauri *et al* suggest that the jump in T_c is related to the phonon softening in the bcc phase, namely with decreasing pressure the phonon anomaly enhances the electron–phonon coupling [9].

Selenium (Se), which is another element of group VIb, also undergoes a structural phase transition from β-Po to bcc phase at 150 GPa [8], but there is neither experimental observation nor *ab initio* calculation for the pressure dependence of T_c.

In this study we carried out first-principles electronic structure calculations for V and Se by using the full-potential linear muffin-tin orbital (FPLMTO) method [10] in order to estimate the equation of state of V and to discuss the pressure-induced phase transition from β-Po to bcc in Se. Then, by calculating the phonon frequencies and electron–phonon coupling constants of both V and Se with use of the linear-response FPLMTO (LR-FPLMTO) method [11, 12] we evaluated the superconducting transition temperature of V and Se as a function of pressure. A part of the results for V has appeared in [13], and the detailed results for Se have been given in [14].

2. Calculational procedure

The calculations of electronic states for V and Se were done according to the following procedure with the use of the FPLMTO program [10]. For the exchange–correlation functional we adopted the formula proposed by Ceperley and Alder [15] for V and by Gunnarsson and Lundqvist [16], and the GGA correction proposed by Perdew *et al* [17] for Se was taken into account. Inside the muffin-tin (MT) spheres, scalar-relativistic calculations were performed for valence electrons, and the core states were recalculated at each self-consistent iteration with relativistic effects. For V the MT radius was taken to be a constant ratio of MT radius to lattice parameter, 0.43. For Se, on the other hand, the MT radius was taken to be constant, 1.07 Å. The $\boldsymbol{k}$-space integration was performed by using the improved tetrahedron method [18] with the use of a (16, 16, 16) [(12, 12, 12)] grid of sampling $\boldsymbol{k}$-points for V [Se]. For V we used the 3κ–spd–LMTO basis set (21 orbitals): $\kappa^2 = -0.1, -1.0$ Ryd for 4s, 4p, 3d and $\kappa^2 = -2.0$ Ryd for 3p, respectively. For Se we used the 3κ–spd–LMTO basis set (27 orbitals): $\kappa^2 = -0.1, -1.0$ and -2.0 Ryd. In the interstitial region the basis functions were expanded in plane waves up to the cutoff corresponding approximately to 86, 140 and 224 [200, 350 and 650] plane waves per s, p, and d orbital, respectively, for V [Se]. The charge densities and the potentials were expanded inside the MT spheres by spherical harmonics up to $\ell_{\max} = 6$ for both V and Se and in the interstitial region by plane waves with the cutoff corresponding to the (26, 26, 26) [(16, 16, 16)] fast-Fourier-transform (FFT) grid in the unit cell of direct space for V [Se]. The final convergence was within 10^{-6} Ryd.

Our calculations of phonon dispersion for V and Se were performed in the framework of the LR-FPLMTO method [11, 12]. We found the dynamical matrix as a function of wavevector for a set of irreducible $\boldsymbol{q}$-points on an (8, 8, 8) reciprocal lattice grid for bcc V and Se and (6, 6, 6) reciprocal lattice grid for β-Po Se. The $\boldsymbol{k}$-space integration needed for constructing the induced charge density and the dynamical matrix was performed over the (16, 16, 16) grid for bcc V and Se and (12, 12, 12) grid for β-Po Se, which was twice as dense as the grid of the

phonon wavevectors $\boldsymbol{q}$. The integration was also performed by using the improved tetrahedron method. However, the integration weights for the $\boldsymbol{k}$-points on the (16, 16, 16) or (12, 12, 12) grid were found to take precisely into account the effects arising from the Fermi surface and the energy bands. This was done with the help of the band energies generated by the original FPLMTO method at the (32, 32, 32) grid for bcc V and Se and the (24, 24, 24) grid for β-Po Se. The procedure allowed us to obtain more convergent results with respect to the number of $\boldsymbol{k}$ points.

