

**Electronic phase transition and superconductivity of vanadium under high pressure**

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We report a theoretical calculation of the electronic band structure, density of states, phase transitions, and superconductivity of vanadium under pressure. The total energies of vanadium corresponding to bcc, fcc, simple cubic (sc), and simple hexagonal structures are computed. From the enthalpy calculation, it is found that up to  $V/V_0=0.685$  vanadium has the bcc structure and a further increase of pressure induces a structural phase transition from bcc to sc structure. Under normal conditions, the superconducting transition of vanadium occurs at 5.97 K ( $T_c$ ). When the pressure is increased it is predicted that  $T_c$  increases at a rate of 10.78 K/Mbar for pressures up to 1.393 Mbar, whereas the experimental increase is 9.6 K/Mbar for pressures up to 1.20 Mbar. The highest  $T_c$  estimated is 20.99 K and the corresponding pressure is 1.393 Mbar. On further increase of pressure  $T_c$  begins to decrease at a rate of 1.42 K/Mbar in bcc structure and 0.2355 K/Mbar in sc structure. Experimental evidence is available up to the 1.2 Mbar pressure region.

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**I. INTRODUCTION**

The discovery of superconductivity with a high transition temperature at normal pressure is of great physical interest. Vanadium (V) is a transition metal. Theoretically Otani and Suzuki<sup>1</sup> applied a first-principles study to bcc vanadium under high pressure. The lattice dynamical studies of vanadium including calculations of phonon dispersion relations, density of states, and the shape of the Fermi surface have been reported.<sup>1</sup> From these results, Otani and Suzuki strongly suggest that vanadium would take another structure other than bcc above 1.37 Mbar. So further theoretical calculations and experimental observations are needed in order to predict the electronic phase transition of vanadium under pressure.

Vanadium metal exhibits a high superconducting transition temperature under normal conditions and the pressure dependence of  $T_c$  has been observed in several experimental works.<sup>2-4</sup> The  $T_c$  of vanadium has been studied up to a maximum pressure of 0.010 Mbar by Gargner and Smith.<sup>2</sup> The rate of increase of  $T_c$  with pressure is (pressure coefficient  $dT/dP$ )  $11 \pm 3$  K/Mbar. Gargner and Smith offered a clear explanation of the observed variation in the sign of the pressure dependence of  $T_c$  in vanadium. More recently,  $T_c$  of vanadium has been observed as a function of pressure up to 1.2 Mbar by Ishizuka *et al.*<sup>5</sup> The results of the superconducting quantum interference device vibrating coil magnetometer measurements performed by Ishizuka *et al.*<sup>5</sup> on vanadium give the characteristic behavior of  $T_c$  under pressure. Under normal conditions, the superconducting transition temperature  $T_c$  is 5.3 K and at 1.2 Mbar pressure the value of  $T_c$  is 17.2 K; this value is the highest value of  $T_c$  among the elemental metals reported so far.<sup>5</sup> There are no theoretical predictions in corresponding to this observation. This motivated the present investigation.

In our calculations, the effect of pressure on the band structure of vanadium is obtained by means of the self-consistent tight-binding linear muffin-tin orbital (TB LMTO) method.<sup>6,7</sup> The superconducting transition temperature  $T_c$  is calculated using McMillan's formula.<sup>8</sup> We present our results on the pressure dependence of  $T_c$  of vanadium in the

bcc phase as well as the simple cubic (sc) phase and the phase transition of vanadium under pressure. In Section II, the details of the calculational procedure, electronic band structure, and density of states corresponding to various pressures of vanadium are discussed. Section III contains the details of the results and a discussion. The conclusion is given in Sec. IV.

**II. BAND STRUCTURE AND DENSITY OF STATES****A. Calculational procedure**

The TB LMTO method within the atomic sphere approximation (ASA) and local density approximation (LDA) is used to compute the band structure and density of states of vanadium. The details of the method are found in Refs. 9–12 and here we give only the computational details. All relativistic effects except spin-orbit coupling are included. The exchange correlation scheme of Von Barth and Hedin is employed.<sup>13</sup> The Brillouin zone (BZ) integrations are performed for 145  $k$  points for both bcc and fcc structures, 165  $k$  points for sc structure, and 270  $k$  points for simple hexagonal (sh) structure of vanadium, within the irreducible wedge of the Brillouin zone. The final convergence in our self-consistent calculation is  $10^{-5}$  Ry. For the sh structure calculation,  $c/a$  is fixed at 1.633 and the total energy is calculated as a function of the lattice spacing  $a$ , keeping the ratio  $c/a$  constant.<sup>14</sup> The electronic configuration of vanadium is  $[\text{Ar}]4s^2 3d^3$ . The valence states assumed in our calculations are  $4s^2$  and  $3d^3$ . There are five valence electrons in vanadium throughout our calculations. The total energy calculation of vanadium is performed as a function of reduced volume for bcc, sc, fcc, and sh structures. The calculated total energies are fitted to Murnaghan's equation of state<sup>15</sup> to determine the phase transition pressure and other ground-state properties of vanadium.

