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AB INITIO STUDY OF SUPERCONDUCTIVITY IN VANADIUM, NIOBIUM AND TANTALUM UNDER PRESSURE

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ABSTRACT

The superconducting transition temperature of group V- B metals Vanadium (V), Niobium (Nb) and Tantalum (Ta) under normal and high pressure are reported. The normal pressure superconducting transition temperature of hcp V, Nb and Ta agree well with the previous calculations. The high-pressure superconductivity exhibits significant deviations from the normal pressure due to s-d transitions. Under normal conditions the superconducting transition of Vanadium occurs at 5,95 K (Tc). When the pressure is increased it is predicted that Tc increases at a rate of 10.8 K/M bar for pressures up to 1.4 M bar, where as the experimental increases is 9.6 K/M bar for pressure up to 1.2 M bar. On further increase of pressure Tc begins to decrease at a rate of 1.4 K/M bar in bcc structure and 0.24 K/M bar in fcc structure. Similar calculations are carried out for Niobium and Tantalum.
Key words: Superconductivity, Vanadium, Niobium, Tantalum, Pressure.

INTRODUCTION

Group-VB transition metals V, Nb, and Ta crystallizes in body-centered cubic (BCC) structure at ambient pressure and temperature conditions. These metals are of great use due to their high thermal, mechanical and chemical stabilities. Recently these metals have been the subject of numerous experimental and theoretical studies in Mbar pressure regions. The Nb is known to have the highest superconducting transition temperature (Tc) among elemental solids at ambient pressure. The Ta is used in high-pressure experiments as a pressure standard. Here bcc is the normal pressure phase and fcc is the high temperature and high pressure phase. The present investigation is aimed at getting detailed information about the high-pressure band structure (fcc - V, Nb and Ta), density of states, structural phase transition and pressure variation of superconducting transition temperature. We have used the full potential linearized muffin tin orbital method (FP-LMTO) method and the details of the calculation are given and here we will give the calculation details. The atomic number of V, Nb and Ta are 23, 41 and 73 respectively. The electronic configuration of V, Nb and Ta are 18[Ar] $4s^2 3d^3$, $_{36}$[Kr] $5s^2 4d^3$

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and $_{54}$[Xe] $4f^{14}$ $6s^2$ $5d^3$ respectively. The valence electronic configuration chosen in our calculations is $4s^2$ $3d^3$ for V, $5s^2$ $4d^3$ for Nb and $6s^2$ $5d^3$ for Ta. The calculated total energies of V, Nb and Ta were fitted to Murnaghan's equation of state and the determined pressure values. There are no theoretical predictions corresponding to this observation. These observations motivated for the present investigation. In our calculation, the superconducting transition temperature *Tc* is calculated using McMillan's formula. Herein we describe the results on the pressure dependence of *Tc* of vanadium in the bcc phase as well as the fcc phase.

SUPERCONDUCTIVITY

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. The manner in which the *d* electron number is increasing as a function of pressure in vanadium is given in Table 1. At normal pressure itself the contribution of 3*d* state is large whereas 4*s* and 4*p* states are small. This will clearly show the possibility of a superconducting transition in solid vanadium under normal conditions. In vanadium the electronic charge distributions and electronic structure under normal conditions are fundamental to our understanding of their superconducting properties. The theory of Gaspari and Glorify in conjunction with McMillan's formula is used to calculate *Tc*.

With the Fermi energy and $N(E_F)$ obtained from the self-consistent calculation, we have calculated the value of the superconducting transition temperature *Tc*. The calculated values of θ_D , λ , μ^* and *Tc* at normal and various pressures for bcc vanadium are given in Table.2. The Debye temperature $\theta_D(P)$ is proportional to the characteristic phonon frequency of the lattice. The path to higher *Tc* lies in the direction of higher $\theta_D(P)$. But under high pressure, a higher Debye temperature can also lower *Tc* . That is because the coupling constant λ can decrease if the phonon frequencies are large. At normal pressure, the value of *Tc* calculated is 5.975 K. This is in good agreement with the experimental observation of (5.3 K) Ishizuka *et al* . The electron-phonon mass enhancement factor λ at normal pressure is 0.598 (Table 1), which is in agreement with the value of 0.6 reported by McMillan. At 1.2 Mbar pressure the calculated value of *Tc* is 18.25 K which is very close to the experimental value of 17.2 K at 1.2 Mbar pressure. The highest value of *Tc* 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.

