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Effect of pressure on the superconducting transition temperature of Nb–Zr and Ti–V

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Abstract

We report a theoretical calculation of band structure and the superconducting transition temperature of Nb–Zr and Ti–V under pressure. The self-consistent tight binding linear Muffin–Tin orbital method have been used to obtain the band structure. Either Allen–Dynes’s formula or McMillan’s formula was used to calculate the transition temperature. A simple but a straight forward method was employed to calculate the effect of pressure on Debye temperature or the phonon frequency. From the present study it is found that the value of T_c increases continuously with pressure for both the compounds. The increase in T_c is attributed to the continuous $s \rightarrow d$ electron transfer under pressure. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The superconducting transition temperature (T_c) of stoichiometric alloy Nb–Zr increases from about 9.5 K at normal pressure by more than 3 K upon the application of a pressure of the order of 13 GPa [1]. Kawamura et al. [2] measured the values of T_c up to approximately 28 GPa and reported that T_c raises to 16.5 K. From the systematic point of view, Kawamura et al. suggested that

analogous binary systems Ti–V, Ti–Nb, Hf–Nb, Hf–Ta may be investigated so that they also show a similar increase of T_c with pressure. From the low temperature specific heat study Cheng et al. [3] measured the electronic specific heat co-efficient γ of Ti–V alloy. On the basis of BCS theory, they reported T_c as 7.3 K at ambient pressure. To our knowledge there is no theoretical calculation of T_c as a function of pressure for the alloys. An attempt is made here to calculate the transition temperature of these alloys and an explanation is given for the increase in T_c under pressure. The rest of the paper is organized as follows. In Section 2, the method of calculation of T_c is outlined. Since the outputs from band structure are used in the

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calculation of T_c , the methodology of band structure is outlined in Section 3. The final section deals with the results and discussion.

2. Calculation of T_c

The superconducting transition temperature is calculated using either Allen–Dynes [4]

$$T_c = \frac{\langle \omega \rangle}{1.2} \exp \left\{ \frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right\} \quad (1)$$

or McMillan's formula [5]

$$T_c = \frac{\Theta_D}{1.45} \exp \left\{ \frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right\} \quad (2)$$

where $\langle \omega \rangle$ is the average phonon frequency, Θ_D is the Debye temperature, λ is the electron–phonon coupling constant and μ^* is the electron–electron interaction constant. Gaspari and Gyroffi [6] have developed a theory to calculate λ in terms of the density of states at the Fermi energy and the electron–phonon matrix element. According to them, λ can be written as

$$\lambda = \frac{N(E_F)\langle I^2 \rangle}{M\langle \omega^2 \rangle} \quad (3)$$

where M is the atomic mass, $\langle I^2 \rangle$ is the square of the electron–phonon matrix element averaged over the Fermi surface.

In the atomic sphere approximation $\langle I^2 \rangle$ can be written in atomic Rydberg units [7] as

$$\langle I^2 \rangle = 2 \sum_l \frac{l+1}{(2l+1)(2l+3)} M_{l,l+1}^2 \frac{N_l(E_F)N_{l+1}(E_F)}{N(E_F)N(E_F)} \quad (4)$$

where, $M_{l,l+1}$ are the electron–phonon matrix elements which can be obtained in terms of the logarithmic derivatives,

$$D_l = \left. \frac{d \ln \phi_l}{d \ln r} \right|_{r=S} \quad (5)$$

evaluated at the sphere boundary.

$$M_{l,l+1} = -\phi_l \phi_{l+1} [(D_l(E_F) - l)(D_{l+1}(E_F) + l + 2) + (E_F - V(S)S^2)] \quad (6)$$

where ϕ_l is the amplitude of the l partial wave function evaluated at E_F , $V(S)$ is the one electron potential at the sphere boundary and N_l is the partial density of states for the angular momentum quantum number l .

3. Band structure calculation

The parameters that are entering into the calculation of T_c are taken from the band structure outputs. The stoichiometric alloys Nb–Zr and Ti–V crystallizes in bcc structure with the space group Im-3m. The Ti atom in Ti–V and Zr atom in Zr–Nb are positioned at (0,0,0) and V in Ti–V and Nb in Nb–Zr are positioned at (0.5,0.5,0.5). For both the compounds the following basis orbitals are used, namely