**B. Band structure under pressure**

We have obtained the band structure of vanadium in the bcc phase and sc phase as a function of various reduced

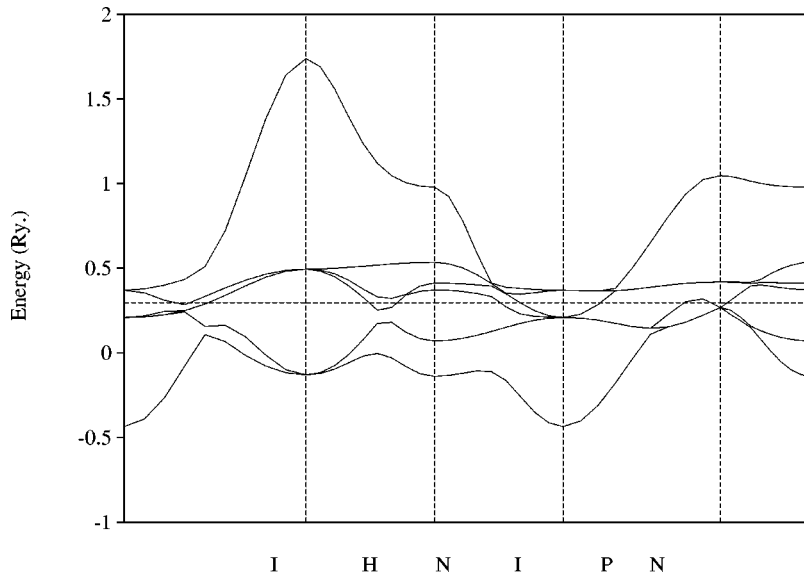


FIG. 1. Band structure of V in bcc structure at  $V/V_0=1.0$ .

volumes. We have done the band structure calculation for different pressures ranging from normal to 23 Mbar corresponding to volume compressions  $V/V_0$  from 1.0 to 0.3. The pressure dependence of the volume is derived from Murnaghan's equation of state.<sup>15</sup> Even though we have obtained the band structure for  $V/V_0$  values from 1.0 to 0.3, we present here the band structures of vanadium along the symmetry directions  $\Gamma$ -H-N- $\Gamma$ -P-N for bcc structure (Figs. 1 and 2) and  $\Gamma$ -R-X- $\Gamma$ -M-X for sc structure (Fig. 3), corresponding to the compressions  $V/V_0=1.0$  (Fig. 1) and 0.685 (Figs. 2 and 3) only. The charge distribution under reduced volume for the bcc phase is given in Table I.

At normal pressure (Fig. 1), band structure of vanadium shows that there is a overlapping of valence band and conduction band, confirming the metallic nature of vanadium under normal conditions. The band structure of vanadium exhibits characteristic features similar to other transition elements Nb, Zr, and Ta.<sup>16-18,1</sup> Similar to previous theoretical band structure calculations of vanadium,<sup>19-22</sup> in the present inves-

tigation also the conduction-band minimum is located at the  $\Gamma$  point. The single band lying well below the Fermi level is the valence band due to  $4s^2$  electrons of vanadium. The nearly half-filled bands with  $3d$  character originate just below the Fermi level. The conduction bands above the Fermi energy  $E_F$  are due to  $4p^0$  state of vanadium. As pressure increases, the entire band structure is slowly shifted up in energy. For comparison, we have given the electronic band structure of bcc vanadium and sc vanadium at the same reduced volume of  $V/V_0=0.685$  (Figs. 2 and 3). It is important to note that in Figs. 2 and 3 the low-lying  $4s$  band never rises above the Fermi level as observed in bcc Zr under pressure.<sup>17</sup> And also the  $3d$  bands lie just below the Fermi level for both structures.

From Figs. 1 and 2, it is seen that the occupied  $d$ -band region increases under pressure while the occupied  $s$ -band region decreases. It is due to the  $s$  to  $d$  transition under pressure. The  $s,p$  electron transfer to the  $d$  shell under pressure is qualitatively a common feature of many band structure

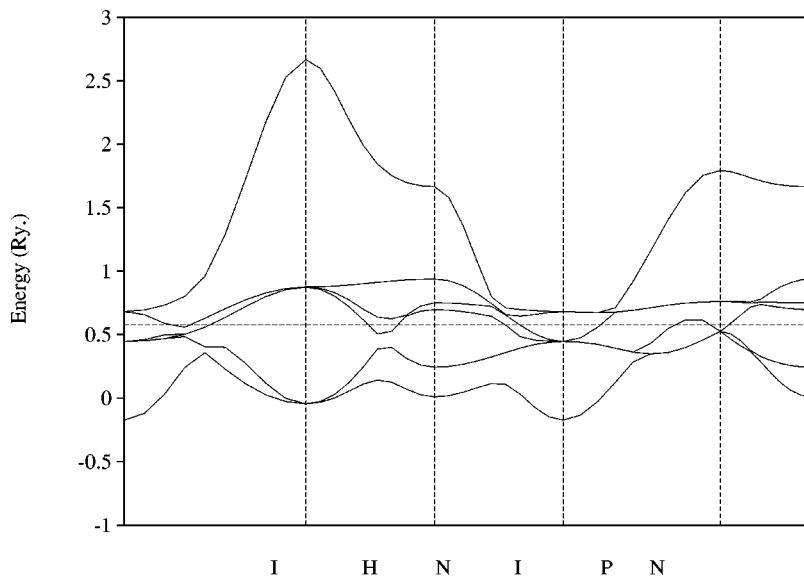


FIG. 2. Band structure of V in bcc structure at  $V/V_0=0.685$ .

