

Electronic and Elastic Properties of Metal Monoxides MO (M=Nb,V): A First-Principles Study

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Abstract— The first-principles calculations based on density-functional theory (DFT) is a very efficient method to study the properties of materials. We report a detailed study of the structural, electronic and elastic properties of the metal monoxides – Vanadium monoxide and Niobium monoxide - MO (M=V, Nb) in the B1 (rock-salt), B2 (CsCl) and B3 (Zinc-blende) phases, under normal and elevated pressures using the first-principles calculations. To understand the structural and electronic properties of MO (M=V, Nb), their lattice parameters, density of states and electronic band structures are analyzed. The lattice parameters are found to be in accord with the available experimental and other theoretical values. From the electronic band structure, we find that both the metal monoxides are metallic in nature at all pressures. We report a phase transition from B1 to B2 phase at a pressure of 58.85 GPa in Vanadium monoxide. Niobium monoxide in its B2 phase, transforms into a super conductor. The elastic constants are computed at normal and elevated pressures to investigate the mechanical stability, anisotropy and hardness of MO (M=V, Nb). The calculated elastic constants obey the stability criteria only for the B1 and B2 phases of Vanadium monoxide. As for Niobium monoxide, its B2 phase alone is stable in the normal and elevated pressures.

Index Terms— Ab-initio calculations, Elastic properties, Electronic structure, Structural phase transition.

1 INTRODUCTION

THE group VB transition metal oxides VO and NbO are stable metal monoxides which crystallize in the cubic phase. VO has diverse applications such as environmental sensors, oxidation catalysts and in optical devices [1], while NbO is widely used as solid state electrolyte capacitors. Most of the theoretical studies based on first principles calculations deal with the structural and electronic properties of MO (M=V, Nb) at ambient pressure only. High pressure studies of these metal monoxides are not done to the best of our knowledge. In this paper the structural, electronic and elastic properties of the metal monoxides – Vanadium monoxide and Niobium monoxide - MO (M=V, Nb) in the B1 (rock-salt), B2 (CsCl) and B3 (Zinc-blende) phases, are investigated under normal and elevated pressures using the first-principles calculations.

2 COMPUTATIONAL METHOD

The first principles calculations were all carried out using the Vienna Ab-initio Simulation Package (VASP) code [2] within the density functional theory frame work, where the PBE form of GGA [3] was employed to describe the electron exchange and correlation. The electronic convergence was set up at

10^{-6} eV and the, sampling of the brillouin zone were performed by Monkhorst-Pack scheme. The vanadium $3s^2 3p^6 3d^3 4s^2$; niobium $4s^2 4p^6 4d^4 5s^1$ and oxygen $2s^2 2p^4$ orbitals were included as valence electrons. In the B1 (NaCl) and B2 (CsCl) structures of VO, the V and O atoms are at the positions (0,0,0) and (1/2,1/2,1/2). For the B3 (ZnB) structure, the atom positions are at (0,0,0) and (1/4,1/4,1/4). As for NbO, it exhibits a defective rock-salt structure with 25% vacancies in the B2 structure which is confirmed by the X-ray investigation of Elliot [4] and in the other two structures, the Nb atom occupies the same position as the V atom.

3 RESULTS AND DISCUSSION

3.1 Structural and Electronic Properties

To find the equilibrium lattice parameters for the three phases of the metal monoxides VO and NbO the total energies for the various volumes are first computed and the optimized lattice parameter which corresponds to minimum energy are calculated. These data are then fitted to the universal Birch-Murnaghan equation of state in order to find the first derivative of the bulk modulus. The calculated values of the lattice parameters are in good agreement with the experimental and other theoretical values as seen in Table 1.

A phase transition from B1 to B2 is found to occur in VO only at a pressure of 58.85 GPa, which is calculated using the relation: $G = E + PV$, is shown in Fig.1.