On further increasing the pressure, the value of *Tc* 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 the elemental transition metal titanium under pressure. From Table.2, we find that the calculated values of *Tc* depend more sensitively on the electron-phonon mass enhancement factor λ than on μ^* . The high *Tc* of bcc vanadium is believed to be the result of the increase in the *d*-electron number and λ . The decrease of *Tc* 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 and the present investigation. From our calculation a discontinuous decrease in *Tc* is obtained at 2.38

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Mbar corresponding to fcc vanadium (Table 3). For the fcc phase, we predict a high *Tc* of 1.72 K at 2.38 Mbar pressure. With a further increase in pressure the *Tc* values decrease with a pressure coefficient of 0.235 K/Mbar. And the calculated values of *Tc* depend more sensitively on the electron-phonon mass enhancement factor λ (Table 3). The decrease in the value of the *Tc* may be due to a stiffening of the lattice and a change in the coordination number from 8 (bcc) to 12 (fcc). The dependence of *Tc* values more sensitively on changes in λ than μ^*, indicating that vanadium is an electron-phonon mediated superconductor. The manner in which the *d* electron number is increasing as a function of pressure in niobium is given in Table 5. At normal pressure itself the contribution of 4*d* state is large whereas 5*s* and 5*p* states are small. This will clearly show the possibility of a superconducting transition in solid niobium under normal conditions. In niobium, the electronic charge distributions and electronic structure under normal conditions are fundamental to our understanding of their superconducting properties. The theory of Gaspari and Glorify in conjunction with McMillan's formula is used to calculate *Tc*.

With the Fermi energy and $N(E_F)$ obtained from the self-consistent calculation, we have calculated the value of the superconducting transition temperature *Tc* of niobium. The calculated values of θ_D , λ , μ^* and *Tc* at normal and various pressures for bcc niobium are given in Table.6. The Debye temperature $\theta_D(P)$ is proportional to the characteristic phonon frequency of the lattice in niobium. The path to higher *Tc* lies in the direction of higher $\theta_D(P)$. But under high pressure, a higher Debye temperature can also lower *Tc* (Table.7). That is because the coupling constant λ can decrease if the phonon frequencies are large. At normal pressure, the value of *Tc* calculated is 9.2425 K. This is in good agreement with the experimental observation of (9.5 K) Ishizuka *et al.* The electron-phonon mass enhancement factor λ at normal pressure is 0.7334 (Table 6), which is in agreement with the value of 0.74 reported by McMillan. At 1.25 Mbar pressure the calculated value of *Tc* is 14.55 K which is very close to the experimental value of 14.8 K at 1.25 Mbar pressure. The highest value of *Tc* 16.55 K, is reached at 2.47 Mbar pressure. On further increasing the pressure, the value of *Tc* goes on decreasing and reaches 1.617 K at 10.26 Mbar pressure. This behavior is similar to the elemental transition metal titanium under pressure. From Table. 5 1nd 6, we find that the calculated values of *Tc* depend more sensitively on the electron-phonon mass enhancement factor λ than on μ^*. The high *Tc* of bcc niobium is believed to be the result of the increase in the *d*-electron number and λ . The decrease of *Tc* above 2.47 Mbar may be due to a structural phase transition in niobium above 1.34 Mbar pressure region.

From our calculation a discontinuous decrease in *Tc* is obtained at 4.88 Mbar corresponding to fcc niobium (Table 6). For the fcc phase, we predict a high *Tc* of 16.55 K at 2.47Mbar pressure. With a further increase in pressure the *Tc* values decrease with a pressure coefficient of 0.127 K/Mbar. And the calculated values of *Tc* depend more sensitively on the electron-phonon mass enhancement factor λ (Table 6). The decrease in the value of the *Tc* may be due to a stiffening of the lattice and a change in the coordination number from 8 (bcc) to 12

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(fcc) of niobium. The dependence of *Tc* values more sensitively on changes in λ than μ^*, indicating that niobium is an electron-phonon mediated superconductor.

