

Computation of Electronic Structure and Ground State Properties of NaZnF₃

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Abstract:

The electronic structure and the ground state properties of fluoroperovskite compound NaZnF₃ in the orthorhombic and cubic phases has been studied by means of self-consistent Tight Binding Linear Muffin - Tin Orbital (TB-LMTO) method. The NaZnF₃ crystallizes in the orthorhombic structure at ambient condition and at high temperature it crystallizes in cubic structure. The total energies for the subjected compound were calculated as a function of reduced volume for both orthorhombic and cubic structure. The calculated total energies as a function of volume were fitted to the Birch EOS to obtain the ground state properties. The calculated ground state properties of these compounds are in good agreement with the experimental results. The total density of states and the band structure of NaZnF₃ were calculated and are plotted at ambient pressure as well as at high pressure. Between the two structures, orthorhombic structure is found to be stable phase. Cubic NaZnF₃ is found to be an indirect bandgap insulator with gap occurring between $\Gamma - R$ points. Whereas orthorhombic NaZnF₃ is found to be a direct band gap insulator with gap occurring at Γ - points.

3.1.INTRODUCTION

There are wide range of properties like electro-optic properties, absorption and luminescence properties called as Fluoroperovskite compounds. They require a shorter wavelength lithographic light which has a technological demand on optical lithography in semiconductors and is basically limited by the bandgap of the materials used. The compound which requires increasingly minute detail. It was been controlled by composition of complex materials selected semiconductor grows wide bandgap like MgZnO, a problem lies in the dissimilar crystal structures between ZnO, with the hexagonal structure and MgO with the rock salt, cubic structure (Shingo and et al 2005). These two devices are tunable with the lattice constant as diamond devices. The wide bandgap are relatively with the main advantage of fluorides.

By Nishimatsu et al (2002) has an addition of Fluorides offer a wide selection of complex materials with wide bandgaps and identical crystal structure, and it is possible to select the band structure, The growth of high quality flawless bulk compound fluoride crystals for the potential applications in Vacuum-ultraviolet-transparent (VUV-transparent) materials for lenses and in optical lithography. Lithography is a technique of fabrication of circuits on a wafer, whereas various various materials can be deposited on or removed from the wafer's surface. By using F2 lasers lithographic optics has been successfully performed in KMgF₃ and LiBaF₃ (Bensalah and et al 2003). The wide range of complex fluorides, has a selection of crystal structure, bandgap energy, band structure and substrate with appropriate lattice constant is possible from the ab-initio calculations within the local density approximation.

Wide bandgaps are the relative of fluoroperovskite compounds in merits. The general formula ABF₃, where A and B refer alkali metals and alkaline earth metals respectively. Fluoroperovskite compounds crystallize in the ideal cubic perovskite structure in their highest

temperature phase, which has an indirect bandgap and it requires for the lithography and other technological applications. Some of the ABF₃ type fluoroperovskite compounds exhibits structural distortion due to the tilting of BF₆ Octahedral tilting in perovskites has given by Glazer (1975). Kassan-ogli and Naish (1986) suggested that the highest temperature phase is not cubic but pseudo-cubic and the lowest temperature called 'ground state' should correspond to static tilts around the three pseudo-cubic axes. Flocken et al (1986) predicted that this ground state structure is orthorhombic from the calculations based abinitio interionic potentials obtained by Gordon-Kim approach. Most of the fluoroperovskite compounds crystallizes cubic structure at the ambient condition and we widely studied. However NaZnF₃ compound has structural ambiguity.

The NaZnF₃ compound is found to crystallize in two different structures. Above 683°C, it crystallizes in cubic structure which is known as α -NaZnF₃ and orthorhombic structure is known as β -NaZnF₃. It has a single crystal X-ray diffraction by Twallin and Zeising (1990). As tetragonal symmetry (Ludekans and Welch 1952) has a powder patterns of β -NaZnF₃ in earlier investigations. Due to the report of NaZnF₃ exhibit orthorhombic symmetry at ambient conditions. The structural distortion and the transition of NaZnF₃ were experimentally studied by Mohamed Mezower et al (2007). The investigation of Pressure induced structural evolution of NaZnF₃ using gas driven diamond anvil cell in the pressure range 0-40 GPa was also performed by them. The Thermoluminescence of pure and Eu doped NaZnF₃ fluoroperovskite compound was studied by Furetta et al (1995). So far no details of band structure calculation for NaZnF₃ are reported.

3.2. PRESENT STUDY

Both Cubic and orthorhombic structures of electronic and stability of NaZnF₃ was been carried out in present work with the addition of high pressure behavior of NaZnF₃ was also studied.

In present work TB-LMTO method was been used, which was advantageous. Since it requires minimal basis set and is computationally very fast. In chapter one and Two brief description was given about various methods and LMTO method was discussed briefly.