For calculation of the electron–phonon coupling the corresponding $\boldsymbol{k}$-space integrations are more sensitive than the dynamical matrices to the number of sampling $\boldsymbol{k}$-points. The calculation was performed with the help of the (32, 32, 32) grid for bcc V and Se and the (24, 24, 24) grid for β-Po Se by means of the tetrahedron method.

The superconducting transition temperature T_c was calculated by using the Allen and Dynes formula [19], which was derived on the basis of the strong coupling theory of the phonon mechanism [20]. Instead of describing the details of the strong coupling theory, here we give only the necessary equations to calculate T_c.

For the electron–phonon spectral distribution functions $\alpha^2F(\omega)$, we employed the expression [21] in terms of the phonon linewidths $\gamma_{\boldsymbol{q}\nu}$

$$\alpha^2F(\omega) = \frac{1}{2\pi N(\varepsilon_F)} \sum_{\boldsymbol{q}\nu} \frac{\gamma_{\boldsymbol{q}\nu}}{\omega_{\boldsymbol{q}\nu}} \delta(\omega - \omega_{\boldsymbol{q}\nu}), \tag{1}$$

where $N(\varepsilon_F)$ is the electronic density of states per atom and per spin at the Fermi level. When the energy bands around the Fermi level are linear in the range of phonon energies, the linewidth is given by the Fermi 'golden rule' and is written as follows:

$$\gamma_{\boldsymbol{q}\nu} = 2\pi\omega_{\boldsymbol{q}\nu} \sum_{\boldsymbol{k}jj'} |g^{\boldsymbol{q}\nu}_{\boldsymbol{k}+\boldsymbol{q}j',\boldsymbol{k}j}|^2 \delta(\varepsilon_{\boldsymbol{k}j} - \varepsilon_F)\delta(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}j'} - \varepsilon_F) \tag{2}$$

where $g^{\boldsymbol{q}\nu}_{\boldsymbol{k}+\boldsymbol{q}j',\boldsymbol{k}j}$ is the electron–phonon matrix element, and is conventionally written in the form

$$g^{\boldsymbol{q}\nu}_{\boldsymbol{k}+\boldsymbol{q}j',\boldsymbol{k}j} = \langle \boldsymbol{k}+\boldsymbol{q}j'|\delta^{\boldsymbol{q}\nu}V_{\text{eff}}|\boldsymbol{k}j\rangle, \tag{3}$$

where $\boldsymbol{k}j$ denotes the one-electron basis $\Psi_{\boldsymbol{k}j}$ and $\delta^{\boldsymbol{q}\nu}V_{\text{eff}}$ is the change in the effective potential induced from a particular $\boldsymbol{q}\nu$ phonon mode. Precisely speaking, the electron–phonon matrix element must be corrected for the incompleteness of the basis functions, but we do not discuss this here. The expression of T_c derived by Allen and Dynes [19] by modifying the McMillan formula [22] is given as

$$T_c = \frac{\omega_{\log}}{1.2} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right), \tag{4}$$

where

$$\lambda = 2\int_0^\infty \mathrm{d}\omega \, \frac{\alpha^2F(\omega)}{\omega}, \tag{5}$$

$$\omega_{\log} = \exp\frac{1}{\lambda}\int_0^\infty \frac{\mathrm{d}\omega}{\omega}\alpha^2F(\omega)\log\omega. \tag{6}$$

Usually λ is called the dimensionless electron–phonon coupling constant, $\omega_{\log}$ the logarithmic-averaged phonon frequency and μ^* the effective screened Coulomb repulsion constant, whose value is usually taken to be between 0.1 and 0.15.