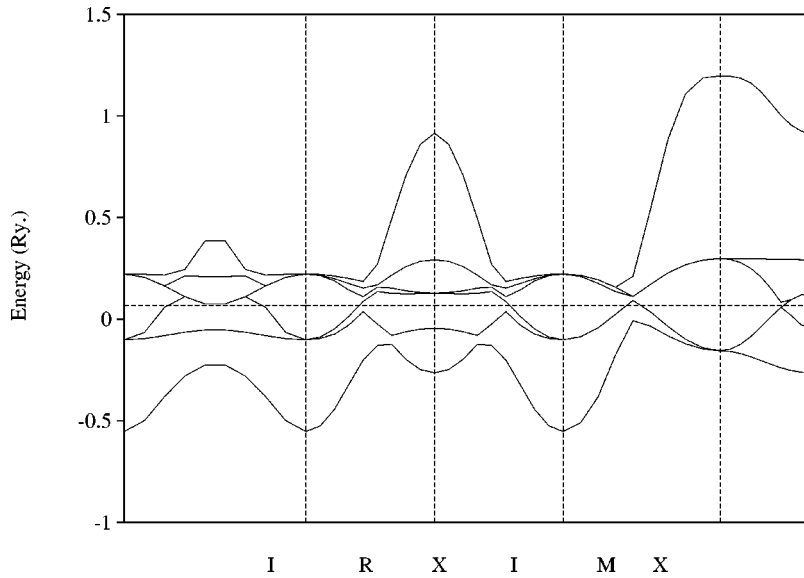


FIG. 3. Band structure of V in sc structure at  $V/V_0=0.685$ .

calculations.<sup>12,23–26</sup> In a similar way, there is  $s,p$  electron transfer to the  $d$  shell in vanadium up to  $V/V_0=0.3$  (Table I). The  $d$ -electron number of vanadium increases from 3.6345 to 4.4775 in the pressure range from normal to 23 Mbar. The dip in the  $4s$  band near the  $\Gamma$  point below the Fermi level (Fig. 1) decreases as the pressure increases (Figs. 2 and 3). It is due to the strong hybridization of the band structure and also the electronic system is strongly coupled to the lattice under pressure.<sup>27</sup> The band structure results are used to calculate the value of  $T_c$  in conjunction with McMillan's formula.<sup>8,18</sup>

### C. Density of states under pressure

The density of states (DOS) (states/Ryd cell) histograms corresponding to various pressures ranging from normal to 23 Mbar are obtained. In Figs. 4–6, we have presented the DOS histograms pertaining to the compressions  $V/V_0=1.0$  (Fig. 4) and 0.685 (Figs. 5 and 6). The calculated DOS at the Fermi energy  $N(E_F)$  corresponding to various pressures of bcc vanadium is given in Table II. For sc vanadium the DOS data are given in Table III. Under normal conditions (Fig. 4), the levels arising from V  $3d$  electrons give a high spike with

narrow width near  $E_F$ . The short spike near the origin is due to  $4s$  electrons of vanadium. The highest spike with a broad width above  $E_F$  is due to the empty  $4p$  state of vanadium.

When pressure increases, the value of Fermi energy increases whereas the density of states at  $N(E_F)$  decreases. It is due to the broadening of the bandwidth with pressure.<sup>1</sup> In Fig. 5, the spikes are of almost equal height below the Fermi level. From Figs. 5 and 6, the DOS at the Fermi level of the bcc structure (13 states/Ry) (Fig. 5) is smaller than that of the sc structure (19 states/Ry) (Fig. 6). This is because, when vanadium is deforming from bcc to sc structure, the energy bands per unit energy region below the Fermi level increases (Fig. 3). As a result, the DOS plot of sc vanadium (Fig. 6) has a relatively large peak just below the Fermi level. This results in a larger DOS at the Fermi level of the sc structure than that of the bcc structure at  $V/V_0=0.685$ . This large peak below  $E_F$  is the reason for the stability of the sc structure above this pressure region. A similar situation is observed in selenium where the structural stability is explained on the basis of a relatively large peak below the Fermi level.<sup>25</sup> This view is supported by our present investigation. The shape of the hole Fermi surface of the third band of vanadium at normal pressure and 1.37 Mbar is evaluated by Otani and Suzuki.<sup>1</sup> They pointed out the possibility of a structural transition from bcc to another phase above 1.37 Mbar pressure.

TABLE I. Electrons in  $s$ ,  $p$ , and  $d$  shells of bcc vanadium at different pressures.

$V/V_0$	Lattice constant $a$ (a.u.)	Pressure	$4s^2$	$4p^0$	$3d^3$
		$P$ (Mbar)			
1.0	5.7278	0.0000	0.6302	0.7352	3.6345
0.9	5.5301	0.2473	0.6157	0.7081	3.6762
0.8	5.3172	0.6321	0.5965	0.6707	3.7328
0.7	5.0857	1.2649	0.5688	0.6212	3.8099
0.6	4.8310	2.3839	0.5252	0.5571	3.9176
0.5	4.5462	4.5655	0.4552	0.4864	4.0584
0.4	4.2203	9.4500	0.3259	0.3944	4.2796
0.3	3.8344	23.0000	0.1560	0.3665	4.4775

## III. RESULTS AND DISCUSSION

### A. Ground-state properties of vanadium

In order to study the phase stability of vanadium, we have calculated the total energy as a function of reduced volume for various structures as shown in Fig. 7. The reduced volume  $V/V_0$  is ranges from 1.2 to 0.4 in steps of 0.05, where  $V_0$  is the experimental equilibrium volume under normal pressure and  $V$  is the volume under pressure.<sup>28</sup> The calculated total energy confirms that the ground-state structure of vanadium is bcc as observed experimentally and reported from other theoretical calculations.<sup>1–5</sup> The calculated total

