Structural Phase Transition and Electronic Properties of NdBi

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Abstract: The structural and electronic properties of NdBi from an electronic structure calculation have been presented. The calculation is performed using self-consistent tight binding linear muffin tin orbital (TB-LMTO) method within the local density approximation (LDA). The calculated equilibrium structural parameters are in good agreement with the available experimental results. It is found that this compound shows metallic behavior under ambient condition and undergoes a structural phase transition from the NaCl structure to the CsCl structure at the pressure 20.1 GPa. The electronic structures of NdBi under pressure are investigated. It is found that NdBi have metalliation and the hybridizations of atoms in NdBi under pressure become stronger.

Keywords: Phase transition, bulk modulus, band structure, density of states.

1. Introduction

The mono-pnictides of rare earth with NaCl structure in recent years have drawn a great attention because of their diversive and unusual properties. The structural properties of several pnictides of lanthanide group, which crystallize in NaCl type crystal structure have been investigated by using high-pressure X-ray diffraction technique [1-5] and reported to undergo to either CsCl or body centered tetragonal (BCT) structure. The X-ray diffraction of cerium mono pnictides has been studied up to 30 GPa at room temperature [5-6]. Amongst all the Ce pnictides, only CeP exhibits an isomorphous transition about 10 GPa, which is associated to an electronic transition involving the change in the valence state of Ce [6]. Furthermore this compound transforms from NaCl structure to CsCl phase around 19 GPa. The high-pressure phases of other pnictides of Ce are either BCT or CsCl. The high-pressure forms of the bismuthides of Ce and Pr are reported as the co-existing cubic CsCl and tetragonal phases [7]. Gd mono pnictides (GdX, X= N, P, As, Sb, Bi) are known to exhibit unusual electric and magnetic [8, 9] phenomena. By use of synchrotron radiation, powder X-ray diffraction studied for LnBi (Ln= La and Pr) with the NaCl –type structure have been carried out up to 30 GPa at room temperature. The structural phase transition of LaBi occurs at about 11.5 GPa. The high-pressure phase of LaBi consists of coexisting of tetragonal (P4/mmm) and cubic (Pm3m) and cubic (Pm3m) modifications at about 14 GPa [10]. Hayashi *et* al. [11] using synchrotron radiation have studied the X-ray diffraction of NdBi with the NaCl-type structure up to 27 GPa at room temperature.

2. Method of Calculation

The total energy, BS and DOS for NdBi are calculated using a similar procedure as reported in our pervious work [12-14] using the TB-LMTO method [15, 16] within the local density approximation (LDA) [17]. Van Barth and Hedin [18] parameterization scheme has been used for exchange correlation potential. The NdBi compound crystallize in the NaCl-type structure (*fcc* lattice with space group, *Fm3m*, No. 225). In the NaCl structure, the Nd and Bi atoms are located at the position: Nd: (0, 0. 0) and Bi: (0.5, 0.5, 0.5). The structure of the high-pressure phase is CsCl-type (B_2-phase) (*sc* lattice with space group, *Pm3m*, No. 221) with positions of Nd: (0, 0, 0) and Bi: (0.5, 0.5, 0.5). As mention earlier work [12, 14, 19], the TB-LMTO method works well for the close-packed structure and since the NdBi compounds belongs to NaCl-type (B_1-phase) structure at ambient conditions, which is not a close-packed one. We have therefore introduced two equivalent empty spheres at position (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75) in such a way that they do not break the crystal symmetry [20]. However, the CsCl-type structure (B_2-phase) is a closed-packed structure, and no such empty spheres were needed. The Wigner-Seitz sphere was chosen in such a way that the sphere boundary potential is minimum and the charge flow between the atoms is in accordance with the electro negativity criteria [14, 19]. The E and *k* convergences are checked subsequently to achieve better accuracy. The calculations were performed for 512 *k* points (grid of 8×8×8) in the Brillouin zone for both the B_1 and B_2 phases. The tetrahedron method [21] of Brillouin zone integration has been used to calculate the DOS. The total energy was computed by reducing the volume from 1.05 V_0 to 0.60 V_0, where V_0 is the equilibrium cell volume. The calculated total energy was fitted to Birch equation of sates [22] to obtain the pressure volume relation. The pressure is obtained by taking the volume derivative of total energy. The Bulk modulus B_T ($-V_0 \, dP/dV_0$) is also calculated from the *P-V* relations. The stability of a particular structure is decided by the minima of the enthalpy. The phase-transition pressure P_t can be obtained by matching enthalpies of both structure such that the difference of enthalpy ΔH ($= H_{B2}-H_{B1}$) becomes zero at transition pressure *(P_t)*.