In the case of monatomic metals, λ can also be expressed in the following form:

$$\lambda = \frac{N(\varepsilon_F)\langle I^2\rangle}{M\langle\omega^2\rangle} = \frac{\eta}{M\langle\omega^2\rangle}, \tag{7}$$

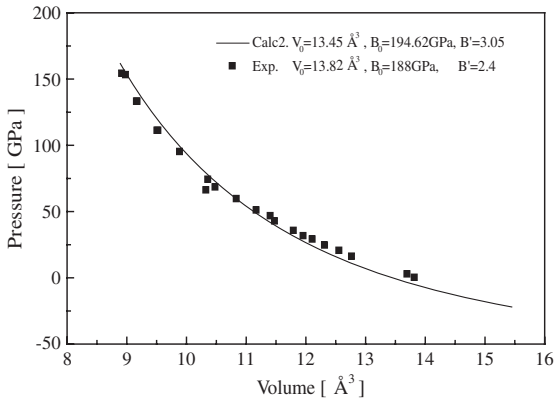

Figure 1. The pressure dependence of the atomic volume of bcc V. The solid line denotes the results of the present calculations and the filled squares indicate the experimental results [7].

where M is the mass of the atoms and $\langle\omega^2\rangle$ denotes the average of the squared phonon frequencies, which is given as

$$\langle\omega^2\rangle = \frac{\int \omega^2 \frac{\alpha^2 F(\omega)}{\omega}\,\mathrm{d}\omega}{\int \frac{\alpha^2 F(\omega)}{\omega}\,\mathrm{d}\omega}. \tag{8}$$

Further, $\langle I^2\rangle$ represents the Fermi surface average of squared electron–phonon coupling interaction, which is defined by

$$\langle I^2\rangle = \frac{\sum_{q\nu}\sum_{kjj'} |g^{q\nu}_{k+qj',kj}|^2 \delta(\varepsilon_{kj}-\varepsilon_{\mathrm{F}})\delta(\varepsilon_{k+qj'}-\varepsilon_{\mathrm{F}})}{\sum_{q\nu}\sum_{kjj'} \delta(\varepsilon_{kj}-\varepsilon_{\mathrm{F}})\delta(\varepsilon_{k+qj'}-\varepsilon_{\mathrm{F}})} \tag{9}$$

and $\eta = N(\varepsilon_{\mathrm{F}})\langle I^2\rangle$ is called the Hopfield parameter.

3. Results for vanadium

First we calculated the electronic band structure and the total energy of bcc V as a function of volume. Then, we evaluated the pressure as a function of volume by fitting the calculated total energies to the Murnaghan equation of state [23]:

$$E(V) = \frac{B_0 V}{B_0'}\left[\frac{1}{B_0'-1}\left(\frac{V_0}{V}\right)^{B_0'} + 1\right] + \text{constant},$$

where B_0 and B_0' is the isothermal bulk modulus at zero pressure and its derivative, respectively. The pressure is determined from

$$P = \frac{B_0}{B_0'}\left[\left(\frac{V}{V_0}\right)^{-B_0'} - 1\right].$$

Figure 1 shows the pressure dependence of the atomic volume. The solid line denotes the results of the present calculations and the filled squares indicate the experimental results [6]. 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 [6] ($B_0 = 188.0$ GPa and $B_0' = 2.4$), and the pressure dependence of volume is in excellent agreement with the experimental results. The density of states (DOS) at the Fermi level [$N(\varepsilon_{\mathrm{F}})$] decreases monotonically from 26.4

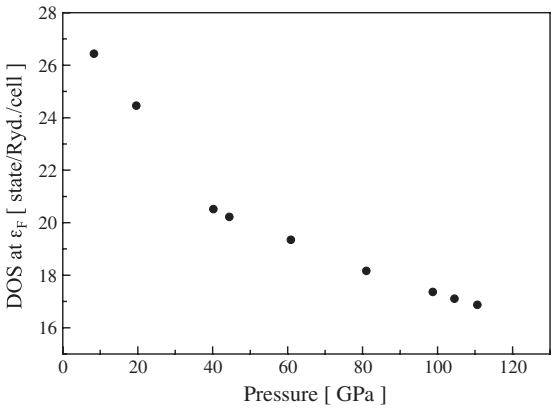

Figure 2. The pressure dependence of $N(\varepsilon_F)$ of bcc V.

