

A First Principle Investigation on the Structural, Electronic and Magnetic Properties of CaNi_2Pn_2 (Pn=P, Sb, Bi) Intermetallic Compounds

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The electronic structures of ThCr_2Si_2 -type compounds namely CaNi_2Pn_2 (Pn=P, Sb, Bi) compounds with space group $I4/mmm$ (139) are studied by means of Full Potential-Linearized Augmented Plane Wave (FP-LAPW) method in order to explore their structural, electronic and magnetic properties. To the best of our knowledge CaNi_2Sb_2 and CaNi_2Bi_2 compounds have not yet been reported elsewhere. The structural parameters of these two compounds are predicted from the experimental study of CaNi_2P_2 and it is understood from literature that CaNi_2P_2 is a low temperature superconductor. The band structure calculations are performed on the present CaNi_2Pn_2 (Pn=P, Sb, Bi) compounds by using WIEN2K code. From this study the optimized structural parameters, bulk modulus, electronic specific heat coefficient, Fermi energy, magnetic moment are obtained and are verified with the available data. From the least magnetic moment value which is obtained by our calculation, it is inferred that these compounds exhibit diamagnetism. Density of States (DOS) histograms and electron density plots are drawn for CaNi_2Pn_2 compounds. The bondings between the atoms of the compounds under study are explored from the charge density plots.

Key Words: Intermetallic Compounds; Electronic Structure; Inter-atomic Bonding; ThCr_2Si_2 -type, *Abinitio* Calculations; Nickel Pnictides

1. Introduction

Some of the ThCr_2Si_2 type structure exhibits superconductivity [1, 2]. Within the ThCr_2Si_2 type family, remarkable discrepancies exist regarding the bonding situation [3]. In some ThCr_2Si_2 -type compounds, Si-Si bonds exist between the adjacent Si-Cr-Si layers and in some ThCr_2Si_2 -type compounds no such bonds exist [4]. Recently, many ThCr_2Si_2 type compounds are synthesized and reported [5-7]. In the formulation of AT_2Pn_2 [122] type, A generally corresponds to alkaline earth metal, T stands for transition metal and Pn are pnictogens (N, P, As, Sb, Bi).

The aim of the present work is to explore the bonding between the transition metal and pnictogen, and hence, to analyze the structural, electronic and

magnetic properties of CaNi_2Pn_2 (Pn=P, Sb, Bi) isostructural compounds where no experimental data is available for CaNi_2Sb_2 and CaNi_2Bi_2 . It is understood from the literature that all the Fe based compounds have the antiferromagnetic ground states, Co based compounds have the ferromagnetic ground states and the Ni, Cu based compounds have the non-magnetic ground states [8-10].

2. Crystal Structure and Computational Aspects

All the considered AT_2Pn_2 where A=Ca, T=Ni and Pn=P, Sb, Bi are crystallize in the quasi-two-dimensional ThCr_2Si_2 -type tetragonal structure, space group $I4/mmm$; $Z=2$. The structure is built up of $[\text{T}_2\text{Pn}_2]$ blocks alternating with 'A' atomic sheets stacked along Z axis. The atomic positions are: A:2a(0,0,0), T:4d (0,0.5,0.25) and Pn atoms :4e

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(0,0, Z_{Pn}), the variable parameter Z_{Pn} determines the relative position of the Pn atom within the unit cell [11].

We have carried out the computations by means of Full Potential Linearized Augmented Plane Wave (FP-LAPW) method implemented in the WIEN2K suite of programs [12]. The Generalized Gradient Approximation (GGA) parameterized by Perdew *et al.* (PBE) is applied for calculating exchange and correlation Energy [13]. The plane wave expansion $R_{MT} \times K_{MAX}$ equal to 7 and K sampling with $10 \times 10 \times 10$ k-points in the Brillouin zone are used. The self consistent calculations are considered to be converged when the difference in the total energy of the crystal did not exceed 0.1mRy and the difference in the total electronic charge did not exceed 0.001e as calculated at consecutive steps. During this process, the structure is fully relaxed until the forces on the atom become smaller than 0.1mRy/a.u. The computations are performed with volume optimization, c/a optimization and position minimization for each of the compounds under study.