$$\text{Ti} \quad 3d^2 \ 4s^2 \ 4p^0$$

$$\text{V} \quad 3d^3 \ 4s^2 \ 4p^0$$

$$\text{Zr} \quad 4d^2 \ 5s^2 \ 5p^0$$

$$\text{Nb} \quad 4d^4 \ 5s^1 \ 5p^0$$

The energy band structure of stoichiometric alloys Nb–Zr and Ti–V are obtained by TB-LMTO method within the atomic sphere approximation (ASA). This is an exact transformation of linear Muffin–Tin method [8] to localized short range or tight binding orbitals within the local density approximation. The exchange correlation potential is calculated using the parameterization scheme of von-Barth and Hedin [9]. The combined correction terms are included which accounts for the non-spherical shape of the atomic spheres and truncation of higher partial waves inside the spheres so that the error in the method is minimized. The sphere radii are chosen in such a way that the discontinuity in the potential at sphere boundary is small and the charge flow between the spheres are as per the electronegativity criteria. The band structure calculations are performed for 8000K points in the entire Brillouin zone and the \mathbf{K} and \mathbf{E} convergence are checked by increasing the number of \mathbf{K} points. The total and partial density of states are calculated by the method of tetrahedra [10].

The total energies are computed in a manner similar to our earlier work [11,12] by reducing the cell volume. The computed total energies are fitted to Birch equation of state [13] to obtain the pressure volume relation. Pressure is calculated from the volume derivative of the total energy. The equilibrium lattice parameter for Nb–Zr (3.365 Å) and Ti–V (3.083 Å) obtained from the present study is in good agreement with the experimental values. The bulk modulus obtained theoretically for Nb–Zr (134.37 GPa) and Ti–V (156.51 GPa) also agrees well with the experimental values.

The band structure and density of states of Nb–Zr and Ti–V are given in Figs. 1–4. From the band structure plots one can observe that the lowest lying bands are due to ‘s’ like electrons from sites

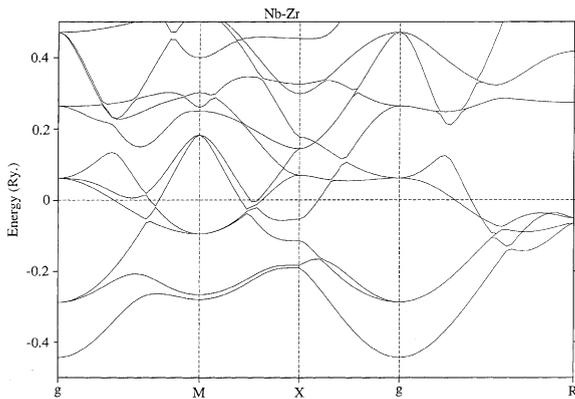


Fig. 1. Band structure of Nb–Zr.

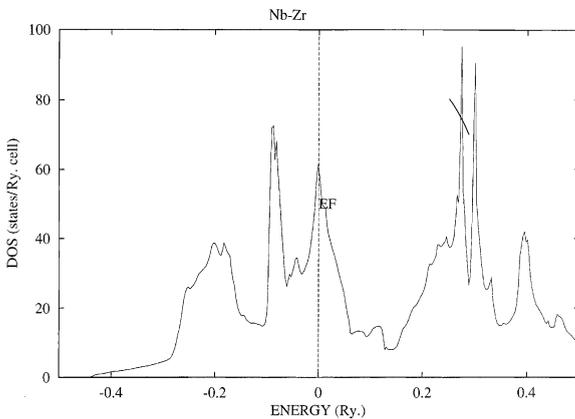


Fig. 2. Density of states of Nb–Zr.

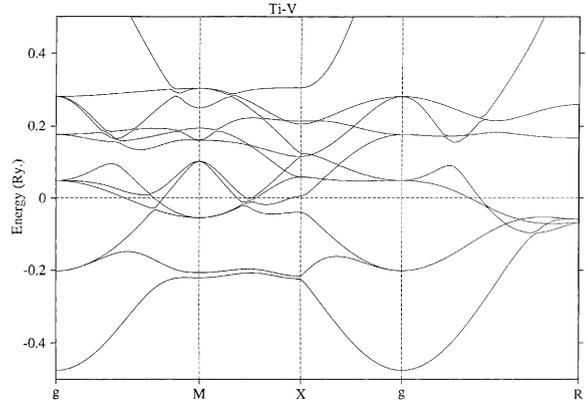


Fig. 3. Band structure of Ti–V.

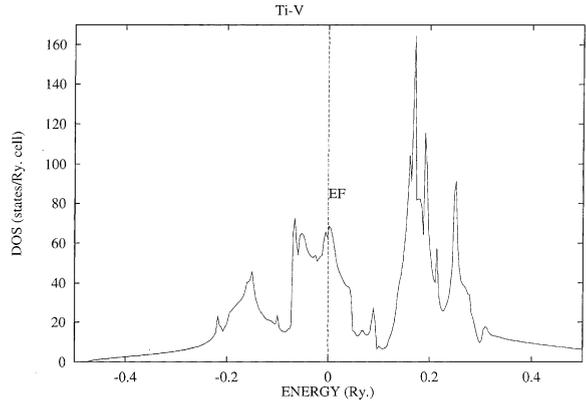


Fig. 4. Density of states of Ti–V.