3.2.1 Crystal structure of NaZnF₃ The fluoroperovskite type NaZnF₃ is found to crystallize in two structures. At low temperatures upto 683°C, form β -NaZnF₃ i.e. orthorhombic structure with the space group Pnma: 62. The lattice constants for orthorhombic structure are, $a = 5.5928 \text{ \AA}$, $b = 7.7747 \text{ \AA}$ and $c = 5.4186 \text{ \AA}$ (Tutov and Surnikov 1968). For the orthorhombic structure the position of zinc atom is (0, 0, 0), sodium atom at (0.05460, 0.25, 0.89867) and fluorine atom is at (0.30045, 0.05301, 0.19697), (Wallin and Zeising, 1990). At high temperature between 683°C form α -NaZnF₃, this is cubic structure with space group Pm $\bar{3}$ m: 221. The lattice constant for cubic structure is $a = 4.060 \text{ \AA}$. For cubic NaZnF₃ the position of zinc atom is (0.5, 0.5, 0.5), sodium atom at (0, 0, 0) and the fluorine atom at (0, 0.5, 0.5). In ideal cubic structure the larger cations (zinc) are cuboctahedrally surrounded by 12 anions (fluorine) and the smaller cations (sodium) are surrounded by 6 anions forming corner sharing octahedra. That is the sodium atoms lie in the space between the octahedra. In ideal cubic structure, the Na-F distances are equal. Fig 3.1(a) and (b) shows the cubic and orthorhombic structures of NaZnF₃ respectively.

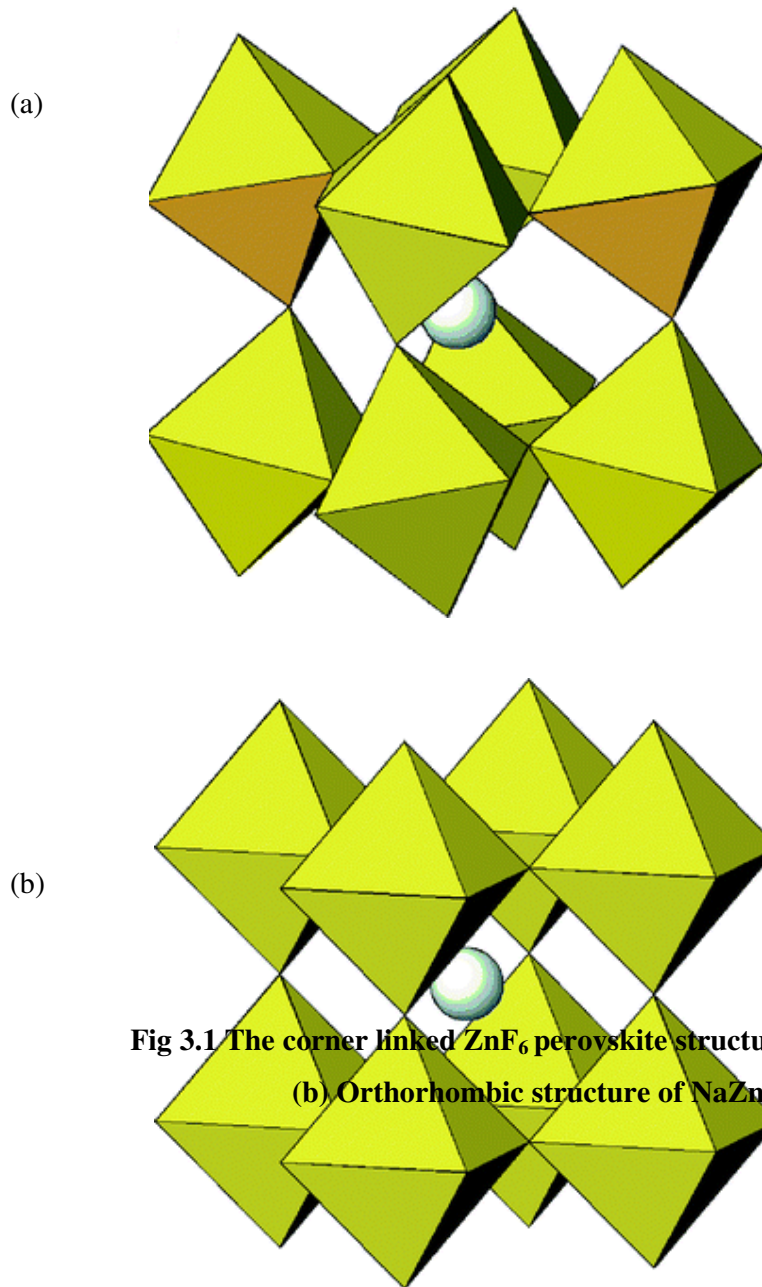


Fig 3.1 The corner linked ZnF_6 perovskite structure of (a) Cubic and (b) Orthorhombic structure of $NaZnF_3$

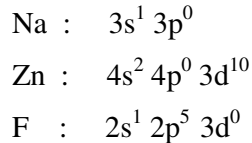
3.3 .COMPUTATIONAL DETAILS

TB-LMTO method has been used to obtain the electronic structure and ground state properties of $NaZnF_3$. They used to calculate the exchange correlation-part of potential, in which Atomic sphere approximation (ASA) was used in the present work. The Crystal was been divided into space filling spheres centered on each of the atomic site.