3. Results and discussion

3.1. Structural properties

The electronic BS calculations are performed to estimate the total energy of NdBi compound by using the first principle TB-LMTO method. The total energies for NdBi compound are plotted against different compressions and are shown in Figure 1.
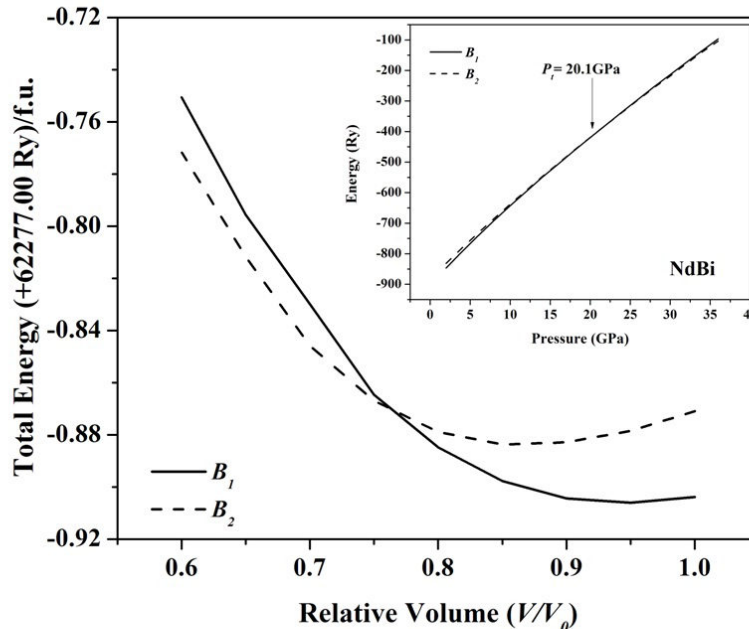

Figure 1.Variation of total energy with relative volume for the B_1 and B_2 phase for NdBi. The inset shows the variation of enthalpies in the B_1 and B_2 phases for NdBi.

The minimum of all the curves define the equilibrium volume V_0 (or equilibrium separation a_0), which is found to be 62.5 Å^3 and the corresponding lattice parameter is 6.3 Å, which is underestimated by 1 % for NdBi as compared to the experimental data [11], which is listed in Table 1.

Table 1. Calculated equilibrium lattice parameter a_0 (Å), bulk modulus B_T (GPa), number of f-states at the Fermi level N(E_f) (states/Ry cell), phase transition pressure P_t in (GPa) of TM Nitrides in the B_1 and B_2 phases.

Solids		a_0 = 2r (Å)		B_T (GPa)		N(E_f) (states/Ry cell)	P_t (GPa)	(V/V_0) %
		B_1	B_2	B_1	B_2			
NdBi	Pres.	6.3	3.9	61.5	54.7	684.07	20.1	2
	Expt	6.4[a]	--	--	--	--	21.1[a]	--

[a] Ref[11],

The present values of lattice parameters are in good agreement with the experimental values [11]. However, experimentally [11] reported values of the lattice parameter for NdBi is little larger than our results. This is primarily due to usage of LDA [17] in the present calculation. Regarding the LDA contraction, it is often found that the LDA leads to some over binding which yields lattice parameters that are somewhat smaller when compared with the experimental.

The calculation of transition pressure is carried out by estimating enthalpy in both the structures, as mentioned in Section 2. We have, therefore, plotted the variation of enthalpy with pressure for NdBi in the B_1 and B_2 phases, shown as inset of Figure 1.

