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Calculations of the Atomic and the Electronic Structures of 4d-Transition-Metal Nitrides

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A systematic study of the zinc-blende-type 4d-transition-metal nitrides, which still need to be synthesized, is carried out by means of spin-polarized first-principles full-potential-linearized-augmented-plane-wave calculations using the local spin density approximation. In particular, lattice constants, bulk moduli, band structures and density of states are reported, and trends are discussed.

Keywords: Electronic structures; 4d-transition-metal nitrides; First-principles

I. INTRODUCTION

Many compounds of the transition elements have certain properties which are not possessed by other compounds, due to the presence of the partially-filled shells of the d electrons in the transition-element ions. Because of interesting magnetic, superconducting, mechanical, and structural properties, they are materials of fundamental importance for magnetic storage devices, superconductors and in the semiconductor industry [1, 2]. Several authors have presented results of electronic-structure calculations for 4d-transition-metal-nitrides (TMN) from different view points [2–5]. Theoretically, the cohesive properties of NaCl-type structure nitrides of the 4d-transition-metals have been performed by Gelatt *et al.* [2] with use of the augmented-spherical-wave method. Their emphasis is on the contribution of the various electron states to the bonding properties. Papaconstantopoulos *et al.* [3] studied the electronic properties of VN, NbN, TaN, CrN, MoN, and WN. Guillemet *et al.* [4] have investigated the electronic, cohesive, and thermodynamic properties of 3d- and 4d-transition-metal monocarbides and mononitrides in the NaCl structure. Recently, Stampft *et al.* [5] investigated the bulk electronic and physical properties of the early 4d-transition-metal mononitrides (YN, ZrN, NbN) also in the NaCl structure. They reported, in particular, lattice constants, bulk moduli, heats of formation, and cohesive energies as well as bulk band structures and densities of states, and discussed trends. We emphasize that all of these theoretical calculations have been done only for NaCl-type 4d-transition-metal nitrides. In this paper we carry out first-principles spin-polarized band calculations for the whole series of 4d-transition-metal nitrides in the zinc-blende phase in order to understand or predict systematically their electronic and structural properties. As it has become increasingly commonplace to prepare compounds in structures which are not the most stable ones, we find it to be worthy to investigate these materials, which have not yet been fabricated in the laboratory. This paper is organized as follows; section II describes the method of calculation and the approximations; section III shows partial results and discussions of the electronic structure, and in section IV contains our conclusions.

II. METHOD OF CALCULATION

We carry out self-consistent, first-principles, spin-polarized calculations using the full-potential linear augmented plane wave method within the local-spin-density functional formalism [6] in the LSDA approach. In particular we use the FP-LAPW method as implemented in the Wien2k code [7]. We have included scalar-relativistic effects for all valence states (including the TM-4d states). Core states are calculated fully relativistically, retaining only the spherical part of the potential. The effects of exchange-correlation are treated within the local spin-density approximation using the Ceperley-Alder data [8] for the electron gas exchange term and their parametrization by Perdew and Wang [9]. The valence part is treated with the potential expanded into spherical harmonics up to $l=6$. The valence wave functions inside the spheres are expanded up to $l=10$. In all cases we use an APW+lo orbital [10, 11] type basis with additional local orbitals for the TM 4s and 4p semi-core states. The muffin-tin radii, k-point set, and plane-wave cutoffs, K_{max} , for the 4d-transition-metal nitrides studied are listed in Table I along with the calculated lattice constants and bulk moduli. We used a zinc-blende structure (space group $\bar{F}43m$) with two atoms in the primitive unit cell to simulate the binary compounds. Self-consistency was achieved by demanding the convergence of both the total energy and the eigenvalues to be smaller than 10^{-6} eV.

III. RESULTS AND DISCUSSION

The equilibrium lattice constants and the bulk moduli, listed in Table I for the 4d-transition-metal nitrides, were obtained by performing total energy calculations for the two-atom unit-cell.

The equilibrium lattice constants and the bulk moduli of those compounds were estimated as follows. First, we calculated the total energy for several discrete values of the unit cell volume, and then the calculated energies were fitted to the Murnaghan equation of states [12]. In Fig. 1 we display the equilibrium lattice constants and the bulk moduli, where two trends can be noted.

TABLE I: Lattice constant, a_o , and bulk modulus B_o for all 4d-transition-metal nitrides in the zinc-blende structure. Also listed are the plane wave cutoffs K_{max} and the muffin-tin radii R_{MT} . The number of k-points used in the irreducible part of the Brillouin zone is 72 in all cases.