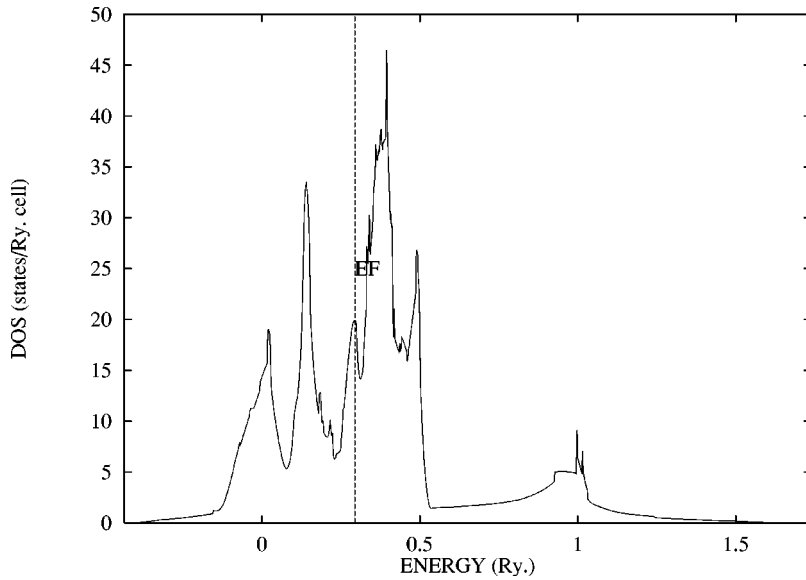


FIG. 4. DOS of V in bcc structure at  $V/V_0 = 1$ .

energies were fitted to Murnaghan's equation of state<sup>15</sup> and the determined pressure is tabulated in Table I. The calculated equilibrium lattice constant  $a_0$ ,  $B_0$ , and  $B_0^1$  in the bcc structure are given in Table IV together with experimental and other theoretical results, where  $B_0$  is the isothermal bulk modulus at normal pressure which is equal to  $(-V_0 dP/dV)$  and  $B_0^1$  is the pressure derivative of isothermal bulk modulus evaluated at normal pressure.<sup>9</sup> The equilibrium lattice constant determined from our calculation is 5.733 87 a.u., which differs from the experimental value by 0.105%. This indicates the accuracy of our calculation. The pressure dependence of the reduced volume obtained from our calculated  $B_0$  and  $B_0^1$  values agrees well with experimental<sup>5</sup> work and exactly coincides with previous theoretical<sup>1</sup> work (Fig. 8). The origin of the discrepancy between theory and experiment at high compression may be due to the difference in the theoretical value of the pressure derivative of the bulk modulus  $B_0^1$  and the experimental  $B_0^1$  (Table IV). The difference between theory and the experimental value of  $B_0^1$  may be due

to the local density approximation and the numerical accuracy of the total energy calculations.

### B. Phase transition under pressure

At ambient conditions, vanadium has bcc structure. Otani and Suzuki<sup>1</sup> obtained phonon dispersion curves along the high-symmetry directions of vanadium. They opined that there could be a phase transition from bcc to another phase other than bcc at high pressure above 1.37 Mbar and suggested further experimental and theoretical investigations in this direction for vanadium.

In general the phase transition pressure and the corresponding reduced volume are studied by performing total energy calculations for various structures. Here total energy calculations are performed for various phases of vanadium [bcc( $A_2$  phase), sc( $A_h$  phase), fcc( $A_1$  phase), and sh( $A_f$  phase)] corresponding to the reduced volume of  $V/V_0 = 1.2-0.4$  and the results are shown in Fig. 7. To ensure the

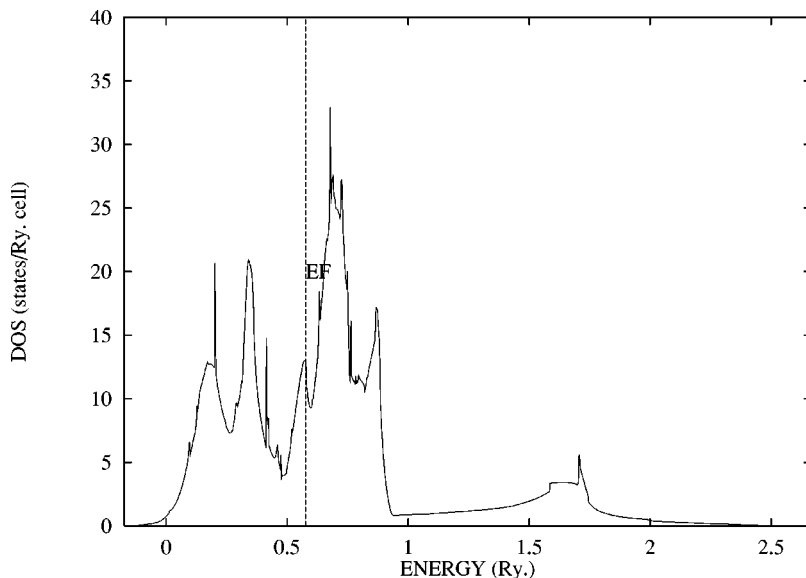


FIG. 5. DOS of V in bcc structure at  $V/V_0 = 0.685$ .