The pressure at which these two phases coexist is phase-transition pressure. The equation of state in terms of pressure variation of relative volume change is given in Figure 2 for NdBi.
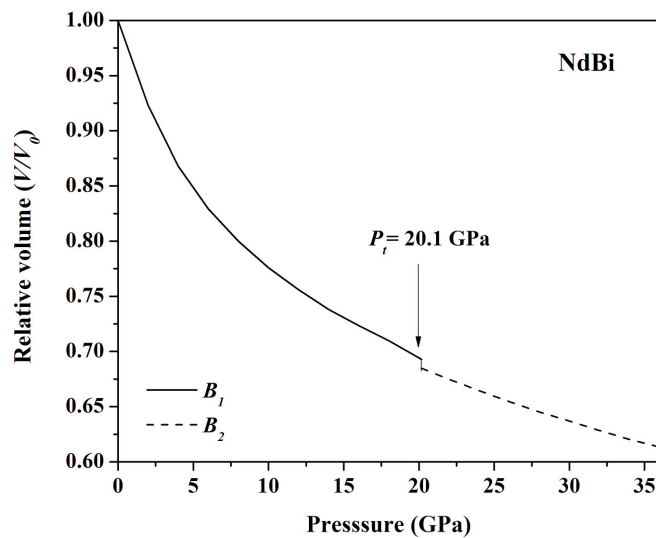
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Figure 2. Equation of states for NdBi compound. Solid line represents the B_1 phase and dotted line represents the B_2 phase.

In the case of NdBi, we have predicted a phase transition pressure of 20.1 GPa with relative volume collapse of 2 %. The calculated values of phase transition pressure for NdBi is compared with experimental results reported so far [11]. The calculated bulk modulus value for NdBi is listed in Table 1.

3.2. Electronic properties

The electronic BS and the DOS for the NdBi in their B_1-phase under ambient conditions are shown in Figure 3. From these figures, it can be noticed that these compounds show metallic property which is manifested by the presence of large number of *d*- and *f*-states at the Fermi level for NdBi respectively, as mentioned in Table 1.
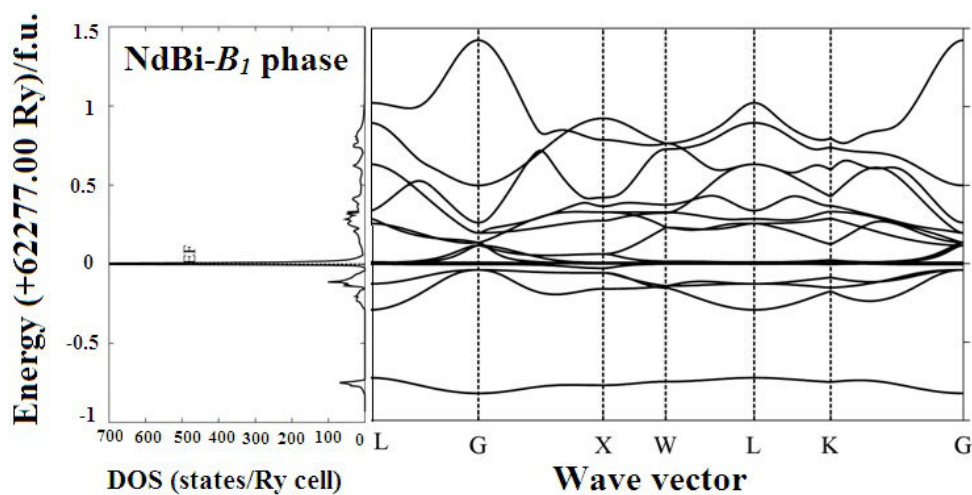

Figure 3 BS and DOS in the B_1 phase for NdBi.