Combined correction terms are also included to minimize the errors in the LMTO method, where the account of non- spherical shape of the atomic cell and the truncation of higher partial waves inside the sphere. The electro negativity Criteria between two atoms has an charge flow with the sphere boundary potential is minimum chooses by the wigner-seitz . In

the Brillouin Zone energy eigenvalues were calculated for 2744 K-Points in irreducible part. LMTO method gives accurate results only for the closed packed structures, Cubic is closed packed structure, Four empty spheres were added without disturbing the crystal symmetry for Orthorhombic structures. s, p and d partial waves are included in the present calculation. The tetrahedron method of Brillouin zone integration has been used to calculate the density of states (Jepsen and Andersen, 1971).

The basis orbitals used in the calculation are as follows:



1. Total energy calculation

The V_0 experimental volume reduces the volume ranging from 1.10 V_0 , which was been calculated by both structures. It depends on the minimum total energy. The minimum total energy to ambient pressure reduces the volume for cubic and orthorhombic structure therefore it is more stable than cubic structure, By concluding total energies were fitted to birch equation of 1988 the volume to obtain the equilibrium properties which has the lattice constant and the bulk modulus.

$$P = \frac{3B_0}{2} \left\{ \left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right\} \quad (3.3.1)$$

The volume drives the total energy by its pressure, which was been calculated by the bulk modulus. (3.3.1).

The calculated ground state properties are given in Table 3.1 it can be seen that the theoretically calculated values of equilibrium lattice constant for cubic NaZnF_3 is $a=4.101\text{\AA}$ and it is 1% higher than the experimental value and for orthorhombic NaZnF_3 the calculated equilibrium lattice constants are 1.7% higher than the experimental values. This order of error in the lattice constant is minimal and can be neglected. This small order of error arises due to various approximations used in the calculations for practical purposes.

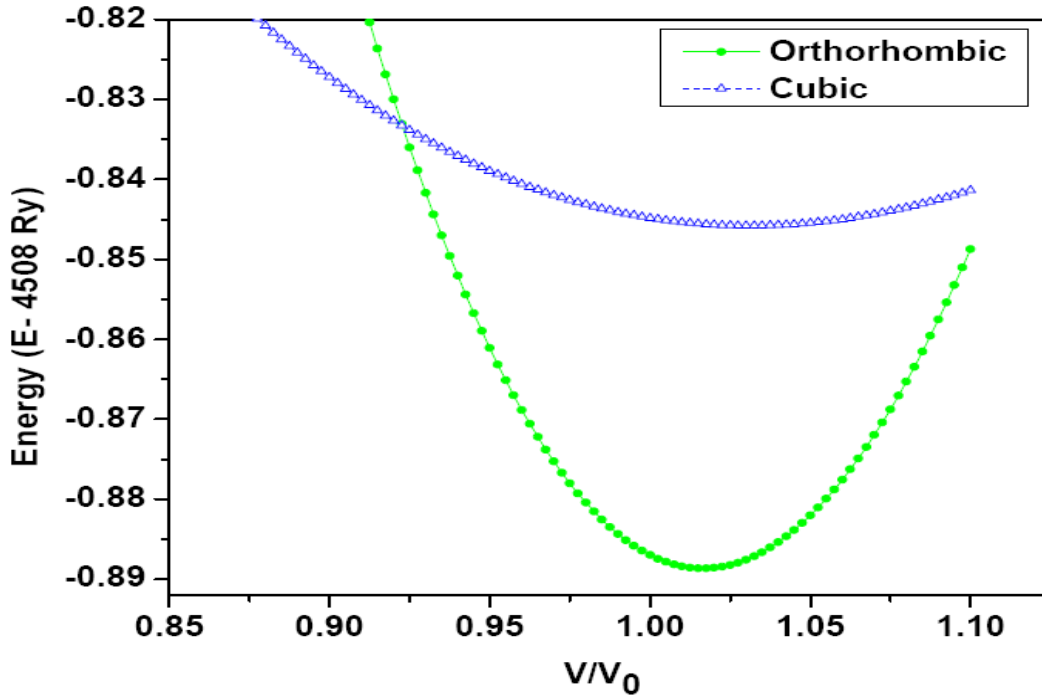


Fig 3.2 Total energies as function of reduced volume of NaZnF₃

Table 3.1 Calculated ground state properties of NaZnF₃

NaZnF ₃	Experimental ¹ Lattice Constant Å	TB-LMTO Lattice Constant Å	Bulk Modulus (B ₀) GPa
Cubic	a = 4.060	a = 4.101	66
Orthorhombic	a = 5.5928; b = 7.7747 c = 5.4186	a = 5.7628; b = 7.8155 c = 5.3219	179

1. ¹ Wallin and Zeising, (1990)

3.4 .BAND STRUCTURE

Self-consistent electronic band structure and the total density of states of NaZnF₃ for both orthorhombic and cubic structures were computed at ambient pressure as well as high pressure. Total density of states of cubic NaZnF₃ was computed at ambient pressure. Figures 3.3 to 3.12 shows the band structure and the total density of state of NaZnF₃ for cubic structure along the high symmetry directions Γ -M-X- Γ -R and for orthorhombic structure, along the Γ -Z-T-Y- Γ -X-S-R-U symmetry directions.