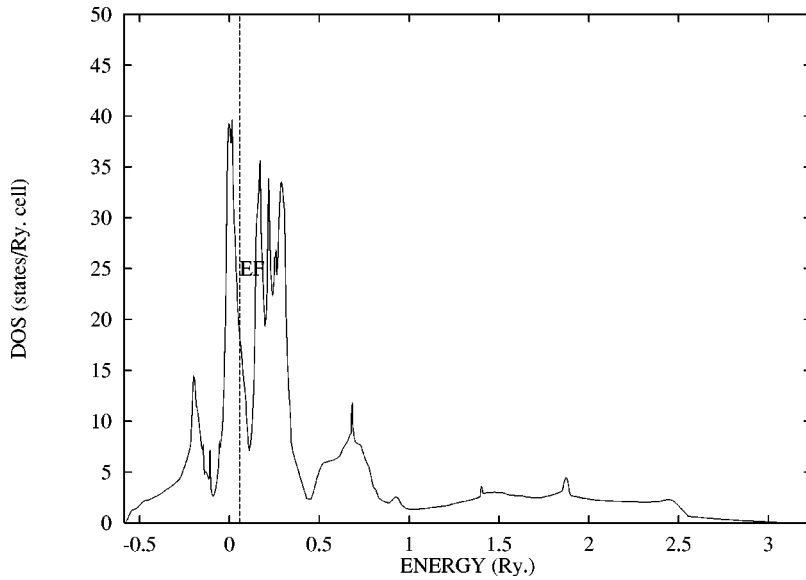


FIG. 6. DOS of V in sc structure at  $V/V_0 = 0.685$ .

high-pressure structure of vanadium, we have also calculated the total energies corresponding to the hcp and diamond structures. From the results we observed, the total energies of vanadium in the above structures are higher than those in the sc, fcc, and sh structures. From Fig. 7, it is found that up to  $V/V_0 = 0.685$ , bcc structure has the lowest energy and further reduction of volume, and sc structure becomes more stable in energy than the bcc structure. Further from the enthalpy calculation, similar to our earlier studies on KI and RbI,<sup>12</sup> we have analyzed the structural phase transition from bcc to sc structure. The enthalpy versus pressure curve is given in Fig. 9. From this, we get the phase transition pressure as 1.393 Mbar and the corresponding reduced volume  $V/V_0$  as 0.685. So it leads to the conclusion that under high pressure (1.393 Mbar) vanadium undergoes a phase transition from bcc structure ( $A_2$  phase) to sc structure ( $A_h$  phase). Thus our present calculation confirms that sc structure is the promising candidate for the new phase one can observe above 1.37 Mbar, which was hinted at in the previous study by Otani and Suzuki.<sup>1</sup> However, our result of the phase transition in vanadium could not be checked by the experiment<sup>29</sup> or theoretical study. So far, no study on the phase transition has been performed as a function of high pressure for vanadium.

### C. Superconductivity in vanadium under pressure

The continuous promotion of  $s, p$  electrons to the  $d$  shell in all solids under pressure is one of the factors which will induce superconductivity<sup>18,23–27</sup>. The manner in which the  $d$  electron number is increasing as a function of pressure in vanadium is given in Table I. At normal pressure itself the contribution of  $3d$  state is large whereas  $4s$  and  $4p$  states are small. This will clearly show the possibility of a superconducting transition in solid vanadium under normal conditions.<sup>25</sup> Thus, in vanadium, the electronic charge distributions and electronic structure under normal conditions are fundamental to our understanding of their superconducting properties.<sup>18,27</sup>

The theory of Gaspari and Gyoffy<sup>30</sup> in conjunction with McMillan's formula<sup>8</sup> is used to calculate  $T_c$ . The electron-phonon mass enhancement factor  $\lambda$  is

$$\lambda = \frac{N(E_F)\langle I^2 \rangle}{M\langle \omega^2 \rangle}, \quad (1)$$

where  $M$  is the atomic mass,  $\langle \omega^2 \rangle$  is an average of the phonon frequency square, and  $\langle I^2 \rangle$  is the square of the electron-

TABLE II. Variation in  $\lambda$ ,  $\theta_D$ , and  $T_c$  of bcc vanadium under pressure.

Pressure $P$ (Mbar)	Fermi energy $E_F$ (Ry)	Density of states $N(E_F)$ (states/Ry)	$\lambda_{e-ph}$	$\theta_D$ (K)	Theory $T_c$ (K)	Expt. $T_c$ (K)
0.0000	0.2958	19.9000	0.5975	380.00	5.97	5.30
0.2473	0.3585	18.5700	0.6379	433.31	7.11	7.61
0.6321	0.4469	16.0940	0.7128	503.17	12.84	11.25
1.2000	0.5593	13.2842	0.8269	587.08	18.25	17.20
1.3930	0.5660	12.8985	0.8414	592.01	20.99	
2.3839	0.7903	11.9328	0.6988	736.43	15.46	
4.5655	0.9831	8.1270	0.5797	872.83	8.85	
9.4500	1.2655	5.5327	0.4417	1066.75	5.44	

TABLE III. Variation in  $\lambda$ ,  $\theta_D$ , and  $T_c$  of sc vanadium under pressure.