Nb and Zr in the case of Nb–Zr, and Ti and V in the case of Ti–V. Followed by this, the bands are from ‘p’ like states of Nb and Zr. Above these bands lie the ‘d’ states of either 3d or 4d transition metals. The total density of states and the number of electrons both at Nb and Zr sites for Nb–Zr and at Ti and V sites for Ti–V are tabulated as a function of pressure and given in Tables 1 and 2. These quantities will be used later in the calculation of T_c . The parameters that are entering into the calculation of $M_{l,l+1}$ are taken from the band structure outputs as a function of pressure. The Debye temperature for Nb–Zr and Ti–V are taken as 190 K [14] and 262 K [3] respectively. The average of the phonon frequency $\langle \omega \rangle$ is calculated by setting $\langle \omega^2 \rangle$ as $0.75\theta_D^2$ [15]. The electron–electron

Table 1
Number of electrons of Nb–Zr at different pressures

<i>P</i> (GPa)	Niobium			Zirconium		
	s	p	d	s	p	d
2.445	0.628	0.626	2.683	0.638	0.558	3.660
6.853	0.619	0.611	2.710	0.628	0.542	3.676
10.12	0.613	0.601	2.729	0.622	0.530	3.686
13.66	0.606	0.590	2.748	0.614	0.519	3.697
17.52	0.598	0.577	2.770	0.606	0.507	3.709
21.72	0.591	0.563	2.794	0.597	0.494	3.722
26.29	0.583	0.549	2.819	0.587	0.481	3.735

Table 2
Number of electrons of Ti–V at different pressures

<i>P</i> (GPa)	Titanium			Vanadium		
	s	p	d	s	p	d
0.1	0.612	0.692	2.638	0.657	0.712	3.686
4.1	0.608	0.686	2.650	0.654	0.705	3.695
8.0	0.604	0.679	2.663	0.649	0.698	3.704
12.0	0.600	0.672	2.677	0.645	0.689	3.714
14.0	0.598	0.668	2.684	0.643	0.685	3.719
16.0	0.596	0.664	2.691	0.640	0.681	3.725
18.2	0.594	0.660	2.699	0.638	0.676	3.730

interaction constant μ^* is calculated using the empirical relation.

$$\mu^* = \frac{0.26N(E_F)}{1 + N(E_F)}. \quad (7)$$

It is very well known that the Debye temperature or phonon frequency varies with pressure. Since the band structure calculations are performed as a function of pressure, one should take into account the variation of Θ_D or $\langle\omega\rangle$ as a function of pressure. In the absence of any experimental data for the variation of Θ_D or $\langle\omega\rangle$ as a function of pressure for most of the materials a very simple but straight forward relation based on harmonic approximation [16] was given by Palanivel et al. [17], which is

$$\frac{\Theta_D(P)}{\Theta_D(0)} = \frac{a(0)}{a(P)} \sqrt{\frac{E_F(P)}{E_F(0)}}. \quad (8)$$

This relation is valid for cubic materials. The validity of this relation is checked for a number of elemental metals and for compounds, for which experimental data are available at ambient and

higher pressures. There is a good agreement between the calculated and experimental results. Palanivel et al. used this formalism to calculate the pressure dependence of T_c of transition metal carbides and nitrides [18–22]. In the above relation a is the lattice parameter and E_F is the Fermi energy. The symbols 0 and P refer to the corresponding quantities in normal and pressurized conditions. a and E_F are taken from the band structure results. The above expression is used to calculate Θ_D as a function of pressure. The atomic mass, which appears in Eq. (3), is taken as the average mass of the constituent atoms since the mass of the individual atoms are almost equal.