3.4.1. Band structure of Orthorhombic NaZnF₃

The calculated band structure of orthorhombic NaZnF₃ and the total density states are shown in figures 3.3 and 3.4. The bottom most band is created by 's' like states of fluorine. The valence band is due to 'p' like state of fluorine and 'd' like states of zinc. In the valence band, the band below the Fermi level, is doublet of '3d' like states of zinc. The next lowest band is the triplet of '3d' like states of zinc. The upper limit of the valence band is at the point Γ . The conduction band arises mainly from 's' like states of zinc and sodium. The lowest limit of conduction band is found at point Γ . The bandgap of orthorhombic NaZnF₃ is direct and it is lying at Γ point. The calculated direct bandgap in this present case is found to be 4.938 eV. Initially the bandgap increases and then decreases for the higher pressure. On compression, broadening of bands is more and moreover the bands move respectively towards the higher energy more, leading to increase in bandgap, upon further compression, the broadening of bands takes place and leading to decrease in bandgap, given in table 3.2.

3.4.2. Band structure for Cubic NaZnF₃

The calculated band structure of cubic NaZnF₃ and the total density of states are shown in figures 3.5 and 3.6. The top of the valence band is situated at the point R and lowest point of conduction band is found at point Γ . The bottom most band is created by 's' like states of fluorine. The valence band is due to hybridization of 'd' like states of zinc and 'p' like states of fluorine. The calculated indirect band gap in this present case is found to be 4.095 eV. In the valence band, the band below the Fermi level is doublet of '3d' like states of zinc. The next lowest band is the triplet of '3d' like states of zinc. The conduction band is arises mainly from 's' like states of zinc and sodium. Upon compression, the bandgap of cubic NaZnF₃ decreases. On compression, broadening of bands is more and moreover the bands move respectively towards the higher energy more, leading to decrease in bandgap, given in table 3.2.

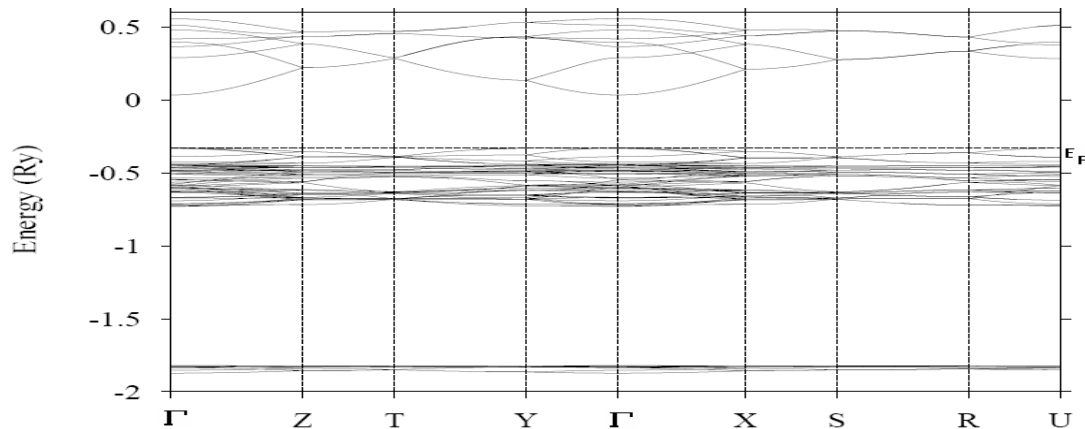


Fig 3.3 Band Structure for Orthorhombic NaZnF₃ at ambient pressure.