To understand the elementary contribution of all atoms, we have studied the partial density of states (PDOS) which are shown in Figure 4. From the PDOS analysis, it has been found that the lower valence band lying around -0.75 Ry is due to the Bi-*s* states for NdBi.
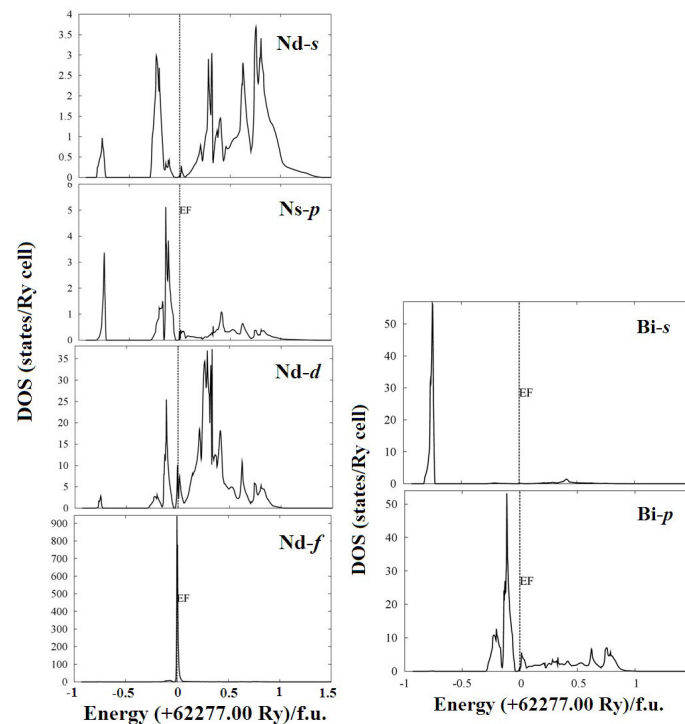
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Figure 4. PDOS in the B_1 phase for NdBi.

The upper valence band lying between -0.5 and 0.0 Ry are due to hybridization of Nd-*s*, *p*-, *d*- and Bi-*p* states for NdBi The Nd-*f* and Bi-*p* states are highly localized at the Fermi level. The conduction bands are due to the hybridization of the Nd-*f* and Bi-*p* states at the Fermi level for NdBi.   As pointed out earlier, the NdBi compound undergoes structural phase transition from the B_1 to B_2 phases at the pressure of 20.1 GPa. Thus, the electronic BS and DOS for both compounds in the B_2-phase are shown in Figure 5.
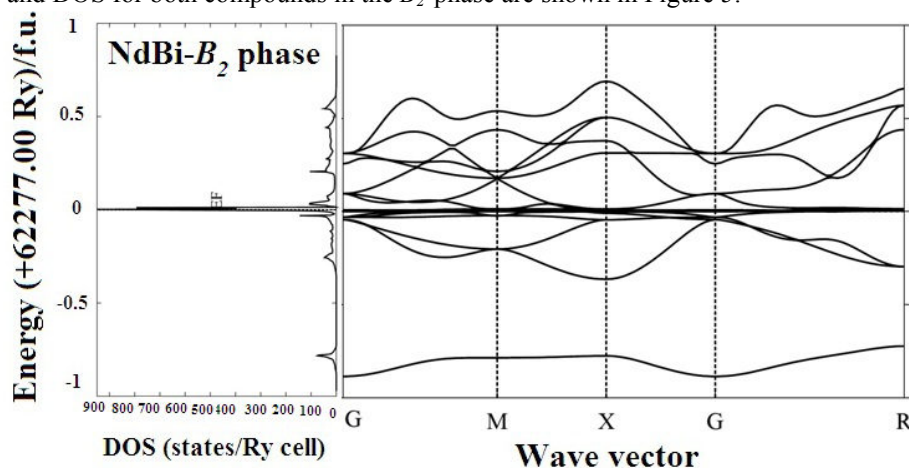

Figure 5. BS and DOS in the B_2 phase for NsBiTiN and NbN respectively.

The NdBi retain their metallic property at high pressure also. The nature of the bands and DOS in the B_2-phase is similar to the B_1-phases, with a minor difference that the lower energy bands are shifted to the higher energy bands near the Fermi level and more compressed bands are seen for NdBi. The hybridization of the Nd-*d*, –*f* and Bi-*p* states in the conduction band increases due to increase in pressure.

4. Conclusions

In summary, we have investigated structural and electronic properties for NdBi using the TB-LMTO method within the LDA. At ambient conditions, this compound is stable in the NaCl-type structure and undergoes structural phase transition to the CsCl-type structure in the pressure 20.1 GPa. The lattice parameters, bulk modulus and the phase transition pressure are obtained which are in good agreement with the experimental data.

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The electronic properties of NdBi under pressure are also calculated, and it is found that NdBi exhibit a metallic behavior and the hybridizations between atoms become stronger under pressure.

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