Syst.	K_{max}	$R_{MT}(\text{bohr})$	$a_o(\text{\AA})$	$B(\text{GPa})$
YN	4.62	2.00(Y), 1.68(N)	5.19	126.19
ZrN	4.85	1.94(Zr), 1.64(N)	4.90	202.10
NbN	4.48	2.10(Nb), 1.74(N)	4.70	260.37
MoN	5.58	1.70(Mo), 1.42(N)	4.58	290.17
TcN	5.53	1.70(Tc), 1.42(N)	4.50	310.30
RuN	5.56	1.70(Ru), 1.42(N)	4.47	307.32
RhN	5.51	1.70(Rh), 1.42(N)	4.51	267.85
PdN	5.52	1.70(Pd), 1.42(N)	4.62	217.18
AgN	4.96	1.90(Ag), 1.60(N)	4.79	149.57

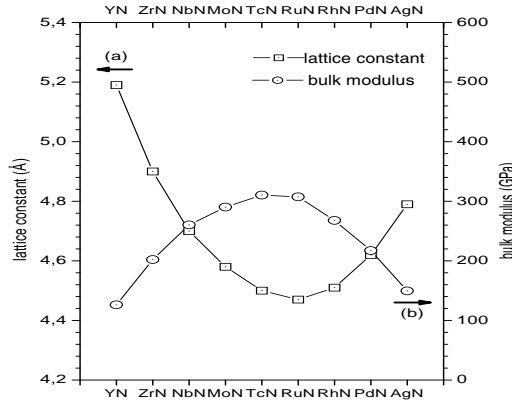


FIG. 1. The equilibrium lattice constants (a) and bulk moduli (b) of zinc-blende-type-structure 4d-transition-metal nitrides.

First, in Fig. 1 (a) it can be seen that the lattice constant decreases rapidly at the beginning of the series reaching the minimum value for RuN, and increases to the end of the series. Second, in Fig 1(b) it can be seen that the bulk modulus has just the opposite behavior as the lattice constant. The bulk modulus reaches a maximum for TcN, for which the lattice constant is close to the minimum value. It is interesting to note that we have obtained larger lattice constants for ZB-type than those reported for NaCl-type TMNs [1–5]. This result seems reasonable because in ZB-type the N atoms are located at the tetrahedral site of the face-centered cubic structure of the transition-metal atoms, and this site is rather closer to neighboring transition-metal atoms as compared to the octahedral site of the N atoms in the NaCl-type structure. The calculated band structures, at the equilibrium lattice constants, are depicted in Fig. 2, which are drawn along symmetry directions in the first Brillouin zone. Firstly we observe that although the calculations were carried out in the spin-polarized mode, no effective polarization of the states occurred at the equilibrium distances. The band structures exhibit the levels originated from atomic states Γ_1 (N-2s), Γ_{15}^v (N-2p + TM-4d),

Γ_{12} (TM-4d), and Γ_{15}^c (N-2p + TM-4d), at the Γ point. It can be seen that all the materials are metallic in the ZB structure except YN, for which the band structure indicates that this material is insulating.

We start by analyzing the trends displayed by the 4d atomic orbitals which originate from the transition-metals. The 4d atomic states are split into the Γ_{12} and Γ_{15} representations at the Γ point. As the atomic number of the TM increases, the characteristic band separations and widths change as shown in and Figure 3. E_g^1 refers to the energy gap between the lower bands Γ_1 and Γ_{15}^v , E_g^2 between Γ_{15}^v and Γ_{12} , and E_g^3 between Γ_{12} and Γ_{15}^c . $E(\Gamma_{15}^v - \Gamma_1)$ refers to the energy difference between the Γ_{15}^v and Γ_1 levels at the Γ point; $E(\Gamma_{12} - \Gamma_{15}^v)$ and $E(\Gamma_{15}^c - \Gamma_{12})$ have analogous meanings. These energy gaps are direct and occur always at the X point of the Brillouin zone. The trends, which can be observed from Table II and Figure 3, are the following: (i) The energy gap, E_g^1 , decreases slowly along the series while the energy gaps E_g^2 decreases steadily from ZrN and E_g^3 has a maximum for NbN and a minimum for RhN. (ii) The energy difference at the Γ point, $E(\Gamma_{15}^v - \Gamma_1)$ decreases slowly along the series, while $E(\Gamma_{15}^c - \Gamma_{12})$ increases and $E(\Gamma_{12} - \Gamma_{15}^v)$ decreases. (iii) The bandwidths $\Delta\Gamma_{15}^v$ and $\Delta\Gamma_{12}$ have both a maximum for MoN.

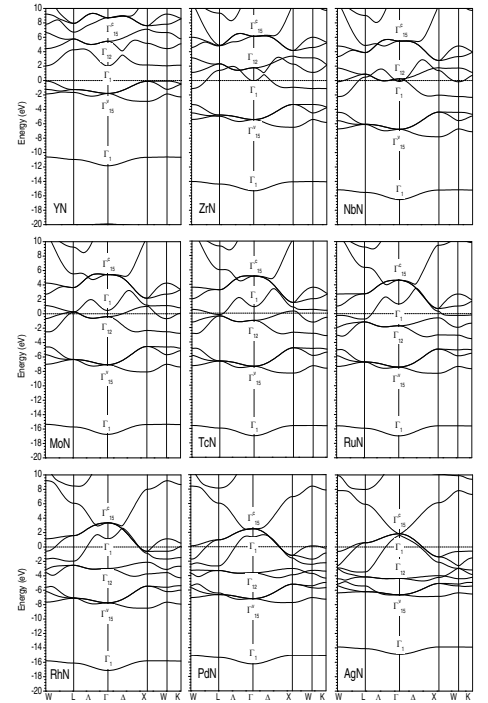


FIG. 2. Band structure for zinc-blende 4d-transition-metal nitrides at the LDA minimum. The horizontal line denotes the position of the Fermi energy.