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TABLE 1
 THE CALCULATED LATTICE PARAMETERS

Phase	Compound	Approach	a (Å)	B ₀ (GPa)	B ₀ '
B1	VO	Present	4.15	251	4.2
		Exp	4.144	277	4.6
		Others	4.186	243	4.6
	NbO	Present	4.5	117	3.7
B2	VO	Present	2.55	229	4
	NbO	Present Exp	4.265 4.21 ^a	115	4
B3	VO	Present	4.51	152	4
	NbO	Present	4.8	103	4

^aReference [5]

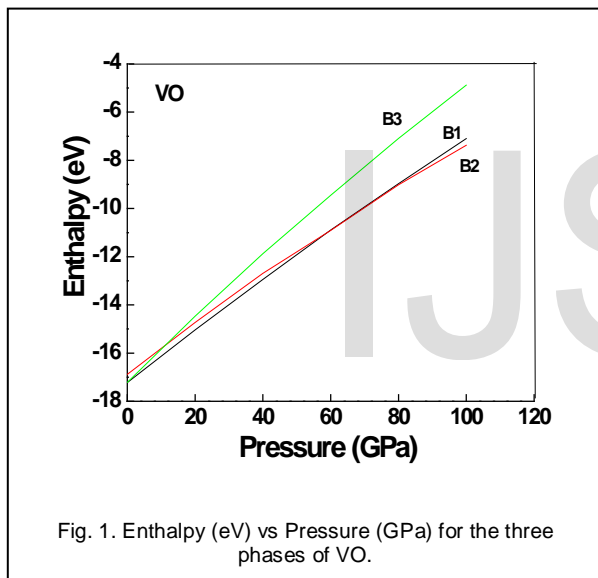


Fig. 1. Enthalpy (eV) vs Pressure (GPa) for the three phases of VO.

The electronic band structure, an important property of any material provides information about its electronic and optical properties. The electronic band structure changes if the composition or atomic arrangements are changed. The normal pressure band structure, at the equilibrium lattice constant are depicted in Fig.2, which are drawn along symmetry directions in the first Brillouin zone for NbO and VO. The Fermi level is indicated by dotted horizontal line. The band structure of these materials is similar to each other. They are all characterized by an energetically low lying band, which is derived from the 2s states of oxygen atom. The remaining bands appearing just below the Fermi level are due to metal-d states and O-2p states. The energy bands at the Fermi level are derived mainly from the mixture of metal-d states and O-2p states. The empty conduction bands above the Fermi level are due to mixture s, p and d states. The band structures of VO and NbO indicate that they are metallic with the metal-d bands well separated from the s bands of oxygen, in all the

three phases at normal and a high pressure as seen in fig 2.

3.1.1 Superconductivity of NbO

The continuous promotion of s electron to d shell in solids is one of the factors which will induce superconductivity. In the NbO, the d – electron number increases as a function of pressures ranging from normal to high pressure. This leads to the improvement of superconducting transition temperature (T_c) value. Therefore, the interaction between the conduction electrons and phonons increases and also electron – phonon coupling constant factor λ_{e-ph} increases. This determines the superconducting nature of a compound. The calculated T_c values depend more sensitively on λ rather than θ_D (Debye temperature) and μ*. NbO is found to have superconducting nature at ambient conditions. For normal pressure, the superconducting transition temperature is estimated by using the McMillan equation modified by Allen and Dynes [6],

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

where λ is the electron- phonon coupling constant, μ* is the electron – electron interaction parameter and ω_{log} is the average phonon frequency. The T_c, μ* and λ values are computed for NbO at normal pressure using the results obtained from the electronic structure calculated using TB-LMTO. Our calculated value of T_c=1.579 K is very close to 1.61K which is reported by Okaz et al. [7].