The manner in which the *d* electron number is increasing as a function of pressure in tantalum is given in Table 7. At normal pressure itself the contribution of 5*d* state is large whereas 6*s* and 6*p* states are small. This will clearly show the possibility of a superconducting transition in solid tantalum under normal conditions. In niobium, the electronic charge distributions and electronic structure under normal conditions are fundamental to our understanding of their superconducting properties in tantalum. The theory of Gaspari and Gyorffy in conjunction with McMillan's formula is used to calculate *Tc*. With the Fermi energy and $N(E_F)$ obtained from the self-consistent calculation, we have calculated the value of the superconducting transition temperature *Tc* of tantalum. The calculated values of θ_D, λ , μ^* and *Tc* at normal and various pressures for bcc tantalum are given in Table.8. The Debye temperature θ_D (*P*) is proportional to the characteristic phonon frequency of the lattice in tantalum. The path to higher *Tc* lies in the direction of higher θ_D (*P*). But under high pressure, a higher Debye temperature can also lower *Tc* (Table.9) . That is because the coupling constant λ can decrease if the phonon frequencies are large. At normal pressure, the value of *Tc* calculated is 4.233 K. This is in good agreement with the experimental observation of (4.483 K) Ishizuka *et al.* The electron-phonon mass enhancement factor λ at normal pressure is 0.576 (Table 9), which is in agreement with the value of 0.574 reported by McMillan. At 1.39 Mbar pressure the calculated value of *Tc* is 10.57 K which is very close to the experimental value of 10.8 K at 1.39 Mbar pressure [1]. The highest value of *Tc* 13.523 K, is reached at 2.667 Mbar pressure (Table.9).

On further increasing the pressure, the value of *Tc* goes on decreasing and reaches 0.012 K at 10.08 Mbar pressure. This behavior is similar to the elemental transition metal titanium under pressure. From Table. 6 and 8, we find that the calculated values of *Tc* depend more sensitively on the electron-phonon mass enhancement factor λ than on μ^*. The high *Tc* of bcc tantalum is believed to be the result of the increase in the *d*-electron number and λ . The decrease of *Tc* above 2.667 Mbar may be due to a structural phase transition in niobium above 1.70 Mbar pressure region. From our calculation a discontinuous decrease in *Tc* is obtained at 5.07 Mbar corresponding to fcc tantalum (Table 9). For the fcc phase, we predict a high *Tc* of 13.523 K at 2.667Mbar pressure. With a further increase in pressure the *Tc* values decrease with a pressure coefficient of 0.124 K/Mbar. And the calculated values of *Tc* depend more sensitively on the electron-phonon mass enhancement factor λ (Table 9). The decrease in the value of the *Tc* may be due to a stiffening of the lattice and a change in the coordination number from 8 (bcc) to 12 (fcc) of tantalum. The dependence of *Tc* values more sensitively on changes in λ than μ^*, indicating that tantalum is an electron-phonon mediated superconductor.

Fig.1 contains the comparison of the relation connecting reduced volume and Lattice constant of vanadium, niobium and tantalum. Fig.2. contains the comparison of the relation

connecting reduced volume and Pressure of vanadium, niobium and tantalum. Fig.3. contains the comparison of the reduced volume, lattice constant and Pressure of vanadium, niobium and tantalum.

Table .1: Electrons in *s,p* and *d* shells of bcc - V at different reduced volumes

V/Vo	Lattice constant *a* a.u.	Pressure Mbar	$4s^2$	$4p^0$	$3d^2$
1	5.728	Normal	0.630	0.735	3.635
0.9	5.530	0.247	0.616	0.708	3.676
0.8	5.317	0.632	0.597	0.671	3.733
0.7	5.086	1.265	0.569	0.621	3.810
0.6	4.831	2.384	0.525	0.557	3.918
0.5	4.546	4.566	0.455	0.486	4.058
0.4	4.220	9.450	0.326	0.394	4.280

Table 2: *Tc* as a function of pressure for vanadium (bcc structure)

Pressure Mbar	λ	θ_D K	μ^*	Theory [60] Tc K	Expt. [37] Tc K
normal	0.598	380.00	0.115	5.970	5.30
0.247	0.638	433.31	0.126	7.111	7.61
0.632	0.713	503.17	0.124	12.84	11.25
1.200	0.827	587.08	0.126	18.25	17.20
1.393	0.841	592.01	0.123	20.99	-
2.384	0.699	736.43	0.122	15.46	-
4.566	0.580	872.83	0.125	8.850	-
9.450	0.442	1066.8	0.116	5.441	-

Table 3: *Tc* as a function of pressure for vanadium (fcc structure)

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Pressure P Mbar	λ	θ_D K	μ^*	Tc K
2.384	0.657	119.01	0.148	1.720
4.566	0.439	192.03	0.151	0.355
9.450	0.323	275.17	0.125	0.056

Table .4: Electrons in *s,p* and *d* shells of bcc - Nb at different reduced volumes

V/Vo	Lattice constant *a* a.u.	Pressure Mbar	$5s^2$	$5p^0$	$4d^2$
1	6.2382	Normal	0.630	0.735	3.635
0.9	6.0231	0.2219	0.616	0.708	3.676
0.8	5.7915	0.5977	0.597	0.671	3.733
0.7	5.5396	1.2556	0.569	0.621	3.810
0.6	5.2624	2.4686	0.525	0.557	3.918
0.5	4.9525	4.8820	0.455	0.486	4.058
0.4	4.5978	10.2641	0.326	0.394	4.280

