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The high-pressure phase transition and superconductivity of VN studied by the LMTO method

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Abstract. In this paper we report on the theoretical investigation of the structural properties and superconductivity of VN under high pressure. The effect of pressure on the band structure is obtained by means of the self-consistent linear muffin-tin orbital (LMTO) method. From total energy studies we predict a structural phase transition in VN from NaCl- (B1-) type to CsCl- (B2-) type at about 65.2 GPa. The superconducting transition temperature (T_c) is calculated using McMillan's formula. The calculated value for T_c at ambient pressure is 9.322 K, which is in agreement with the experimental value of 8.5 K. Values for T_c increase with increasing pressure, with a pressure coefficient of 27 mK kbar⁻¹, which is in good agreement with the experimental value of 12 mK kbar⁻¹.

1. Introduction

Refractory metal compounds, especially carbides and nitrides, are of great interest to technologists and theoreticians. This is because they exhibit unusual combinations of physical and chemical properties, such as ultrahardness, high melting point and good electrical and thermal conductivity. It is well known that the superconductivity of these compounds is connected with crystallographic structure and the superconducting temperature depends mainly on the composition. Experimental observations of low values for the specific heat capacity in these compounds stimulated interest in band structure calculations. A number of band structure calculations of oxides, carbides and nitrides of transition metals with the NaCl-type structure using the APW and LAPW methods exist.

Under normal conditions VN crystallizes in the NaCl structure. The first band structure calculation of VN by the APW method was reported by Neckel *et al* (1976). Blaha and Schwarz (1987) calculated the band structure and electron densities of VN by the LAPW method. The relationship between crystal structure, chemical bonding and hardness in refractory metal compounds has been discussed by Nowotny (1953). Theoretical work on chemical bonding as well as a detailed comparison with experimental data are given in reviews by Neckel (1983) and Schwarz (1987). Zhukov *et al* (1988) calculated the energy band structure of VN_x for $x = 1$ and 0.75 by the LMTO-ASA (atomic sphere approximation) method. They calculated the equilibrium lattice constant, the bulk modulus, the cohesive energy and the energy of vacancy formation for nitrides and compared them with the available experimental data. More recently, Haglund *et al* (1991) studied the cohesive properties of transition metal compounds with the NaCl structure using the LMTO method. With their calculations,

they established trends for the cohesive energy of carbides and nitrides as a function of the average number of valence electrons per atom in the compound.

In this paper we report on the investigation of the structural properties of VN under high pressure. The total energies are obtained by means of the LMTO method as a function of volume in the NaCl as well as the CsCl structure. We also present our results on the pressure dependence of the superconducting transition temperature of VN in the NaCl structure. The organization of the paper is as follows. The methodology of the band structure calculation and the structural properties of VN are given in section 2. Section 3 deals with the calculation of the superconducting transition temperature. The final section is devoted to results and discussion.

2. Method of calculation

The energy bands of VN have been obtained by means of the LMTO-ASA method (Andersen 1975) in its scalar relativistic form, in conjunction with the local density approach. The self-consistent calculations were carried out using 161 k -points in the irreducible wedge of the Brillouin zone (IBZ). We used a minimal basis set consisting of s , p and d orbitals on the metal atom and s and p orbitals on the non-metal atom. The basis set is corrected by including the correction terms for overlapping sphere geometry. The exchange and correlation parametrization scheme of von Barth and Hedin (1972) is used in the present work. In the LMTO-ASA method the crystal is divided into 'space filling' spheres centred on all atomic sites. We have taken the ratio of the radii of spheres of V and N to be equal to 0.68.

At ambient conditions VN crystallizes in the NaCl structure. To find the equilibrium lattice constant in the NaCl structure, the total energies (valence electrons) are computed by varying the cell parameter from 4.398 Å to 3.491 Å. The Birch equation of state is fitted to the total energies for the valence electrons. The theoretically calculated equilibrium volume in the NaCl structure corresponds to a value for the lattice constant equal to 4.07 Å, which is in good agreement with the experimental value of 4.139 Å (Zhao *et al* 1984). The bulk modulus, which is obtained from the derivatives of fitted total energies, is 2.324 Mbar, whereas the experimental value is 2.328 Mbar (Francevitsh 1980).