Pressure $P$ (Mbar)	Fermi energy $E_F$ (Ry)	Density of states $N(E_F)$ (states/Ry)	$\lambda_{e-ph}$	$\theta_D$ (K)	Theory $T_c$ (K)
2.3839	0.1134	16.6128	0.6574	119.01	1.720
4.5655	0.2615	13.3100	0.4390	192.03	0.355
9.4500	0.4627	11.5900	0.3232	275.17	0.056

phonon matrix element averaged over the Fermi energy.  $\langle I^2 \rangle$  (in rydbergs) can be written as

$$\langle I^2 \rangle = 2 \sum_l \frac{(l+1)}{(2l+1)(2l+3)} M_{l,l+1}^2 \frac{N_l(E_F)N_{l+1}(E_F)}{N(E_F)N(E_F)}, \quad (2)$$

where

$$M_{l,l+1} = -\phi_l \phi_{l+1} \{ [D_l(E_F) - 1][D_{l+1}(E_F) + l + 2] + [E_F - V(S)]S^2 \}.$$

The necessary parameters to calculate  $M_{l,l+1}$  are taken from the band structure results.<sup>23-27</sup>

The average of the phonon frequency square is

$$\langle \omega^2 \rangle = 0.5 \theta_D^2, \quad (3)$$

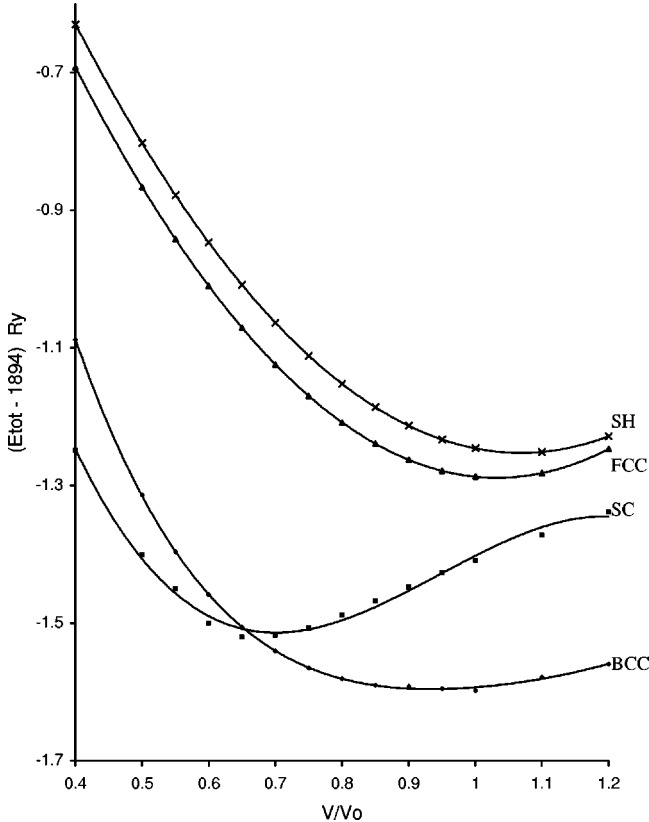


FIG. 7. Total energy vs reduced volume curve for vanadium in different structures.

TABLE IV. Comparison in equilibrium lattice constant  $a_0$ , bulk modulus  $B_0$ , and its derivative  $B_0^1$  of vanadium at ambient pressure.

Ground-state properties	Present study	Experiment <sup>a</sup>	Previous theory <sup>b</sup>
$a_0$ (a.u.)	5.7338	5.7278	5.7586
$B_0$ (Mbar)	2.0020	1.8800	1.9460
$B_0^1$	2.9500	2.4000	3.0000

<sup>a</sup>Reference 5.

<sup>b</sup>Reference 1.

where  $\theta_D$  is the Debye temperature. The variation of  $\theta_D$  with pressure can be estimated from a relation which is obtained assuming a free electron approximation. The ratio of Debye temperature  $\theta_D$  to the Fermi temperature  $T_F$  can be written as<sup>31</sup>

$$\frac{\theta_D}{T_F} = \frac{2K_D}{K_F} \frac{C}{V_F}, \quad (4)$$

where  $K_D$  is the Debye wave vector,  $K_F$  is the Fermi wave vector,  $V_F$  is the Fermi velocity, and  $C$  is the velocity of sound. Under the harmonic approximation, one can obtain the Debye temperature which is proportional to the square root of the Fermi energy divided by the cell parameter, i.e.,

$$\theta_D(P) = \frac{\sqrt{E_F}}{\sqrt{E_F^0}} \frac{a_0}{a} \theta_D^0, \quad (5)$$

where  $\theta_D^0$ ,  $a_0$ , and  $E_F^0$  are normal pressure quantities.<sup>18,32</sup>

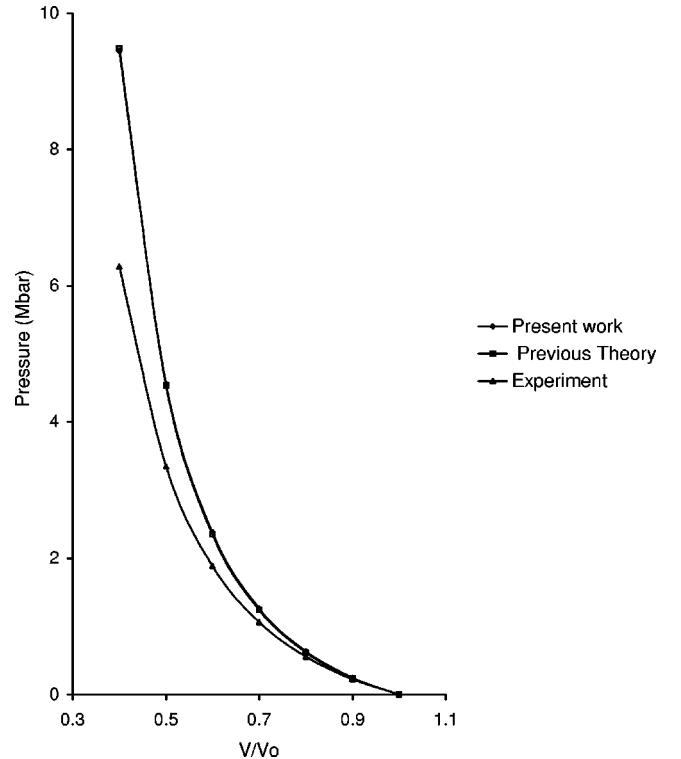


FIG. 8. Pressure dependence of reduced volume in vanadium.