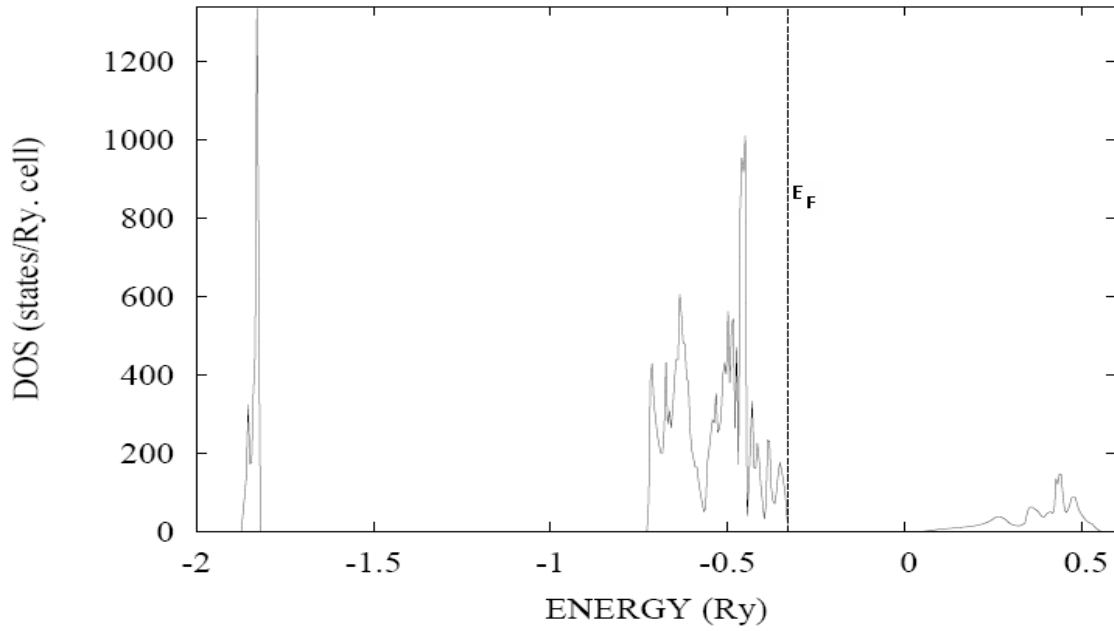


Fig 3.4 Density of States for Orthorhombic NaZnF₃ at ambient pressure.

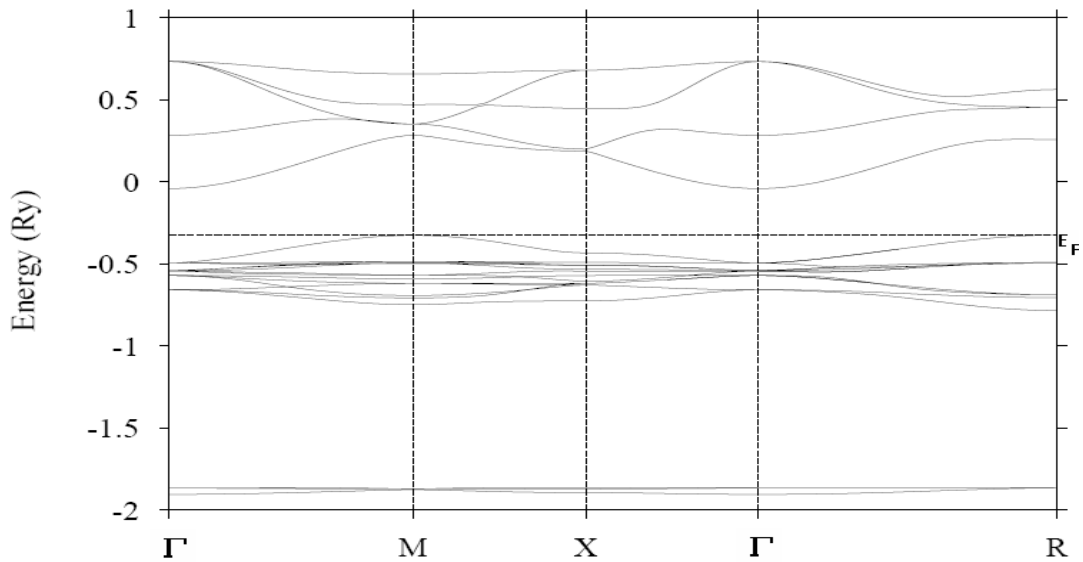


Fig 3.5 Band Structure for Cubic NaZnF₃ at ambient pressure

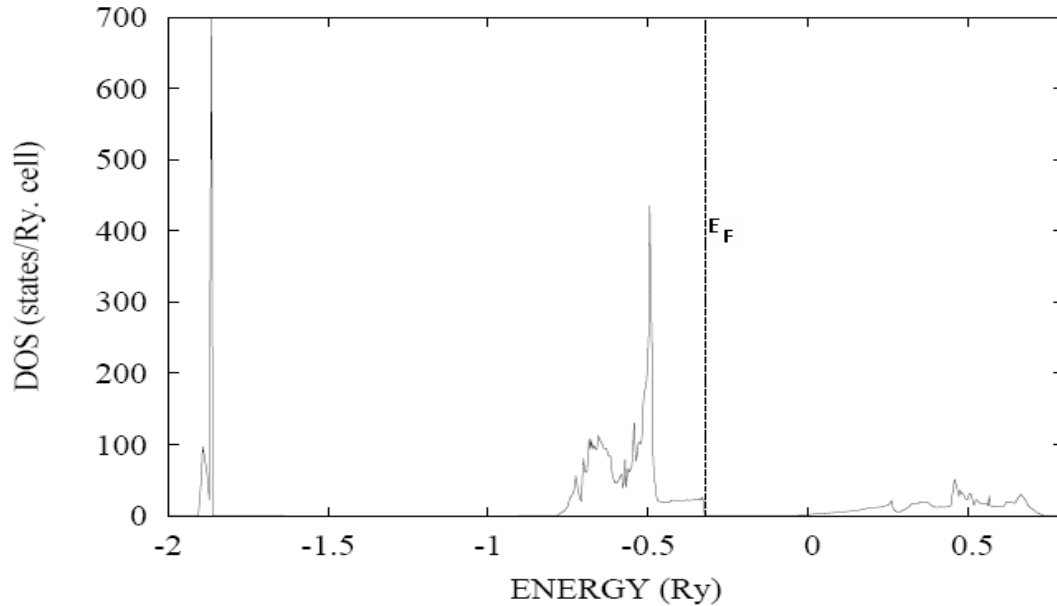


Fig 3.6 Density of States for Cubic NaZnF₃ at ambient pressure.