4. Results and discussion

The superconducting transition temperature of Nb–Zr and Ti–V are calculated using Eqs. (1) and (2) as a function of pressure in a manner similar to our earlier works [18–22]. The values of T_c along with other parameters that enter into the expression to calculate T_c are given in Tables 3 and 4 for

Table 3
Variation of superconducting transition temperature with pressure for Nb–Zr

P (GPa)	$\langle\omega\rangle$ (K)	λ	T_c (K)
2.445	164.55	0.984	9.56
6.853	169.90	1.034	10.76
10.12	173.67	1.073	11.68
13.66	177.61	1.134	13.01
17.52	181.72	1.170	13.93
21.72	186.02	1.173	14.31
26.29	190.51	1.258	16.12

Table 4
Variation of superconducting transition temperature with pressure for Ti–V

P (GPa)	Θ_D (K)	λ	T_c (K)
0.1	262.0	0.674	5.155
4.1	267.4	0.672	5.217
8.0	273.1	0.721	6.548
12.0	279.0	0.765	7.819
14.0	282.0	0.780	8.315
16.0	285.1	0.789	8.641
18.2	288.3	0.824	9.675
20.2	291.6	0.850	10.487

Nb–Zr and Ti–V respectively. From the tables one can observe that the values of T_c for both the alloys increase as a function of pressure. When compared to Ti–V, the increase in the value of T_c is much more rapid for Nb–Zr. Both these alloys have a positive pressure co-efficient of T_c which falls in line with the behavior of pure transition metals with e/a ratio < 5 . Since there is a continuous transfer of s to d electron transfer under pressure, these alloys show a positive pressure co-efficient. By looking at Tables 1 and 2, one can easily find that there is a continuous transfer of ‘s’ and ‘p’ like electrons to ‘d’ like states at both the sites. In the case of Nb–Zr, the transfer is at a faster rate when compared to Ti–V. This may be one of the reasons why there is an increase of T_c by roughly 7 K when the pressure is raised to 26.3 GPa, when compared to Ti–V in which the raise in T_c is about 5 K when the pressure is raised to 20.2 GPa.

In summary the band structure and superconducting transition temperature of Nb–Zr and Ti–V were calculated as a function of pressure using

either McMillan’s or Allen–Dynes’s formula. The effect of pressure on the phonon frequency or Debye temperature was taken into account by a simple procedure. The transition temperature increases with the increase of pressure. From the present calculation, it is found that the value of T_c of Nb–Zr increases at a faster rate when compared with the T_c value of Ti–V. This may be due to the continuous transfer of s to d electron in both the compounds. Since the transfer of s \rightarrow d electron is more in Nb–Zr when compared with Ti–V, Nb–Zr shows a steep increase in T_c with pressure.

References

- [1] P. Hohnberg, W. Gey, W. Buckel, unpublished.
- [2] H. Kawamura, J. Wittig, B. Bireckoven, W. Buckel, Physica B 126 (1984) 485.
- [3] C.H. Cheng, K.P. Gupta, E.C. Van Reuth, P.A. Beck, Phys. Rev. 126 (1962) 2030.
- [4] P.B. Allen, R.C. Dynes, Phys. Rev. B 12 (1975) 905.
- [5] W.L. McMillan, Phys. Rev. B 167 (1968) 331.
- [6] G.P. Gaspari, B.L. Gyroffi, Phys. Rev. Lett. 28 (1972) 801.
- [7] H.L. Skriver, I. Mertig, Phys. Rev. B 32 (1985) 4431.
- [8] O.K. Anderson, Phys. Rev. B 12 (1975) 3060.
- [9] U. VonBarth, L. Hedin, J. Phys. C 5 (1972) 1629.
- [10] O. Jepsen, O.K. Anderson, Solid State Commun. 9 (1971) 1763.
- [11] G. Kalpana, B. Palanivel, M. Rajagopalan, Phys. Rev. B 50 (1994) 12318.
- [12] G. Kalpana, B. Palanivel, M. Rajagopalan, Phys. Rev. B 52 (1995) 4.
- [13] F. Birch, J. Geophysics. Rev. 83 (1978) 1257.
- [14] F.J. Morin, J.P. Maitha, Phys. Rev. 129 (1963) 1115–1120.
- [15] D.S. Papaconstantopoulous, W.E. Pickett, B.M. Klein, L.L. Boyer, Phys. Rev. B 31 (1985) 752.
- [16] N.W. Aschcroft, N.D. Mermin, Solid State Physics, Holt–Saunders, Philadelphia, PA, 1981.
- [17] B. Palanivel, M. Rajagopalan, K. Iyakutti, J. Phys. Cond. 4 (1992) 413.
- [18] B. Palanivel, M. Rajagopalan, S. Natarajan, High Press. Res. 8 (1992) 587.
- [19] B. Palanivel, M. Rajagopalan, J. Phys. Cond. Matt. 4 (1992) 10377.
- [20] B. Palanivel, G. Kalpana, M. Rajagopalan, Phys. Stat. Solidi. B 176 (1993) 195–202.
- [21] B. Palanivel, M. Rajagopalan, Phase Transition 38 (1992) 61.
- [22] G. Vaitheeswaran, I.B. Shameen Banu, M. Rajagopalan, Solid State Commun. 116 (2000) 401.