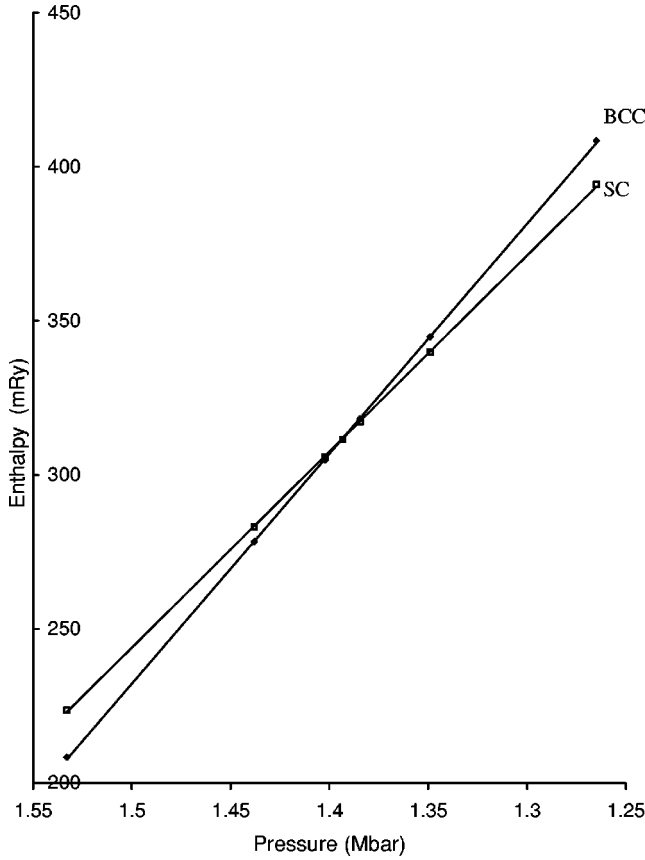


FIG. 9. Enthalpy vs pressure curve for V in bcc and sc structures.

$\theta_D^0$  for V is 380 K. The superconducting transition temperature is calculated using McMillan's formula,<sup>8</sup>

$$T_c = \frac{\theta_D}{1.45} \exp \left[ \frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right], \quad (6)$$

where  $\mu^*$  is the electron-electron interaction parameter. With the Fermi energy and  $N(E_F)$  obtained from the self-consistent calculation, we have calculated the value of the superconducting transition temperature  $T_c$  using Eq. (6). The calculated values of  $\theta_D(P)$ ,  $\lambda$ , and  $T_c$  under various pressures for bcc vanadium are given in Table II.

The Debye temperature  $\theta_D(P)$  is proportional to the characteristic phonon frequency of the lattice. The path to higher  $T_c$  lies in the direction of higher  $\theta_D(P)$ . But under high pressure, a higher Debye temperature can also lower  $T_c$ . That is because the coupling constant  $\lambda$  can decrease if the phonon frequencies are large.<sup>25</sup> At normal pressure, the value of  $T_c$  calculated is 5.975 K. This is in good agreement with the experimental observation of Ishizuka *et al.*<sup>5</sup> The measured value of  $T_c$  is 5.3 K at atmospheric pressure. The electron-phonon mass enhancement factor  $\lambda$  at normal pressure is 0.5975 (Table II), which is in agreement with the value of 0.6 reported by McMillan.<sup>8</sup>

At 1.2 Mbar pressure the calculated value of  $T_c$  is 18.21 K which is very close to the experimental value of 17.2 K at

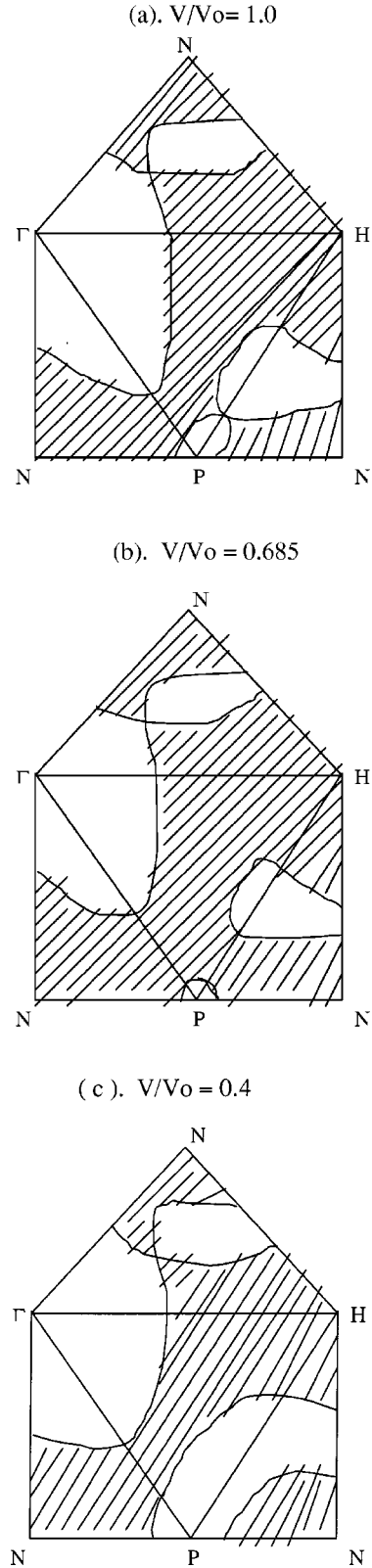


FIG. 10. Fermi surface cross section of V in central (100) and (110) planes.