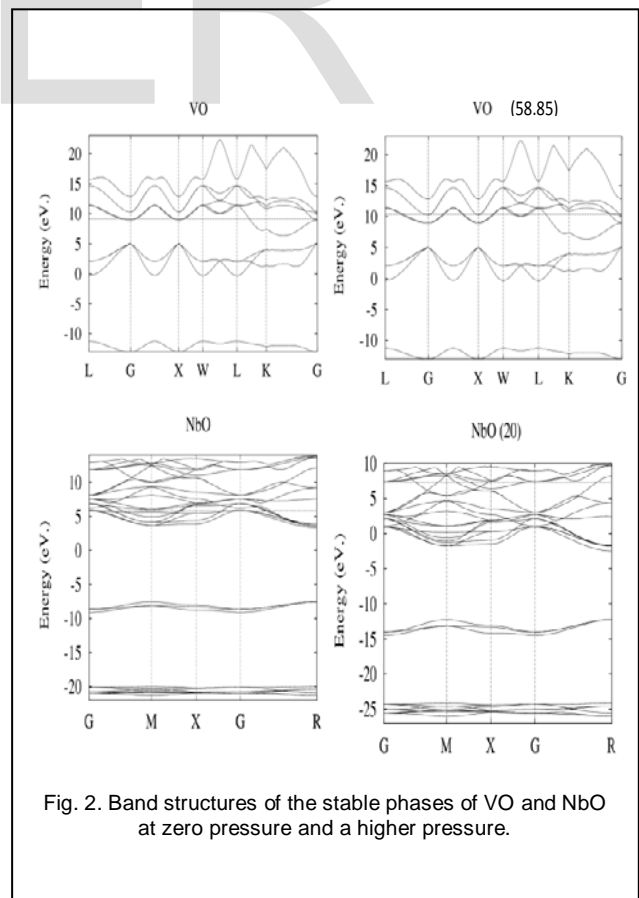


Fig. 2. Band structures of the stable phases of VO and NbO at zero pressure and a higher pressure.

TABLE

Calculated elastic constants C_{11} , C_{12} , C_{44} (GPa), Young's modulus E (GPa), shear modulus G(GPa), Poisson's ratio(ν), B/G ratio, Anisotropic factor and (A) and micro hardness parameter h_v for vanadium monoxide and Niobium monoxide.

		C_{11}	C_{12}	C_{44}	E	G	ν	B/G	A	Hv
VO	B1	484.6	134.3	18.2	152.8	54.6	0.398	4.59	0.057	8.6
	B2	339.4	174.2	39.7	148.9	53.5	0.39	4.29	0.16	8.83
	B3	111.6	143.5	-48.4	-	-	-	-	-	-
NbO	B1	174.2	89.03	-45.8	-	-	-	-	-	-
	B2	241.8	51.8	59.5	178.4	71.8	0.24	1.6	0.41	20.3
	B3	96.7	107.2	-39.4	-	-	-	-	-	-

3.2 Elastic Properties

The elastic constants are essential for applications related to mechanical properties of solids. The high pressure study of these constants is important to predict and understand the material response, strength and its mechanical stability. In order to obtain the mechanical stability description of these systems, a set of elastic constants is obtained from the resulting change in total energy deformation. The elastic constants C_{ij} are calculated within the total energy method [8-10], where the unit cell is subjected to a number of finite size strains along several strain directions.

In this work the elastic constants at normal and high pressures are calculated to investigate the mechanical stability of VO and NbO in their stable phases. Now, there are three independent elastic constants - C_{11} , C_{12} and C_{44} for the cubic structure. VO is stable in the B1 phase up to a pressure of 58.85 GPa. And it transforms to the B2 phase, whereas NbO is stable only in the B2 phase even at high pressures. The calculated values of elastic constants (C_{ij}), Young's modulus, shear modulus, poisson's ratio, B/G ratio, anisotropic factor and hardness for VO and NbO with possible considered phases at ambient pressure are given in Table.2. The negative values of C_{44} indicate that these oxides are highly unstable even at ambient condition. However the elastic constants are found to increase with pressure for these oxides in their stable phases as expected. The variation of the various moduli and their corresponding micro hardness for the stable phases of VO and NbO are shown in fig 3. The Bulk modulus B_0 , Young's modulus E and shear modulus G increase monotonously with pressure. This indicates that these oxides resist both volume and shape changes. The hardness also increases with pressure, very slowly indeed. Also, NbO is found to be more stiffer and more harder than VO, as it's young's modulus and hardness values are higher.