3. Results and Discussion

The optimized lattice parameters, position of the atoms, computed bulk modulus, electronic specific heat coefficient, Fermi energy and magnetic moment are reported in Table 1 for the $CaNi_2Pn_2$ (Pn=P, Sb, Bi) compounds under study. For $CaNi_2P_2$, the obtained

results are compared with the available results and there is a good agreement between them. The results show that replacements of the pnictogens from $CaNi_2P_2$ - $CaNi_2Sb_2$ - $CaNi_2Bi_2$ i.e., when going from a smaller P atom to larger atoms like Sb and Bi, the lattice parameters, namely both 'a' and 'c' increases and this leads to isotropic deformations of the crystal structure. The bulk modulus decreases from $CaNi_2P_2$ - $CaNi_2Sb_2$ - $CaNi_2Bi_2$. The electronic specific heat coefficient values are found to be more or less same for $CaNi_2P_2$ and $CaNi_2Sb_2$ due to their same range of $N(E_F)$. The obtained least value of magnetic moment implies that these compounds exhibit diamagnetism.

Fig. 1 shows the band structures of $CaNi_2Pn_2$ (Pn=P, Sb, Bi) phases as calculated for equilibrium geometries. Here the common features of the band structure for these phases will be illustrated using $CaNi_2Sb_2$ as an example. Here the lowest lying band below the Fermi level arises mainly from Sb-5s states and are separated by a gap from the near Fermi valence bands. The bands in the vicinity of Fermi level are formed predominantly by Ni-3d and Sb-5p states. Several bands cross the Fermi level confirming the metallic properties of $CaNi_2Pn_2$. Thus the near Fermi region is formed mainly by the states of $[Ni_2Sb_2]$ blocks and it is noteworthy that the contributions from the valence states of Ca are negligible. Fig 2 shows the total and partial Density of States of $CaNi_2 Pn_2$

Table 1: The optimized lattice parameters, internal coordinates (Z_{Pn}), c/a ratio, bulk modulus, electronic specific heat coefficient, Fermi energy, magnetic moment for $CaNi_2P_2$, $CaNi_2Sb_2$ and $CaNi_2Bi_2$

Phase/Parameter	$CaNi_2P_2$	$CaNi_2Sb_2$	$CaNi_2Bi_2$
a (a.u.)	7.4167 (7.4010 ^a)	8.3842	8.7048
c (a.u.)	17.7334 (17.6958 ^a)	20.0446	20.8115
c/a	2.3910 (2.3910 ^a)	2.3908	2.3908
$Z_{P,Sb,Bi}$	0.3762 (0.3774 ^a)	0.3641	0.3566
Bulk modulus in GPa	122.7277	82.1009	67.0646
Electronic specific heat coefficient (\bar{a}) in Gamma in mJ/(mol cell K**2)	5.45	5.45	5.65
Fermi energy in Ryd.	0.6107	0.5317	0.4996
Magnetic moment in μ_B	0.00004	-0.00003	-0.00004

a. Reference [10] - (reported exptl.work)

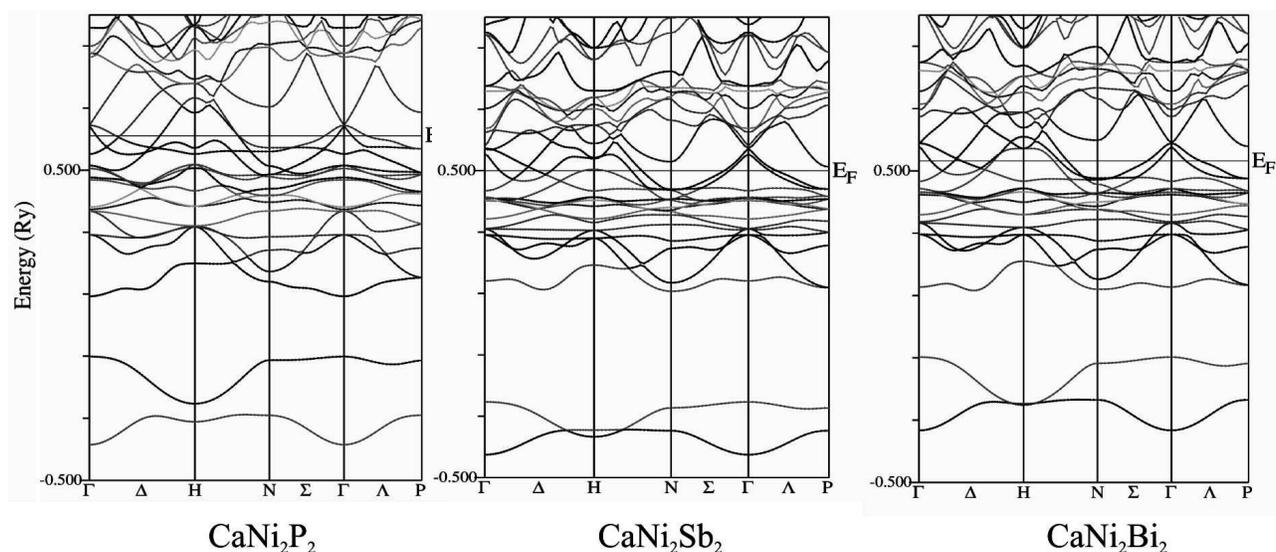


Fig. 1: The total and partial density of states of CaNi_2Pn_2 ($\text{Pn}=\text{P}, \text{Sb}, \text{Bi}$)

