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Research Article

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Analysis of chemical bonding nature on $CaNi_2Sb_2$ compound under compressions

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ABSTRACT

The electronic structure of $ThCr_2Si_2$-type compound namely $CaNi_2Sb_2$ with space group I4/mmm (139) were studied by means of Full Potential –Linearized Augmented Plane Wave Method (FP-LAPW) method in order to explore their existence and changeable chemical bonding nature in between the atoms on $CaNi_2Sb_2$ compound at ambient condition and under compressions. Based on this bonding nature the possibility of iso structural transition in this compound is disclosed.

Keywords: intermetallic compounds, electronic structure, inter-atomic bonding, $ThCr_2Si_2$-type, ab-initio calculations.

INTRODUCTION

The $ThCr_2Si_2$ type structure is well known for accommodating a superconducting state with heavy fermion community [1, 2]. Furthermore a great variety of interesting physical properties have been observed such as valence fluctuation and mixed valance in $EuNi_2P_2$ and $EuCu_2Si_2$ compounds as well as a wide range of magnetic properties. 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 there is no such bonds exist [4]. From this type of compounds, here we discussed in the formulation of AT_2Pn_2 [122-group] group, A generally corresponds to alkaline earth metal, T stands for transition metal and Pn are pnictogens (N, P, As, Sb, Bi). From the electron density plots the bonding nature between the atoms is thoroughly can explain. From literature it is observed that the calcium based compound namely $CaNi_2P_2$ which belongs to AT_2Pn_2 type, there is an existence of interlayer bonding [5,6] and in strontium and barium based compound namely $(Sr/Ba)Ni_2P_2$, there is an absence of interlayer bonding and presence of intra layer bonding [7,8]. From literature [9] it is observed that iso structural transition is might possible by the formation / breaking of bond between the Pn-Pn atoms in AT_2Pn_2 type compounds.

The aim of this work is of two folds viz., (i) At ambient condition we were discussed about all the structural, electronic, bonding and magnetic properties of the compound $CaNi_2Sb_2$, here we would like to extend our study in view of its bonding nature under compression [10] (ii) From our previous study [6], it is observed that the parent (or) isostructural compound of our present compound namely $CaNi_2As_2$, exhibits diverse bonding nature from ambient condition to the states of compression and the same revealed its phase transition.

COMPUTATIONAL DETAILS

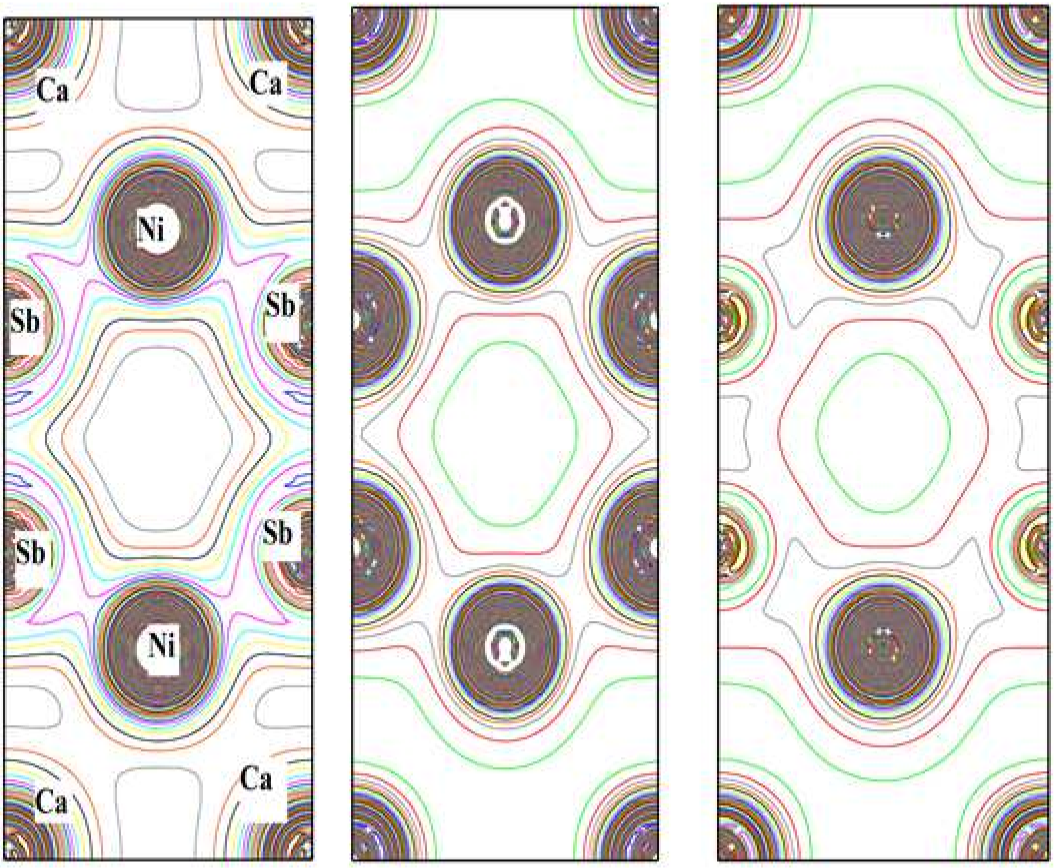
In this study, calculations are carried out by means of the all-electron full potential-linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN2K code [11]. The generalized gradient approximation (GGA) parameterized by Perdew et al. [12] has been applied to calculate the exchange correlation potential. Muffin tin spheres radii (R_{MT}) are chosen in such a way that there is a minimal charge leakage from the core. The non-spin polarized calculations are performed with 1000 k-points in Brillouin zone. The plane wave expansion (R_{MT} * K_{MAX}) has been taken as 7. The SCF cycle comes to an end upon convergence at a specified tolerance for energy, charge and forces to an accuracy of 0.0001Ry, 0.1mRy and 0.001|e| respectively. Computations are performed to find the total energy of given system and obtained total energies are then fitted into Birch–Murnaghan equation of state [13] to get pressure – volume relation. The theoretically calculated equilibrium lattice parameters are used to optimize c/a ratio, which are then used to optimize position of the pnictogen atoms.