The mechanical stability conditions also depend on the elastic constant values. The elastic stability criteria for cubic crystals under pressure are: $K = C_{11} + 2C_{12} + P > 0$; $K_1 = C_{44} - P > 0$; $K_2 = C_{11} - C_{12} - 2P > 0$. The stable phases of both oxides obey elastic stability criteria suggesting they are mechanically stable. Moreover, the anisotropy $A = 2C_{44} / (C_{11} + C_{12})$ is found to weaken as the pressure is enhanced.

4 CONCLUSION

The band structure, phase transition and elastic properties of VO and NbO were studied in detail using the first principles calculations. Our results indicate that at normal pressure VO and NbO are stable in the B1 and B2 phases respectively. A phase transition from B1 to B2 at a pressure of 58.85 GPa in VO is reported. The band structure calculations indicate that these oxides are metallic. NbO is a super-conductor at normal pressure, with $T_c = 1.578K$, which is in accord with the experimental value. The pressure dependent study of the elastic constants showed that NbO is stiffer and harder than VO and both these oxides are mechanically stable in their stable phases. The first principles study has thus helped us to explore the behavior of VO and NbO at extreme conditions.

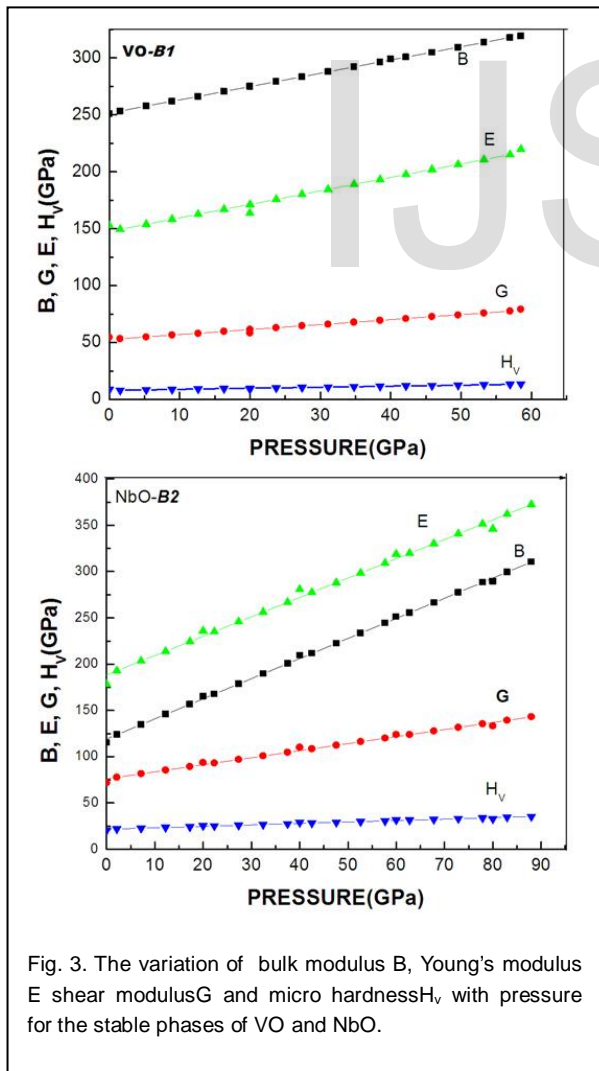


Fig. 3. The variation of bulk modulus B, Young's modulus E shear modulus G and micro hardness H_v with pressure for the stable phases of VO and NbO.

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