3.5.METALLIZATION UNDER PRESSURE

Within the one electron theory, the metallization may be described as due to the broadening of bands under pressure and subsequent overlap of the filled valence bands and the empty conduction bands.

We find that both the structures, under high pressure exhibit a transition to metallic phases. From figures 3.7 to 3.12 it can be seen that NaZnF₃ goes to the metallic phase at a larger pressure. The band overlap metallization is found to occur on 40% compression for both structures.

Table 3.2 shows the variation of bandgap E_g (eV) as a function of reduced volume in both orthorhombic and structures. The bandgap is found to increase for small compression and decreases for large compression in orthorhombic structure.

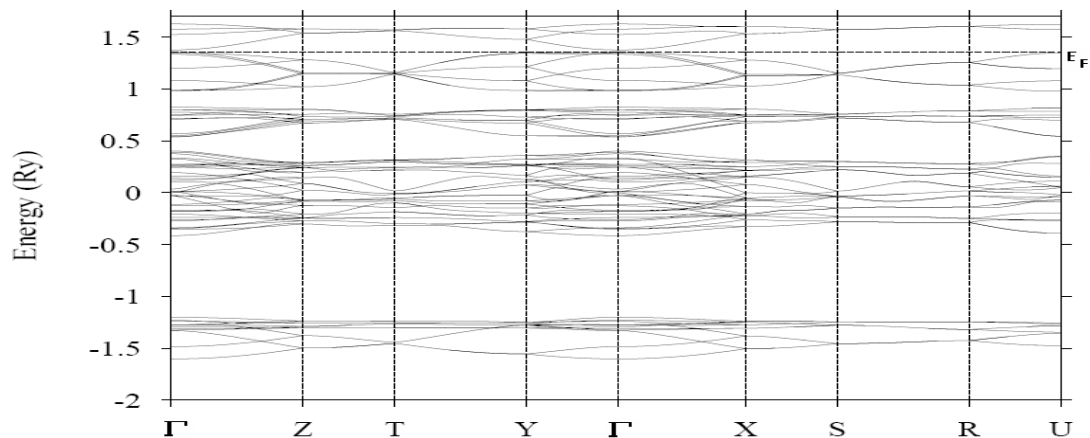


Fig 3.7 Band Structure for Orthorhombic NaZnF₃ at $V/V_0=0.65$

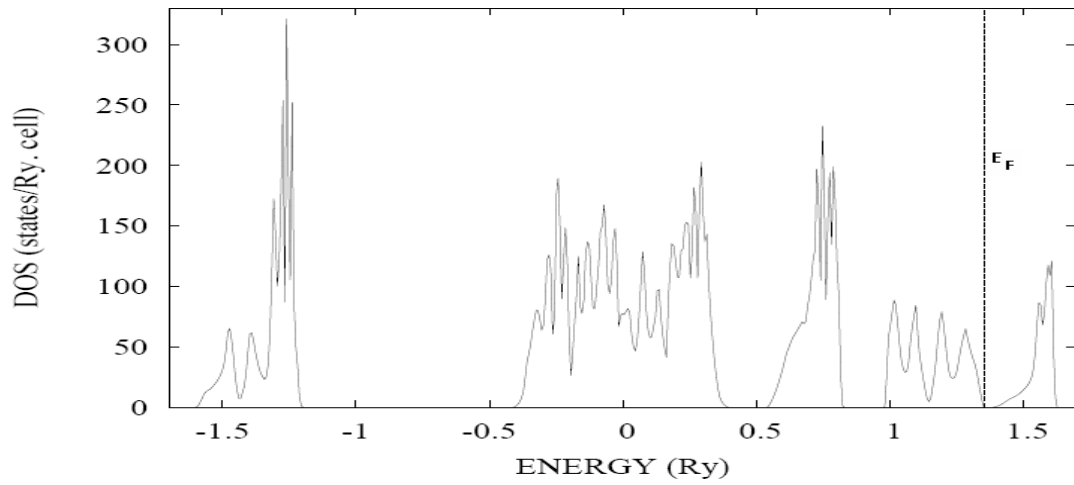


Fig 3.8 Density of States for Orthorhombic NaZnF₃ at V/V₀=0.65

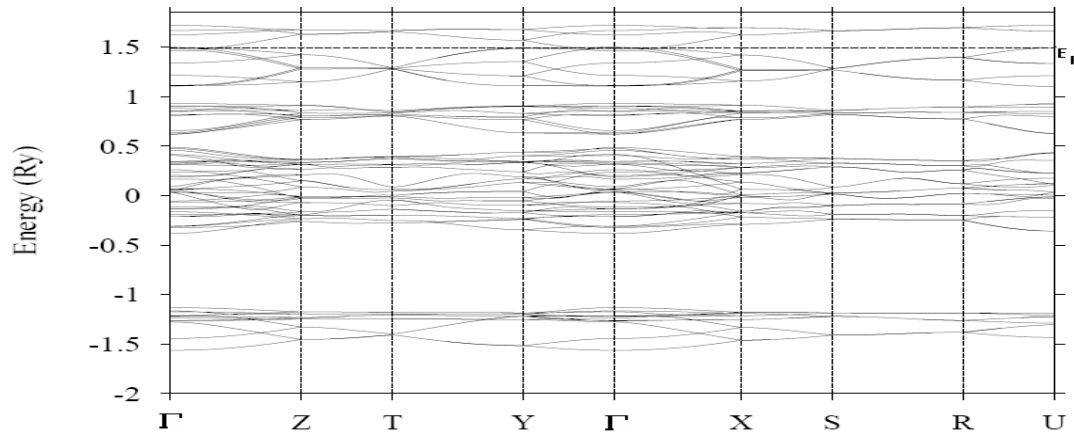


Fig 3.9 Band Structure for Orthorhombic NaZnF₃ at V/V₀=0.60

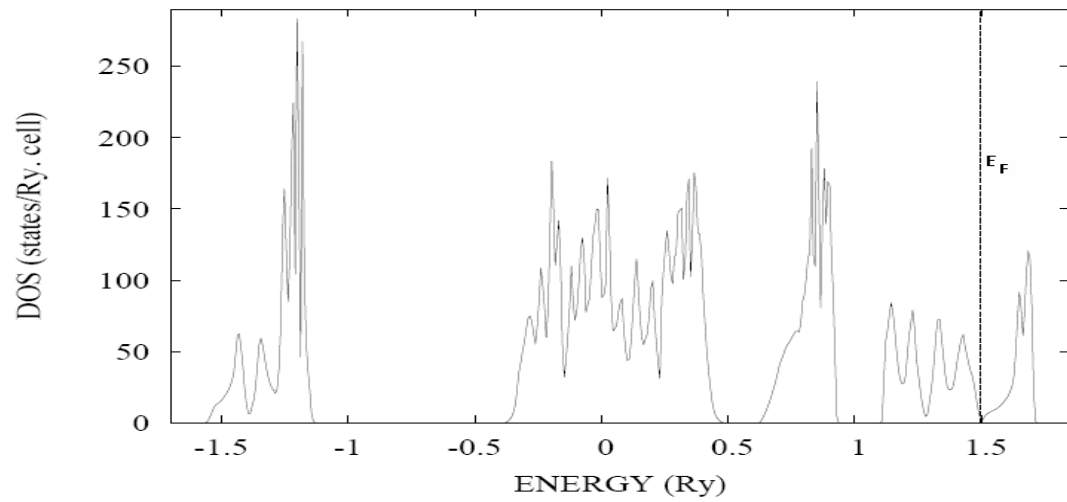


Fig 3.10 Density of States for Orthorhombic NaZnF₃ at V/V₀=0.60

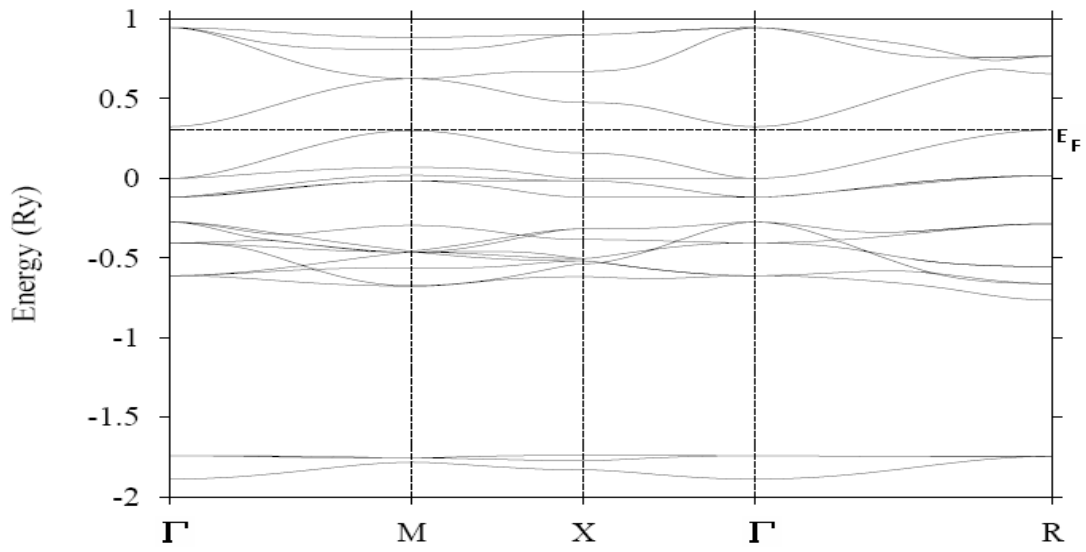


Fig 3.11 Band Structure for Cubic NaZnF₃ at V/V₀=0.65

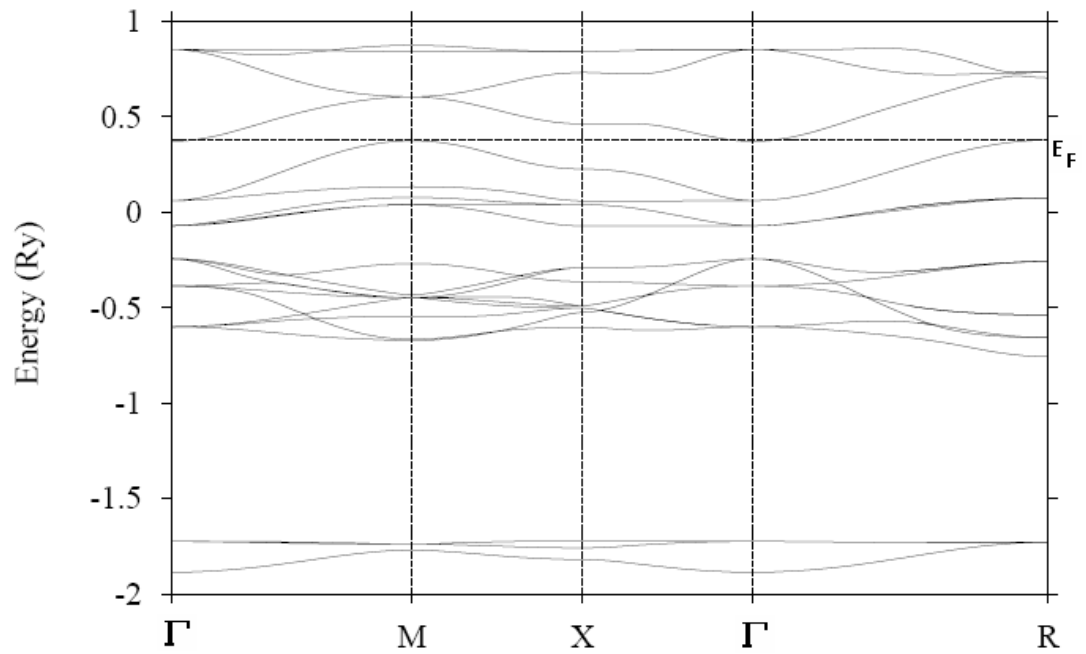


Fig 3.12 Band Structure for Cubic NaZnF₃ at V/V₀=0.60

Table 3.2 Variation of bandgap as a function of reduced volume for orthorhombic NaZnF₃