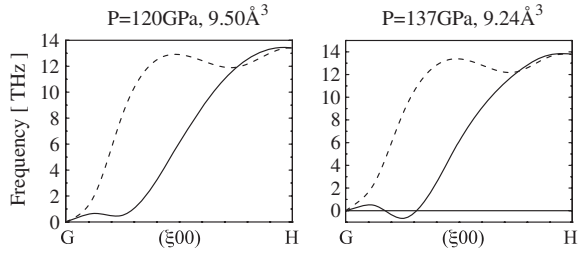

Figure 3. The phonon dispersion of bcc V along the Γ–H line at 120 and 137 GPa. The dashed and solid lines denote the longitudinal and transverse mode, respectively.

(state/Ryd/atom) at 8.3 GPa to 16.6 (state/Ryd/atom) at 120 GPa (see figure 2). This decrease of the DOS results in the decrease of the dimensionless electron–phonon coupling constant λ defined by equation (7).

To see the pressure dependence of the phonon frequency, we calculated phonon dispersion curves along high-symmetry lines for several volumes (pressures). As the pressure increases, the overall tendency of increase of phonon frequency is seen. At the same time we found a remarkable phonon anomaly, 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. Figure 3 shows the phonon frequencies along the Γ–H line obtained for 120 and 137 GPa. As is seen from the figures, the phonon frequencies around a quarter of the Γ–H line show complete softening at 120–137 GPa, indicating a possibility of a structural transition from bcc to another phase. As is shown later, a similar anomaly was obtained for the phonon frequencies of the transverse mode around the middle of the Γ–N line in bcc Se with decreasing pressure.

In order to clarify the origin of the characteristic pressure dependence of the observed T_c we calculated the electron–phonon interaction of bcc V. Knowledge of the electron–phonon interaction enables us to calculate T_c. Actual calculations of T_c were performed by using the Allen–Dynes formula given by equation (4). With respect to the value of μ^*, the conventional value is usually taken to be ∼0.13. Vaitheeswaran *et al* [24], however, estimated μ^* as 0.248 by using an empirical relation proposed by Bennemann and Garland [25]. Savrasov [13] solved the Eliashberg equation and found the value of μ^* to be 0.30. Since it is difficult to estimate

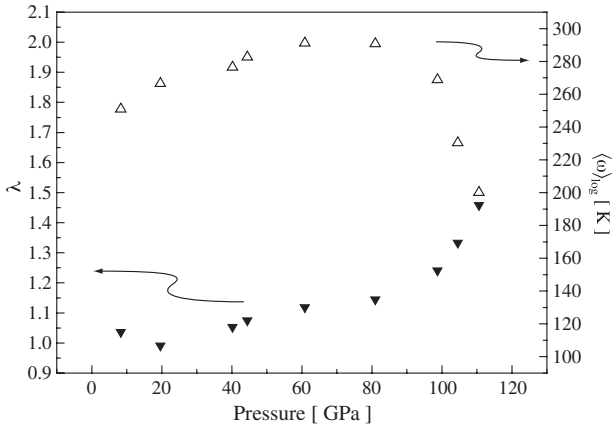

Figure 4. The electron–phonon coupling constant λ and the logarithmic-averaged phonon frequency $\langle\omega\rangle_{\log}$ as a function of pressure.

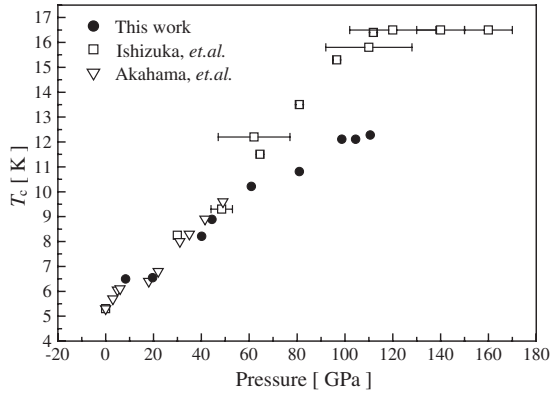

Figure 5. The pressure dependence of T_c. The filled circles represent our work and the squares and triangles denote the experimental results obtained by Ishizuka *et al* [4, 5] and by Akahama *et al* [26], respectively.

the value of μ^* in an *ab initio* manner, as a first step in estimating the pressure dependence of T_c we adopted $\mu^* = 0.25$ for the whole range of pressure, which well reproduces the value of T_c at 8 GPa.