In order to find the high-pressure phase of VN we decided to examine another simple structure, namely the CsCl structure. The total energies are computed by reducing the cell volume in a manner similar to the NaCl structure and fitting to the Birch equation of state. Figure 1 shows the total energy (valence electrons) of VN in the NaCl and CsCl structures as a function of the reduced volume, namely V/V_0 where V_0 is the equilibrium experimental volume in the NaCl structure. From the theoretically calculated values for total energy, we predict a structural phase transition in VN from NaCl to CsCl at about 65.2 GPa. For want of experimental data we are unable to compare our results.

The band structure of VN in the NaCl structure along the high-symmetry directions is presented in figure 2 under ambient conditions. The band profile of VN is in agreement with that of APW results (Neckel *et al* 1976). The lowest-lying band originates mainly from the N 2s state. The next three bands originate mainly from the N 2p states. The states above 2p have predominantly V 3d character and are termed as the 'd' band.

The total and 'l' partial state densities are calculated by means of the tetrahedron method (Jepson and Andersen 1971). The total density of states (DOS) determined

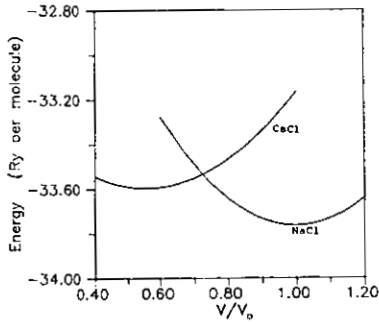


Figure 1. The total energy as a function of the reduced volume for the NaCl and CsCl structures of VN.

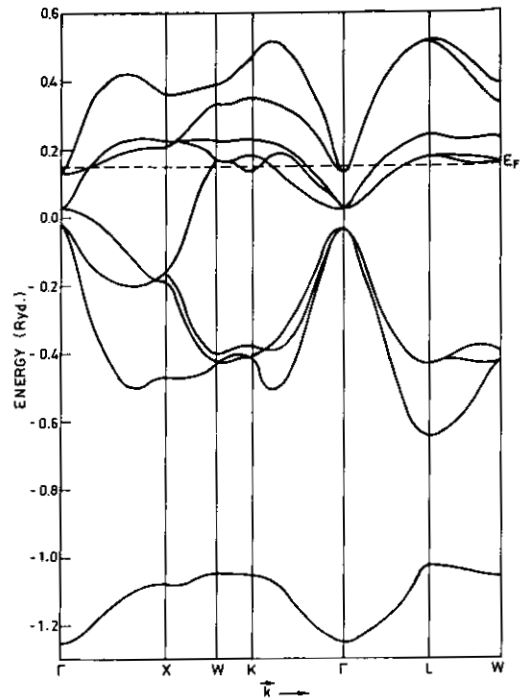


Figure 2. The LMTO band structure of VN in the NaCl structure.

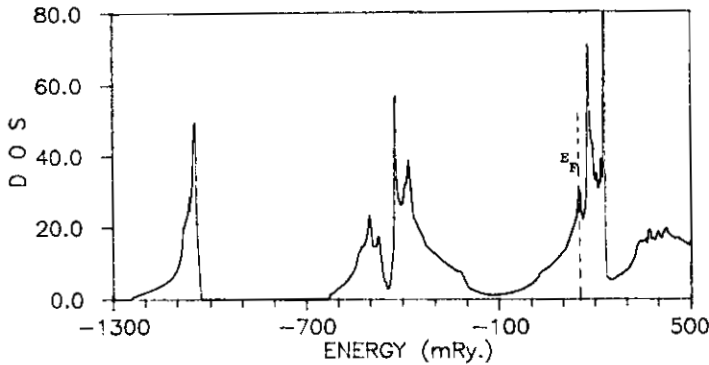


Figure 3. The density of states for VN with the NaCl structure.

at ambient conditions is given in figure 3, which is in good agreement with those obtained by the LAPW method (Blaha and Schwarz 1987). The Fermi energy, and the total and partial density of states evaluated at the Fermi energy, are given in table 1 along with the number of electrons for different pressures. The total and the partial density of states at E_F are used in the calculation of T_c .

The electronic specific heat coefficient ν , which is related to the density of states at E_F through the relation

Table 1. Fermi energies E_F , the total and partial densities of states at E_F , and the number of electrons.