Table 5: *Tc* as a function of pressure for Niobium (bcc structure)

Pressure P Mbar	λ	θ_D K	μ^*	Theory Tc K	Expt. Tc K
Normal	0.7334	275	0.094	9.2425	9.5
0.2219	0.7587	314	0.103	10.6526	10.35
0.5977	0.7728	386	0.116	13.6358	13.65
1.2556	0.7943	448	0.123	14.5521	14.8

Table 6: *Tc* as a function of pressure for niobium (fcc structure)

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Pressure P Mbar	λ	θ_D K	μ^*	Tc K
2.4686	0.8176	517	0.134	16.551
4.8820	0.399	843	0.041	8.874
10.2641	0.286	796.5	0.048	1.617

Table .7: Electrons in *s,p* and *d* shells of bcc - Ta at different reduced volumes

V/Vo	Lattice constant *a* a.u.	Pressure Mbar	$6s^2$	$6p^0$	$5d^2$
1	6.2571	Normal	0.630	0.735	3.635
0.9	6.0414	0.2569	0.616	0.708	3.676
0.8	5.8091	0.6796	0.597	0.671	3.733
0.7	5.5564	1.3961	0.569	0.621	3.810
0.6	5.2784	2.6670	0.525	0.557	3.918
0.5	4.9674	5.0716	0.455	0.486	4.058
0.4	4.6117	10.0784	0.326	0.394	4.280

Table 8: *Tc* as a function of pressure for Tantalum (bcc structure)

Pressure P Mbar	λ	θ_D K	μ^*	Theory [60] Tc K	Expt. [37] Tc K
Normal	0.576	240	0.095	4.233	4.483
0.2569	0.615	282	0.105	5.455	5.5
0.6796	0.674	342	0.118	7.594	7.55
1.3961	0.727	412	0.125	10.568	10.8

Table 9: *Tc* as a function of pressure for Tantalum (feck structure)

Pressure P Mbar	λ	θ_D K	μ^*	Tc K
2.6670	0.775	498	0.138	13.523
5.0716	0.249	763.7	0.036	1.005
10.0784	0.161	732.9	0.043	0.012

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Fig.1.The relation connecting reduced volume and Lattice constant of vanadium, niobium and tantalum

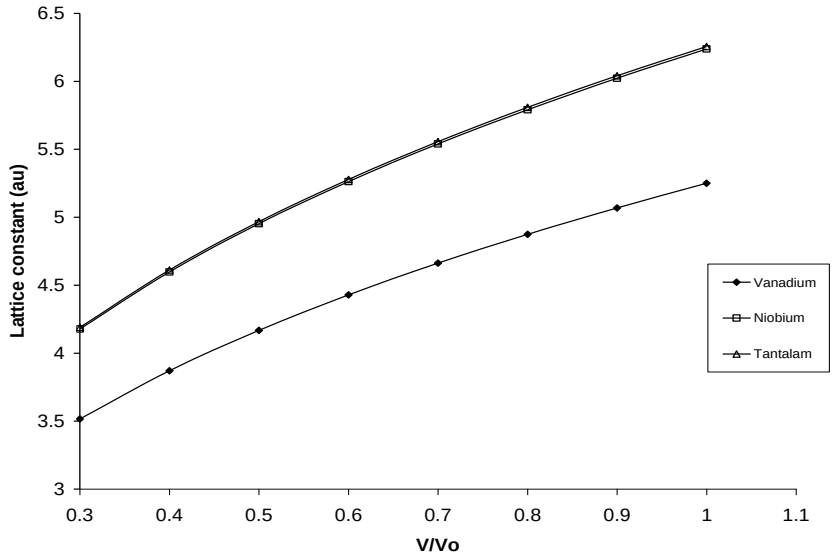


Fig.2.The relation connecting reduced volume and Pressure of vanadium, niobium and tantalum