Figure 4 shows the results of calculations for the pressure dependences of λ and $\langle\omega\rangle_{\log}$. As is seen from the figure, the value of λ increases gradually as the pressure is increased from ambient pressure. With further increasing pressure it increases rapidly at pressures above ∼80 GPa, reflecting a remarkable phonon softening 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 (4) are shown in figure 5, together with the experimental data [4, 5, 26]. 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 to 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 around a quarter of the Γ–H line. Finally, we emphasize that the results of our lattice 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 desired.

Recently, Louis and Iyakutti [27] performed theoretical calculations of the electronic band structure and superconductivity of V under pressures. The band structures of bcc, sc, fcc and sh phases were computed by means of the tight-binding linear muffin-tin orbital method, and they predicted that a structural phase transition from bcc to sc would occur at 139.3 GPa. The superconducting transition temperature T_c of bcc V under pressures was calculated up to 945 GPa with the use of the theory of Gaspari and Gyoffy for the dimensionless electron–phonon coupling constant λ as well as the Debye model for the lattice dynamics. The value of T_c calculated increases monotonically with increasing pressure and reaches the highest value, 20.99 K, at 139.3 GPa. On further increasing the pressure it goes on decreasing, and reaches 5.44 K at 945 GPa. The value of T_c evaluated for sc V is much lower than that of bcc V, i.e., 1.72 K at 238 GPa and 0.056 K at 945 GPa (the value of T_c at 139.3 GPa is not given in [27]).

Experimentally, on the other hand, as mentioned in section 1, the crystal structure of V is reported to be bcc from ambient pressure up to 150 GPa [6], and the value of T_c is almost constant from 120 to 150 GPa [5]. Therefore, in order to obtain a better understanding of the structural and superconducting properties of V under high pressures, refinements of the theoretical calculations as well as experimental measurements at pressures higher than 150 GPa are desired.

4. Results for selenium

First we calculated the total energies of β-Po and bcc Se as a function of volume in order to investigate the pressure-induced structural transition, bcc $\rightarrow$ β-Po. The β-Po type structure is rhombohedral, and it can be described as a simple cubic lattice deformed along the [111] direction keeping the edge length unchanged. By changing the ratio c/a of the rhombohedral lattice we obtain the bcc structure when $c/a = \sqrt{6}/4$. For the β-Po structure we optimized c/a at each volume, namely, we calculated the total energy of β-Po Se as a function of c/a with the atomic volume V_A being kept constant. The pressure of each structure was evaluated as a function of volume by fitting the calculated total energies by the Murnaghan equation of state [23].

In order to estimate the transition pressure from β-Po to bcc we calculated the Gibbs free energy (or enthalpy) as a function of pressure. The Gibbs free energy is defined by $G(P) \equiv E_{tot}(P) + PV(P)$ and the transition pressure between the two phases is obtained from the relation $G_\beta(P) = G_b(P)$, where G_β and G_b are the Gibbs free energies of the β-Po and the bcc structures, respectively. Figure 6 shows the Gibbs free energies of bcc and β-Po Se (the origin of energy is taken to be the Gibbs free energy of bcc Se). From this plot the transition pressure P_c from β-Po to bcc was estimated as 120 GPa. This value is higher than other calculated transition pressures, 95 GPa (FLAPW method without GGA) [28] and 110 GPa (pseudo-potential method without GGA) [29], but still lower than the experimental value of 150 GPa [30]. The origin of this discrepancy between theory and experiment may be ascribed to the LDA with GGA itself and/or the numerical accuracy of the total energy.