Pressure (GPa)	E_F (Ryd)	$N(E_F)$ (states Ryd ⁻¹ / unit cell)	Density of states (states Ryd ⁻¹ /unit cell)						Number of electrons per unit cell					
			V			N			V			N		
			s	p	d	s	p	d	s	p	d	s	p	d
0.18	0.1479	28.940	0.104	0.129	26.792	0.089	1.829	0.504	1.023	3.871	1.356	1.356	3.246	
2.93	0.1536	28.659	0.103	0.129	26.517	0.089	1.820	0.505	1.026	3.875	1.354	1.354	3.242	
5.76	0.1594	28.381	0.103	0.129	26.249	0.088	1.811	0.505	1.028	3.879	1.349	1.349	3.238	
9.27	0.1665	28.060	0.102	0.129	25.940	0.088	1.801	0.506	1.032	3.883	1.345	1.345	3.234	
14.16	0.1761	27.587	0.101	0.129	25.486	0.087	1.785	0.506	1.037	3.889	1.339	1.339	3.228	
19.31	0.1858	27.141	0.100	0.129	25.056	0.086	1.770	0.507	1.042	3.895	1.334	1.334	3.222	

$$\nu = (\pi^2/3)k_B^2 N(E_F) \quad (1)$$

where k_B is Boltzmann's constant, is calculated at ambient conditions. From the theoretically calculated value for ν , one can estimate the electron-phonon mass enhancement factor λ through the relation

$$\nu_{\text{exp}} = \nu_{\text{theor}}(1 + \lambda). \quad (2)$$

Since the experimental value for ν is available at ambient conditions, we have estimated the value for λ_{theor} using the above expression. From table 2 it is clear that our value is in good agreement with the experimental value.

Table 2. A comparison of the theoretical value for λ with the experimental value.

Pressure (GPa)	ν (mJ mol ⁻¹ K ⁻²)		λ	
	Exp.	Theory	Present	Exp.
0.18	8.6	5.016	0.702	0.715

3. Calculation of superconducting transition temperature

The superconducting transition temperature (T_c) is calculated using McMillan's formula (1968), which is

$$T_c = (\Theta_D/1.45) \exp \{-1.04(1 + \lambda)/[\lambda - \mu^*(1 + 0.62\lambda)]\} \quad (3)$$

where λ is the electron-phonon coupling constant, μ^* the electron-electron interaction constant and Θ_D the Debye temperature.

The electron-phonon coupling constant is calculated for this compound using Phillips' formula (1971) in the two-compound system

$$\lambda = \lambda_A + \lambda_B \quad (4)$$

that is

$$\lambda = N_A(E_F)\langle I_A^2 \rangle / M_A \langle \omega_A^2 \rangle + N_B(E_F)\langle I_B^2 \rangle / M_B \langle \omega_B^2 \rangle \quad (5)$$

where A and B stand for a metallic and a non-metallic atom in a compound having the chemical formula AB. Such a separation is valid only when the difference in masses is large, which is the case in nitrides. By virtue of this inequality, the heavy metallic atom mainly oscillates in the acoustic frequency range, and the light atom nitrogen in the optical range. In the same approximation it turns out that

$$\langle \omega_A^2 \rangle \sim 1/M_A \quad \text{and} \quad \langle \omega_B^2 \rangle \sim 1/M_B$$

so that the denominators in the expression for λ are weakly dependent on mass and are of the same order of magnitude. $\langle I^2 \rangle$, which appears in equation (5), is

the square of the electron-phonon matrix element averaged over the Fermi surface. Gaspari and Gyorffy (1972) have shown that $\langle I^2 \rangle$ can be expressed within the rigid muffin-tin approximation (RMTA) in terms of the scattering phase shifts. However, in the ASA, the usual phase shift notation becomes meaningless and $\langle I^2 \rangle$ can be written in atomic Rydberg units (Skriver and Mertig 1985) as

$$\langle I^2 \rangle = 2 \sum_l \frac{l+1}{(2l+1)(2l+3)} M_{l,l+1}^2 \frac{N_l(E_F)N_{l+1}(E_F)}{N(E_F)N(E_F)} \quad (6)$$

where $M_{l,l+1}$ is the electron-phonon matrix element, which can be expressed in terms of the logarithmic derivatives

$$D_l = \left. \frac{d \ln \phi_l}{d \ln r} \right|_{r=s} \quad (7)$$

evaluated at the sphere boundary.