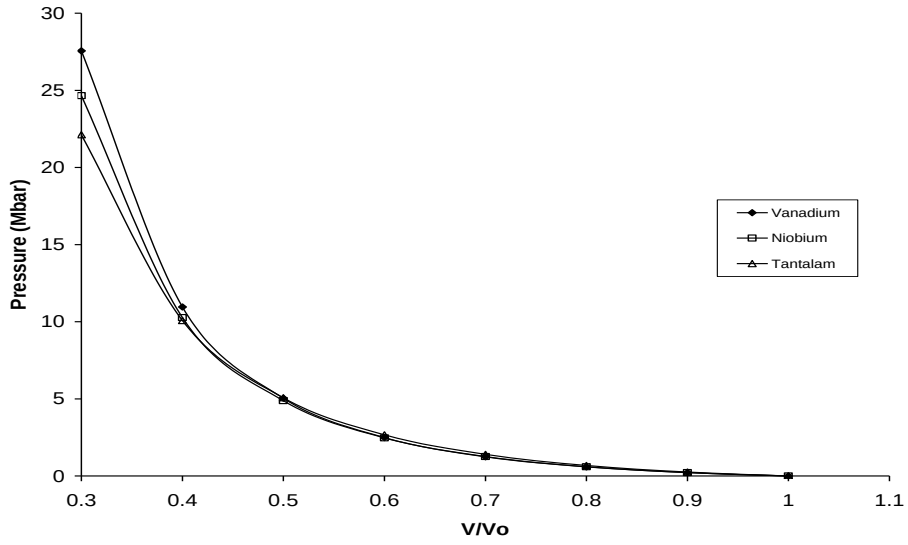
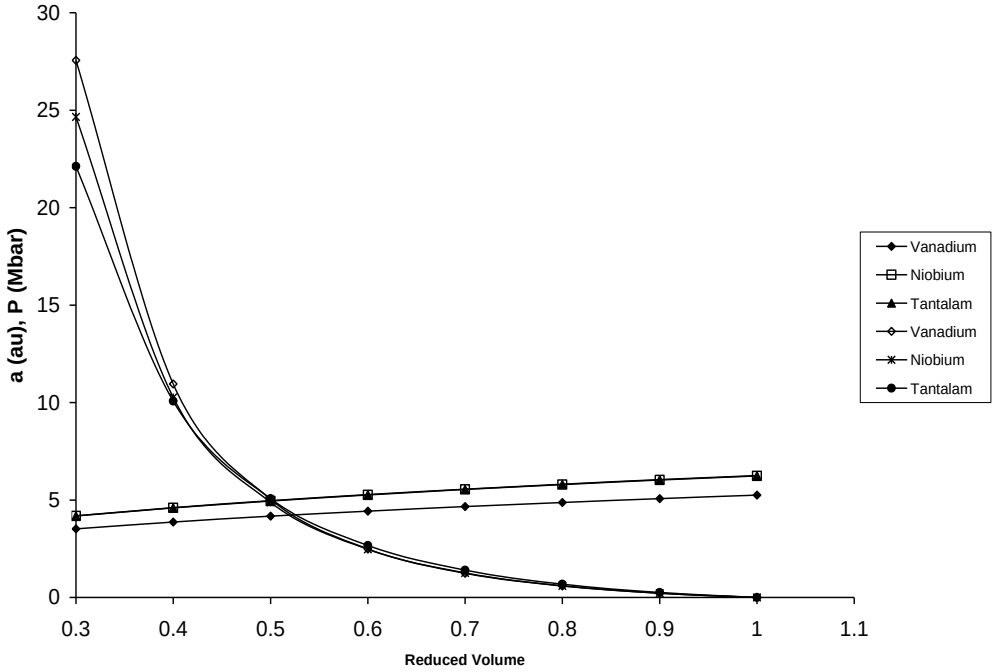


Fig.3.The comparison of reduced volume , lattice constant and Pressure of vanadium, niobium and tantalum



CONCLUSION

In summary, we have investigated the pressure dependent band structure, density of states, structural phase transition and superconductivity of vanadium, niobium and tantalum using FP-LMTO method. The total energies of vanadium, niobium and tantalum are computed and the results are used to study the structural phase transition and superconductivity under pressure. In vanadium, niobium and tantalum, we could find a phase transformation sequence of *bcc* $\rightarrow$ *fcc* under pressure. From our analysis we predict hexagonal closed packed, simple cubic and diamond phases are not stable at any high pressures. We have analyzed the structural phase transition from bcc to fcc structure in vanadium, niobium and tantalum at 1.24Mbar, 1.34 Mbar and 1.70 Mbar respectively. The phase transition pressure of vanadium as 1.24 Mbar and the corresponding reduced volume V/V_o as 0.7, the phase transition pressure of niobium as 1.34 Mbar and the corresponding reduced volume V/V_o as 0.68 and the phase transition pressure of tantalum as 1.70 Mbar and the corresponding reduced volume V/V_o as 0.65. When the pressure is increased, it is predicted that, *Tc* increases and reaches a maximum value thereafter *Tc* starts to decrease.

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