Besides the pressure dependence of the atomic volume V_A of both the structures, for β-Po Se we also calculated the lattice constants a and c, and the bond lengths r_1 and r_2, which

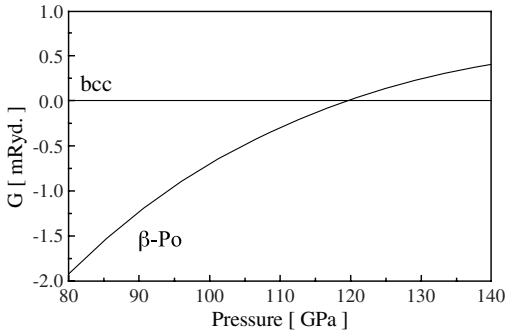

Figure 6. The Gibbs free energies of β-Po and bcc Se.

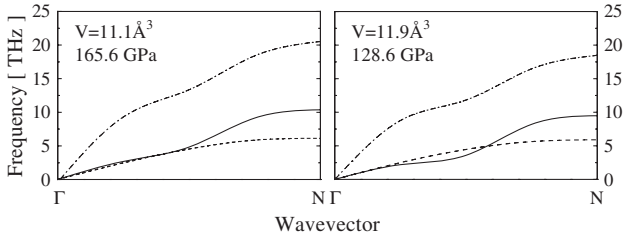

Figure 7. The phonon dispersion curve along the high-symmetry line (Γ–N) of bcc Se calculated at 165.6 and 128.6 GPa.

are defined as the nearest neighbour (nn) and next nn (nnn) atomic distances, respectively. We note here that the volume variation as a function of pressure below 120 GPa (β-Po) and above 150 GPa (bcc) shows good agreement with the observations [30]. It is also noted that the obtained pressure dependence of a, c and the bond lengths of the β-Po phase agree well with the experimental results [30]. Furthermore, the volume reduction at the transition from the β-Po to the bcc phase is estimated to be 0.06 Å^3, which is in good agreement with the experimental volume (about 0.08 Å^3) [30].

As for the lattice dynamics, we first calculated the phonon dispersion curve along the high-symmetry line (Γ–N) for bcc Se at different four volumes (pressures), 10.37 Å^3 (214.2 GPa), 11.11 Å^3 (165.6 GPa), 11.85 Å^3 (128.6 GPa), and 12.59 Å^3 (103.4 GPa). The results for 165.6 and 128.6 GPa are shown in figure 7. As the pressure decreases, the overall tendency of decrease of phonon frequency is seen. In particular, the frequency softening is remarkable for one of the transverse modes (shown by the solid curve), and this mode exhibits a notable phonon anomaly, i.e., a dip in the middle of the line. The same phonon anomaly is obtained in S [31]. This softening of the transverse mode does not directly cause the bcc $\rightarrow$ β-Po transition with decreasing pressure, because both of the β-Po and bcc phases have one atom per unit cell. However, Zakharov and Cohen [31] have pointed out that it plays an important role in changing the coordination number from eight to six during the bcc $\rightarrow$ β-Po transition.

Mauri *et al* [9] performed an *ab initio* linear-response calculation for the lattice dynamics of bcc Te under pressures. They reported the same anomaly for the transverse mode along the Γ–N line and found that with decreasing pressure the phonon frequencies in the middle of the Γ–N line become imaginary in a pressure region where the β-Po structure is stable. In our calculation, complete softening of the transverse mode was not observed even at 100 GPa, where the β-Po structure is stable. Complete softening may occur at even lower pressures.

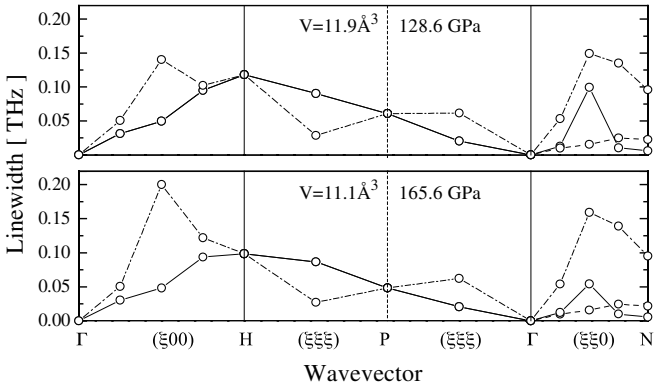

Figure 8. The mode and wavevector dependences of the phonon linewidths $\gamma_{q\nu}$ along the symmetry lines of bcc Se calculated at 165.6 and 128.6 GPa.