1.2 Mbar pressure.<sup>5</sup> The highest value of  $T_c$  20.99 K, is reached at 1.393 Mbar pressure with a pressure coefficient of 10.78 K/Mbar, whereas the experimental pressure coefficient is 9.6 K/Mbar.<sup>5</sup> On further increasing the pressure, the value

of  $T_c$  goes on decreasing and reaches 5.44 K at 9.45 Mbar pressure with the pressure coefficient of 1.42 K/Mbar. This behavior is similar to a number of elemental transition metals Nb, Zr, and Ta under pressure.<sup>16–18</sup> From Table II, we find that the calculated values of  $T_c$  depend more sensitively on the electron-phonon mass enhancement factor  $\lambda$ .<sup>25</sup> The high  $T_c$  of bcc vanadium is believed to be the result of the increase in the  $d$ -electron number and  $\lambda$ .<sup>33–35</sup> In general, at greater  $d$ -electron contribution to the band structure results in a stronger electron-lattice interaction<sup>25</sup> ( $\lambda=0.84$  at  $P=1.393$  Mbar). The decrease of  $T_c$  above 1.393 Mbar may be due to a structural phase transition in vanadium in this pressure region. This view is supported by the previous theoretical work<sup>1</sup> and the present investigation.

From our calculation a discontinuous decrease in  $T_c$  is obtained at 2.38 Mbar corresponding to sc vanadium (Table III). For the sc phase, we predict a high  $T_c$  of 1.72 K at 2.38 Mbar pressure. With a further increase in pressure the  $T_c$  values decrease with a pressure coefficient of 0.2355 K/Mbar. Here, also, the calculated values of  $T_c$  depend more sensitively on the electron-phonon mass enhancement factor  $\lambda$  (Table III). The decrease in the value of the  $T_c$  may be due to a stiffening of the lattice and a change in the coordination number.

#### D. Fermi surface cross section

Fermi surface cross sections of vanadium under different pressures along the central (100) and (110) planes are shown in Figs. 10(a)–10(c). The Fermi surface cross sections are due to the III band of vanadium. In the above figure the hole regions are shaded like in Ref. 36. In Fig. 10(a), electron surfaces are present along  $\Gamma$ - $N$ ,  $N$ - $H$ (neck),  $\Gamma$ - $P$ ,  $P$ - $H$ , and  $P$ - $N$  directions.<sup>21</sup> At normal pressure, the complex third zone hole surface consists of a multiply connected hole tube (jungle gym) along the  $\Gamma$ - $H$  direction (100) and distorted ellipsoids centered around  $N$ . The ellipsoids are connected to the jungle gym surface by necks along  $\Gamma$ - $N$  direction. This is in good agreement with the experimental Fermi surface study of vanadium.<sup>36</sup>

The area of the cross section of the electron surface decrease with an increase of pressure [Fig. 10(b)], which is also predicted in the earlier theoretical calculation.<sup>1</sup> The electron

region along the  $P$ - $H$  direction is modified, giving rise to a hole region along the  $P$ - $H$  direction. The size of the electron packet around the  $P$  point is reduced whereas the neck along the  $\Gamma$ - $N$  direction is increased at  $V/V_0=0.685$ . On further increasing of pressure [Fig. 10(c)], the hole region along the  $P$ - $H$  direction and the tiny electron packet around the  $P$  point are again joined with the electron region along the  $P$ - $H$  direction. At this pressure, the size of the necks along the  $\Gamma$ - $N$  direction gets reduced.

As in the case of Nb and Ta, in vanadium also the nonlinearities in  $T_c(P)$  could be explained by the creation and destruction of new parts of the Fermi surface at high pressure.<sup>17</sup> The creation of the hole region along the  $P$ - $H$  direction may be the reason for the high value of  $T_c$  at 1.393 Mbar pressure. Similarly the destruction of the hole region and the increased area of the cross section of the electron region led to the lowering of the  $T_c$  value above 1.393 Mbar. This is an indication of a Lifshitz transition of order 2.5.<sup>37</sup>

#### IV. CONCLUSIONS

In the present investigation, the pressure dependence of the superconducting transition temperature ( $T_c$ ) of vanadium is well brought out and is in good agreement with a recent experimental observation.<sup>5</sup> This trend is similar to other  $T_c$  calculations.<sup>16–18</sup> We have performed  $T_c$  calculations up to the compression  $V/V_0=0.4$  which corresponds to a high pressure of 9.45 Mbar for both bcc and sc structures of vanadium. Experimental evidence is available up to the 1.2 Mbar pressure region.<sup>5</sup> We have also predicted the phase transition of vanadium from bcc to sc structure under pressure (1.393 Mbar). The phase transition is one of the reasons for the decrease in the  $T_c$  above 1.393 Mbar. Experimental findings are needed to confirm the phase transition in vanadium under pressures above 1.2 Mbar.

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