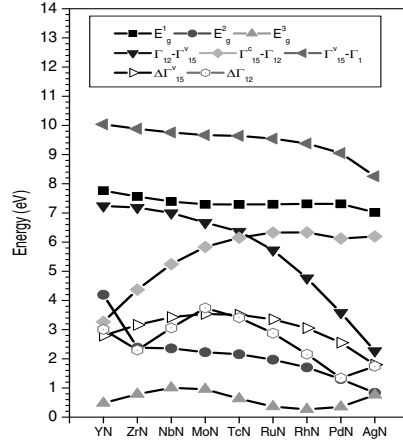


FIG. 3. Characteristic band separations and band widths (see Table II and text.)

In order to obtain a deeper insight into the changes in electronic band composition we give the total and partial density of states for all 4d-transition-metal nitrides in Fig. 4.

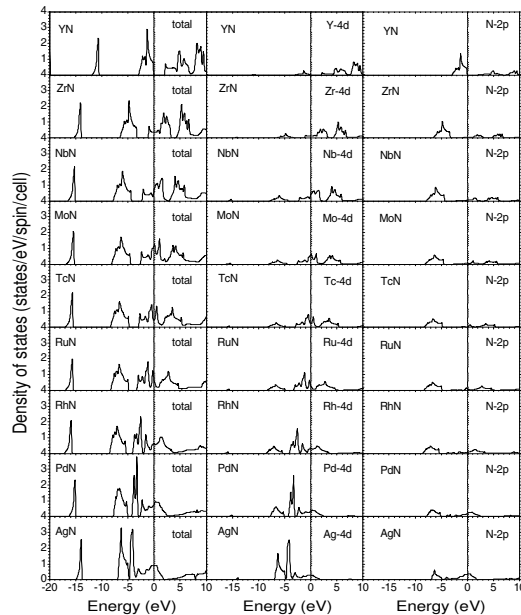


FIG. 4. Total and partial density of states for the zinc-blende 4d-transition-metal nitrides at the LDA minimum. The vertical line denotes the position of the Fermi energy.

The DOS features for all systems show close similarity. From the DOS features we see that the N-p states hybridize strongly with the TM-4d states. The DOS for all systems lies mainly in four energy regions: (i) the lowest region stemming

mainly from N-2s states; (ii) the region at the bottom of the valence band complex, originating from TM-5s and N-2p states; (iii) the region at the top of the valence band complex. This region, except for YN, is cut by E_F , and is mainly due to TM-4d states mixed with some N-p states; (iv) the energy region just above E_F dominated by unoccupied 4d-transition metal states. It can be seen that the total valence band width increases with the increasing of the atomic number. Moreover, along the series, the d-character of the valence band increases steadily with the increasing of the atomic number. In Fig. 5 we show the behavior of the Fermi-level density of states $N(E_F)$, and also of the Stoner enhancement, S_F , as calculated considering the Stoner parameter $I_F=0.47$ eV, constant along the series [3].

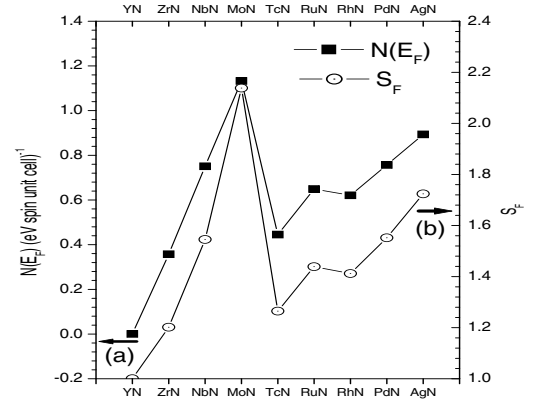


FIG. 5. The density of states $N(E_F)$ at the Fermi energy, and the Stoner enhancement S_F .

Aside MoN, these nitrides show moderate enhancements and the paramagnetic state is predicted to be the stable one for the whole series.

IV. CONCLUSIONS

This work reports partial results of a systematic study on the electronic and structural properties of zinc-blende-type 4d-transition-metal nitrides using spin-polarized first-principles full potential linearized augmented plane wave (FP-LAPW) calculations within the local spin density approximation (LSDA). The calculations show that all the materials are metallic except for YN, for which the band structure indicates that this material is insulating. We observe that when the lattice constant decreases, the bulk modulus increases, i. e., when going to the center of the series the material becomes harder. The paramagnetic state is predicted to be the stable one for the whole series.

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