($\text{P}_n = \text{P}, \text{Sb}, \text{Bi}$) phases. Considering the Density of States (DOS) of CaNi_2Sb_2 , in the vicinity of the Fermi level, the major contribution arises from Ni-3d states (green line) to the total density of states and is hybridized with the Sb(Pn)-5p state (pink line). Thereby it may lead to the Ni-Sb bonding. Comparatively, the flat portion of DOS of Sb (Bi)-p and Ni-d states seen at the Fermi level suggests the possibility of metallic bonding between Sb (Bi)-p and Ni-d.

To probe the bonding properties of these compounds, the charge density plots along (100) plane is obtained and is shown in Fig. 3. From the plot, in CaNi_2P_2 , a directional bond exists between P-P atoms in between the adjacent Ni-P layers and also between Ni-P atoms in the same Ni-P layer. No such covalent interaction is seen between Sb(Bi)-Sb(Bi) atoms that exist between Ni-Pn layers of other compounds namely, CaNi_2Sb_2 and CaNi_2Bi_2 , wherein smaller P atom is replaced by Sb and Bi atoms. The symmetry of directionality between Ni-Sb (Bi) atoms gets disturbed, thereby it may lead to partial ionic and metallic bond in the corresponding compounds. This may be attributed to the decrease in the bulk modulus values as one moves from CaNi_2P_2 - CaNi_2Sb_2 - CaNi_2Bi_2 since the covalent nature and hence the hardness does not remain the same as in CaNi_2P_2 . From these plots one can infer the presence of mixed