$$M_{l,l+1} = -\phi_l \phi_{l+1} [(D_l(E_F) - l)(D_{l+1}(E_F) + l + 2) + (E_F - V(s))s^2] \quad (8)$$

where $V(s)$ is the one-electron potential and ϕ_l the sphere boundary amplitude of the l partial wavefunction evaluated at E_F . N_l in equation (6) is the partial density of states function for the angular momentum quantum number l . The matrix elements are calculated in a manner similar to our earlier work on Zr (Palanivel *et al* 1992) and NbC (Palanivel *et al* 1991). The value for λ calculated at ambient pressure is 0.7015, which is in good agreement with an earlier reported value of 0.72 (Haufe *et al* 1975). $\langle \omega^2 \rangle$, which appears in equation (5), is set equal to $0.5\Theta_D^2$.

It is a well established fact that the phonon spectrum alters under pressure. The variation of Debye temperature with pressure can be obtained using the relation

$$\nu_G = -\partial \ln \Theta_D / \partial \ln V \quad (9)$$

where ν_G is the Grüneisen parameter. Since no experimental data for the variation of ν_G with pressure are available, a simple procedure was adapted in one of our earlier calculations (Palanivel *et al* 1991). The same procedure is followed now to obtain the variation of Θ_D with pressure. The electron-electron interaction constant μ^* is obtained from the empirical relation given by Bennemann and Garland (1971):

$$\mu^* = 0.26N(E_F)/[1 + N(E_F)]. \quad (10)$$

The calculated value for μ^* at ambient pressure, using the above relation, is 0.17, which is slightly greater than the earlier reported value of 0.13 (Haufe *et al* 1975). In the present calculation the value for μ^* is taken as 0.13. The values for the superconducting transition temperatures are obtained as a function of pressure and are given in table 3, along with other parameters that feature in the calculations. The calculated value for T_c at ambient conditions is 9.322 K, which is in good agreement with the experimental value of 8.5 K (Kyoichi Kinoshita 1990), as well as the earlier reported value of 9.1 (Haufe *et al* 1975). From the table one can see that T_c increases with increasing pressure. The theoretically calculated value for the pressure coefficient is 27 mK kbar⁻¹, whereas the experimental value is 12 mK kbar⁻¹ (Grewe 1987). From our band structure calculations we observe that the 'd' electron number at the V site increases at the expense of 's' electrons from the N site. This may be a possible reason for the increase of T_c with increasing pressure.

Table 3. The variation in λ , Θ_D and T_c with pressure.

Pressure (GPa)	λ	Θ_D (K)	T_c (K)	
			Present	Exp.
0.18	0.7015	420	9.322	8.5
2.93	0.7192	423	10.074	
5.76	0.7198	425	10.413	
9.27	0.7607	429	11.872	
14.16	0.7913	433	13.214	
19.31	0.8237	437	14.675	

4. Results and discussion

We have obtained the band structure of VN in the NaCl structure as a function of pressure using the self-consistent LMTO method. Under normal conditions VN crystallizes in the NaCl structure. The calculated values for the lattice constant and the bulk modulus are in good agreement with experimental values. To investigate any possible structural transformation in VN we have calculated the total energies of VN in the NaCl as well as the CsCl structures by reducing the cell volume. From total energy studies we predicted a structural phase transition in VN from NaCl to CsCl at about 65.2 GPa. The LMTO band structure and DOS of VN at ambient conditions are in good agreement with the earlier work using the APW and LAPW methods.

The band structure outputs are used to calculate the electron-phonon coupling constant in the two-component formalism of Phillips (1971). From our calculation we find that the value for λ_A is large when compared with λ_B , which supports the views expressed by Klein and Papaconstantopoulos (1974) that the contribution λ_A is important in the nitrides of transition metals. The superconducting transition temperature is calculated as a function of pressure using McMillan's formula. The calculated value for T_c at ambient conditions is 9.322 K, which is in good agreement with the experimental value of 8.5 K. The theoretically calculated value for the pressure coefficient of T_c is 27 mK kbar⁻¹, which is in good agreement with the experimental value of 12 mK kbar⁻¹. Our band structure results show that the 'd' electron number at the V site increases at the expense of 's' electrons from the N site. This may be the reason for the increase in T_c with increasing pressure. Also, the calculated values for T_c and λ at ambient conditions are in good agreement with other earlier reported values (Haufe *et al* 1975).

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