RESULTS AND DISCUSSION

Equilibrium lattice parameters of $CaNi_2Sb_2$ compounds are derived from their experimentally reported parent compounds namely $CaNi_2P_2$ and $CaNi_2As_2$ [14-16]. Initially the structure file is generated for newly proposed compounds with the derived parameters. The total energy of the compound is calculated for different cell volumes. It is then fitted into the Birch-Murnaghan equation of state to obtain the optimized volume. The equilibrium volume is used to optimize the c/a ratio. All the lattice parameters including z_{Sb} are optimized in the present calculation.

Table 1: The optimized lattice parameters (a&c), minimized z-parameter (Z_{Sb}), distance between Sb-Sb in between two layers (d_{Sb-Sb}), distance between Ni-Sb atoms in the same layer (d_{Ni-Sb}) and Angle between the atoms in the same layer ($\theta_{Sb-Ni-Sb}$) are listed for the compound $CaNi_2Sb_2$ at ambient condition and under compressions

V/V_0	a (a.u)	c (a.u)	Z_{Sb}	d_{Sb-Sb} (a.u)	d_{Ni-Sb} (a.u)	$\theta_{Sb-Ni-Sb}$ (degree)
1	8.3842	20.0446	0.3641	5.45	4.78	122.77
0.95	8.2421	19.7051	0.3629	5.40	4.68	123.28
0.9	8.0949	19.3532	0.3655	5.21	4.62	122.18
0.85	7.9421	18.9879	0.3737	4.80	4.61	118.79
0.8	7.7832	18.6081	0.3674	4.94	4.46	121.38



(a) **(b)** **(c)**

Fig.1 Electron density plots of $CaNi_2Sb_2$ (a) V/V_0 =1 (b) V/V_0 =0.9 and (c) V/V_0 =0.8

The optimized structural parameters such as lattice parameter, Variable positional parameter, distance between Ni–Sb atoms in the same layer, distance between Sb– Sb atoms in between the successive layers and angle between the atoms in the same layer are listed for the compound $CaNi_2Sb_2$ at ambient condition and for compressions up to 20% in steps of 5% of its ambient volume are reported in Table 1. The optimized structural and variable positional parameters are then used to perform band structure calculation. From the table, it is observed that the lattice parameters both *a* and *c* are decreases from ambient state to the compression states. It leads to Isotropic deformation of crystal structure. Due to the compression of volumes the distances between the atoms in the same and adjacent layers are gradually decreases and there is not much variation in angle between them. We would like to analyze the bonding nature between the atoms with respect to the decrement of distance between them; it is explained as follows.

The electron density plots are drawn to analyze the bonding nature between the atoms, shown in Fig.1. From Fig. 1(a) it is observed that, there is an existence of directional charge density contours that enclosed Ni and Sb atoms, it meant a strong covalent bonding is exist in between Ni and Sb atoms in the same layer. When we notice the Ni-Sb block, it is observed that there is no directional charge density contours between Sb atoms, but an existence of metallic bonding between the sb atoms in between the two adjacent layers and ca contributes ionic bonding to the Ni-Sb block. Hence it is to be stated that there is no strongest bonding is presence in between the layers, so structural transition is might be possible from this ambient condition. The evidence is also available for the same [17]. From ambient condition to compressions there is no change in the ionic bonding in between Ca and Ni-Sb block. In Fig. 1(b) it is observed that the metallic nature of the compound is enhancing due to the complete existence of metallic bonding between the atoms in the same and successive layers. The covalent bond, which is broken in between Ni-Sb atom at 10% of compression (V/V_0=0.9) and again the covalent bonding is formed in between Sb-Sb atoms at 20% of compression (V/V_0=0.8). The same is used to explain its structural transition from ambient condition.

CONCLUSION

The structural changes lead to isotropic deformation of crystal structure from ambient to under compressions. At ambient and under compressions, the alkali earth metal (Ca) offer ionic bonding to the Ni-Sb block and there is a fluctuation of metallic and covalent bonding in Ni-Sb block. At ambient there is no existence of interlayer covalent bonding between the Sb-Sb atoms in between the two adjacent layers. At 20% of volume compression from ambient state, it is observed that the existence of covalent bonding between the Sb-Sb atoms in between the two adjacent layers. Hence the iso-structural transition might be possible in this range of volume in the compound under study.

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