Table 1. The values of $N(\varepsilon_F)$, η, ω_{log}, $\langle\omega^2\rangle$, λ and T_c calculated for bcc Se at 165.6 and 128.6 GPa. The two values for T_c correspond to two different values of μ^* (0.10 and 0.12). The units of $N(\varepsilon_F)$ and η are state/Ryd/atom/spin and Ryd Å^{-2}, respectively.

P (GPa)	$N(\varepsilon_F)$	η	ω_{log} (K)	$\langle\omega^2\rangle$ (K^2)	λ	T_c (K)
128.6	2.73	0.018	224.73	291.95^2	0.83	11.29, 9.90
165.6	2.55	0.019	264.62	335.11^2	0.66	8.03, 6.64

By using the Allen–Dynes formula, we estimated the superconducting transition temperature T_c of bcc Se. In table 1 we give the values of T_c together with those of the density of states $N(\varepsilon_F)$, the Hopfield parameter η, the logarithmic-averaged frequency ω_{log}, the average of the squared phonon frequencies $\langle\omega^2\rangle$, and the electron–phonon coupling constant λ, calculated at 165.6 and 128.6 GPa. As for the value of μ^*, we tentatively adopted two typical values, $\mu^* = 0.10$ and 0.12. With decreasing pressure, the value of ω_{log} decreases, while the value of λ increases, but the rate of change of λ exceeds that of ω_{log}. As a result, the value of T_c increases considerably with decreasing pressure. Since λ can be expressed by $\lambda = \frac{N(\varepsilon_F)\langle I^2\rangle}{M\langle\omega^2\rangle}$, the frequency softening (decrease of $\langle\omega^2\rangle$) is considered to contribute to the increase of λ with decreasing pressure.

In order to obtain a more physical insight into the characteristic pressure dependence of T_c, we calculated the mode and wavevector dependences of the phonon linewidths $\gamma_{q\nu}$ along the symmetry lines. The results obtained for 165.6 and 128.6 GPa are shown in figure 8. The figure shows that $\gamma_{q\nu}$ is almost independent of pressure, except for the longitudinal mode along the Γ–H line and one of the transverse modes along the Γ–N line. With decreasing pressure, $\gamma_{q\nu}$ of the longitudinal mode along the Γ–H line decreases whereas that of the transverse mode along the Γ–N line increases considerably. Generally speaking, a large phonon linewidth increases the dimensionless electron–phonon coupling λ. Therefore, it is expected that the transverse mode along the Γ–N line plays an important role in giving rise to the characteristic pressure dependence of T_c.

To clarify the role of the transverse mode along the Γ–N line in more detail, we calculated the quantity $\alpha^2(\omega)$, defined by

$$\alpha^2(\omega) = \frac{\alpha^2 F(\omega)}{D(\omega)}, \tag{10}$$

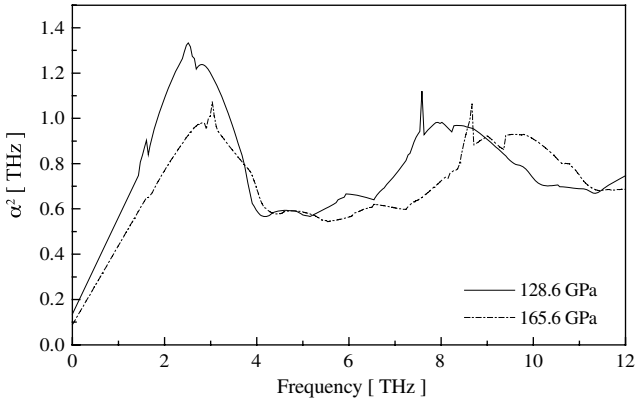

Figure 9. The frequency dependence of $\alpha(\omega)^2$ of bcc Se obtained for 165.6 and 128.6 GPa.