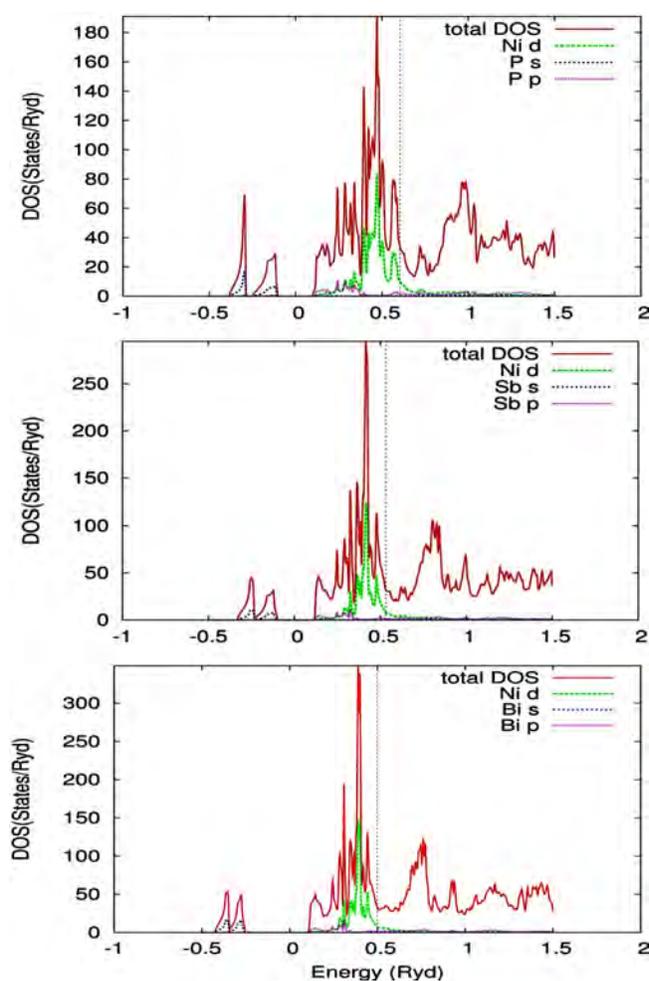


Fig. 2: Density of States histograms of CaNi_2P_2 , CaNi_2Sb_2 and CaNi_2Bi_2

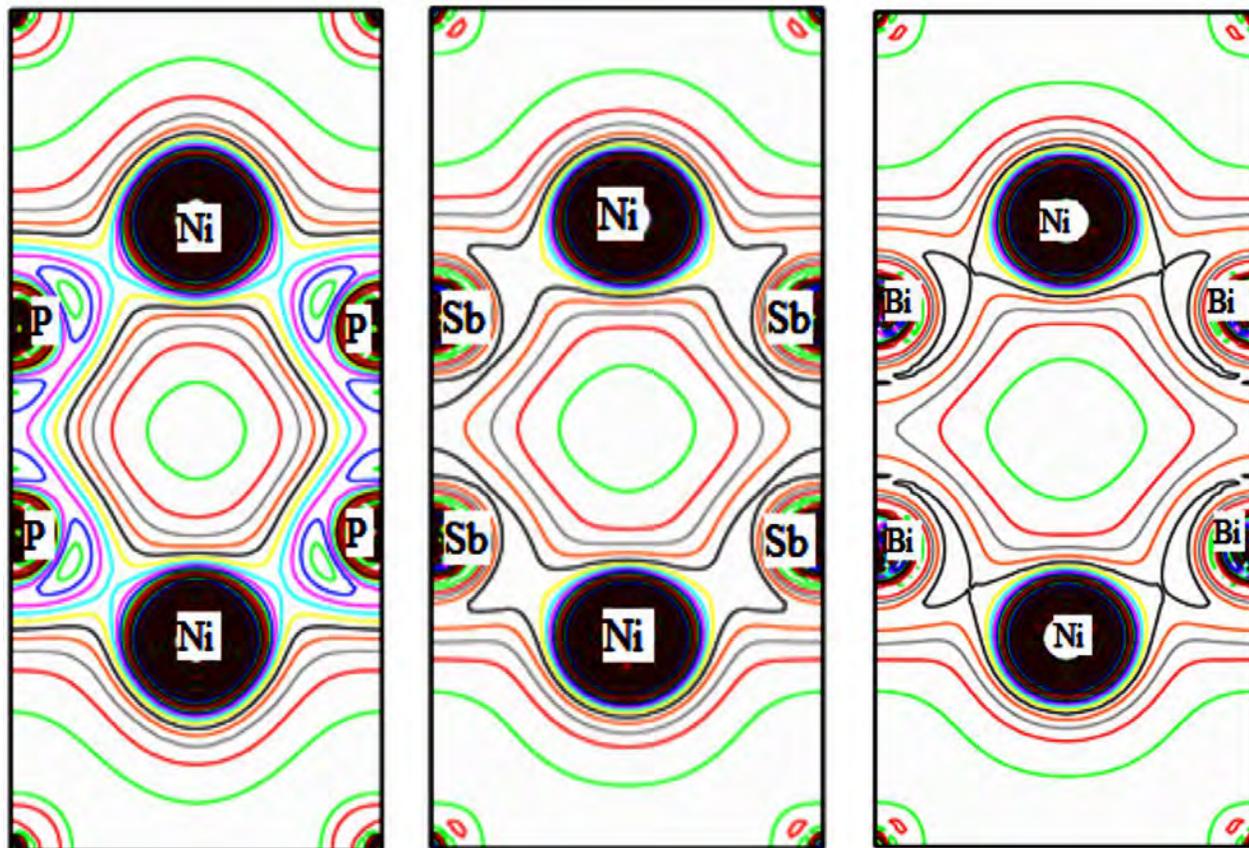


Fig. 3: Electron density plots of CaNi_2P_2 , CaNi_2Sb_2 and CaNi_2Bi_2

covalent, metallic and ionic bonding in the compounds under study.

4. Conclusion

In summary, by means of the FLAPW-GGA approach, we have systematically studied the structural, electronic and magnetic properties of CaNi_2Pn_2 ($\text{Pn}=\text{P}, \text{Sb}, \text{Bi}$) intermetallic compounds. The electronic band structures of CaNi_2Pn_2 ($\text{Pn}=\text{P}, \text{Sb}, \text{Bi}$) phases are similar and are derived from the Ni $-3d$ states with an admixture of the Pn $-3P, -5P$ and $-6P$ states respectively. Indeed we have assumed the same crystal structure for these compounds. They have been identified as diamagnetic materials due to their low magnetic moment values. Hence, we propose the existence of new hypothetical compounds namely CaNi_2Sb_2 and CaNi_2Bi_2 which may be of low T_c superconductors. Our results show that replacements

of pnictogen lead to isotropic deformations of the crystal structure. The charge density plots exhibit a mixed covalent and ionic behavior.

5. Future Study

Our future study will be focused on the resistivity calculations of the newly proposed hypothetical compounds CaNi_2Sb_2 and CaNi_2Bi_2 which may give a lead for the possibility of these compounds to exist as superconductors.

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