V/V₀	Bandgap for orthorhombic NaZnF₃ (eV)	Bandgap for cubic NaZnF₃ (eV)
1.10	4.054	4.312
1.05	4.516	4.204
1.00	4.938	4.095
0.95	5.305	3.972
0.90	5.564	3.90
0.85	5.496	3.442
0.80	5.278	2.966
0.75	4.598	2.503
0.70	1.959	1.305
0.65	0.326	0.367
0.60	-	-

RESULTS AND CONCLUSIONS:

The decisive remarks on the outcome of the theoretical calculations performed are presented in this chapter. The electronic, physical, structural properties and the phase stability of fluoroperovskite type compound NaZnF₃ has been studied using the TB-LMTO method. This compound at ambient conditions crystallizes in the orthorhombic structure and at high temperature crystallizes in cubic structure. The calculations were performed for 2744 k-points in the irreducible part of the Brillouin Zone (IBZ).

The total energies were calculated as a function of reduced volume for both cubic and orthorhombic structures. The calculated total energies were fitted to the Birch EOS to obtain the equilibrium lattice constant and bulk modulus. From the total energy calculations we found that orthorhombic structure is the most stable structure. The theoretically calculated values of equilibrium lattice constants are compared with the

experimental values for cubic and orthorhombic structures. The theoretically calculated values of equilibrium lattice constant is 1% and 1.7% higher than the experimental values for cubic and orthorhombic NaZnF₃ respectively. Even though the calculated values are slightly higher than the experimental values, this order of error in the lattice constant is minimum and can be neglected. This small order of error arises due to various approximations used in the calculations for practical purposes. The bulk modulus for both structure were calculated. From the bulk modulus calculation we found that the orthorhombic NaZnF₃ has less compressibility than cubic structure.

The self-consistent electronic band structure along the high symmetry directions Γ -Z-T-Y- Γ -X-S-R-U and Γ -M-X- Γ -R, and the total density of states for both orthorhombic and cubic structures of NaZnF₃ were obtained at ambient pressure as well as high pressure. The orthorhombic NaZnF₃ is an ionic insulator with direct bandgap occurring between the symmetry points Γ . The calculated direct bandgap in this present case is found to be 4.938 eV. However for cubic structure, indirect bandgap occurring between the symmetry points Γ and R, is found to be 4.095 eV.

The variations of the bandgap values as a function of reduced volume were examined. On applying pressure, we found that there is a decrease in bandgap in both orthorhombic and cubic structures. We conclude that both orthorhombic and cubic phases, under pressure exhibit a transition to metallic phase.

Being a direct bandgap material, NaZnF₃ will be used in technological applications like lithography and vacuum ultraviolet transparent materials; this theoretical work may be useful for future experimental work.

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