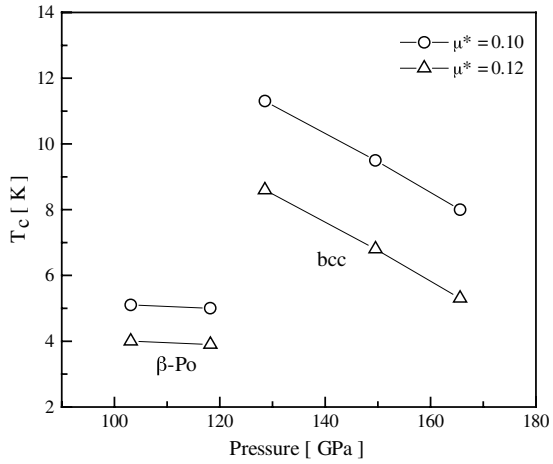

Figure 10. The values of T_c calculated for β-Po and bcc Se as a function of pressure. The circles and triangles denote the computed values of T_c with $\mu^* = 0.10$ and 0.12, respectively.

where $\alpha^2 F(\omega)$ is the spectral function and $D(\omega)$ denotes the phonon density of states. We consider that by inspecting the frequency dependence of $\alpha^2(\omega)$ we can discern which phonons make dominant contributions to the dimensionless electron–phonon coupling λ. Figure 9 shows the calculated $\alpha^2(\omega)$ as a function of frequency for three pressures. The peak around 2 THz originates from transverse phonons along the Γ–N line and the peak around 7–10 THz from longitudinal phonons along the Γ–H line. As is seen from the figure, both peaks move towards the lower frequency side with decreasing pressure. It should be noted, however, that the magnitude of $\alpha^2(\omega)$ around 2 THz increases remarkably with decreasing pressure, whereas the magnitude of $\alpha^2(\omega)$ around 7–10 THz is less dependent on pressure. Therefore, we can say again that transverse phonons in the middle of the Γ–N line make a dominant contribution to λ.

Combining all of the above results, we conclude that the origin of the remarkable increase of T_c of bcc Se with decreasing pressure is mainly attributed to the phonon anomaly (the remarkable frequency softening) in the middle of the Γ–N line.

To see the pressure dependence of T_c in β-Po Se, we calculated T_c at pressures 103.1 and 118.2 GPa with the use of the lattice constants determined experimentally. The calculated values of T_c are given in table 2, together with those of $N(\varepsilon_F)$, η, ω_{log}, $\langle\omega^2\rangle$ and λ.

Table 2. The values of $N(\varepsilon_F)$, η, ω_{log}, $\langle\omega^2\rangle$, λ and T_c of β-Po Se calculated for 103.1 and 118.2 GPa. The two values for T_c correspond to two different values of μ^* (0.10 and 0.12). The units of $N(\varepsilon_F)$ and η are state/Ryd/atom/spin and Ryd Å^{-2}, respectively.

P (GPa)	$N(\varepsilon_F)$	η	ω_{log} (K)	$\langle\omega^2\rangle$ (K^2)	λ	T_c (K)
103.1	2.45	0.015	250.11	311.71^2	0.58	5.14, 4.04
118.2	2.43	0.016	255.88	324.58^2	0.57	5.01, 3.91

Figure 10 shows the values of T_c calculated for β-Po and bcc Se as a function of pressure. As is seen from the figure, the superconducting transition temperature T_c is almost pressure independent in the β-Po phase, and there is a large jump in T_c at the transition from β-Po to bcc. Almost the same results have been obtained by Rudin *et al* [32] for the pressure dependence of T_c of β-Po and bcc Se. Recently, high-pressure measurements have been done for Se up to 180 GPa, and superconductivity has been observed at 150–170 GPa in the bcc phase [33]. The observed values of T_c are very close to our calculated results.

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