

Structural and Mechanical Properties of Bulk Scandium Trifluoride Investigated by First-Principles Calculations

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Abstract—Cubic Scandium Trifluoride (ScF_3) is a material that contracts when exposed to heat. Not many materials are known to behave this way. Such a material has many interesting technological applications yet some of its properties are yet to be fully explored using *ab initio* methods. This paper engaged the state-of-the-art *ab initio* methods to study the Structural and Mechanical properties of ScF_3 at ambient conditions. All calculations were done within the Density Functional Theory (DFT) framework and a plane wave basis set as implemented in the QUANTUM ESPRESSO computer code. A comparison with previous DFT and Experimental studies was done. The Projector Augmented Wave pseudo-potentials were used to describe the core-valence electron interactions with the GGA (PBE,PBEsol,PW91,WC) and LDA chosen for the exchange –correlations. The cubic ScF_3 was modeled using 4-atoms. The calculated lattice parameters for cubic ScF_3 were found to be in good agreement with previous studies and differed by -1.17% to 1.07% from the experimental value. The calculated elastic constants ($C_{11}=231.65\text{GPa}$ to 280.15GPa , $C_{12}=16.41\text{GPa}$ to 18.18GPa and $C_{44}=17.74\text{GPa}$ to 18.61GPa) were also in agreement with the existing cited data. This paper points out the fact that ScF_3 is a ductile material at ambient conditions and will deform under tensile stress.

Keywords—Structural, elastic constants and first principles calculations.

1. INTRODUCTION

Scandium Trifluoride (ScF_3) is a trivalent metal fluoride that belongs to the family of perovskite-type compounds that have a general formula ABX_3 , but in this case, A-Cation site is vacant. The crystal structure of ScF_3 can be cited as ReO_3 -type. ScF_3 portrays thermomiotic characteristic from 10K to 1100K. Thermomiotics are

promising materials that are able to form composites for thermal regulation [1]. It is therefore necessary to study their properties to conceive suitable thermomiotics for special applications. The study of thermomiotics is essential since it helps understand the process of Negative Thermal Expansion (NTE). Most NTEs are characterized by a network of polyhedral groups of atoms that are connected through sharing of corner atoms or shared ligands. Thermomiotic materials have sparked an interest over a decade now due to their much novel functionality [2]. ScF_3 contracts upon heating and has a capability of forming composites to compensate for the positive thermal expansion of other materials [3]. To date, there has not been any formal consensus amongst researchers on the real cause of NTE [3]. One school of thought that we have adopted in this work describes NTE phenomena in ScF_3 as a consequence of the quartic oscillation of the Fluorine atoms. A general orientation of atoms in ScF_3 crystal structure is that a Scandium atom is bound to three Fluorine atoms. When atoms get more excited as the temperature increases, the Fluorine atom oscillates more perpendicularly to its bonds and hence causing the Scandium atom to move close to another Scandium atom in the entire bulk material and hence a contraction [4]. This movement in essence implies that the interaction between Scandium atoms become stronger with increase in temperature. Naturally, very few materials are known to behave in such a manner. A common phenomenon is where materials get weaker when exposed to extreme temperatures. This unique behavior of ScF_3 is analogous to anomalous behavior of water between 0°C and 4°C . ScF_3 has a simple cubic structure and it is a very good material for novel functionalities. Unlike other NTE materials, ScF_3 exhibits strong isotropic behavior over a wide temperature range while maintaining its original Cubic structure.

Increased activities in theoretical design of new materials based on metal fluorides have been made possible by the advancements in the modern *ab initio* methods based on Density Functional Theory (DFT) [5]. DFT is a proved tool for designing new materials based on knowledge of quantum mechanics. This tool is widely used in developed

countries unlike in developing countries that lag behind due to limited equipment and research facilities. One well known challenge of DFT is reproducing existing results. Herein, we employ various techniques used in DFT to reproduce previous theoretical results and compare them with experimental results. In particular, we focus on the Structural and Mechanical properties of ScF₃. These two properties are fundamentally significant in any study of physical properties of materials. Failure to predict a correct ground state structure of a material implies that one is unlikely to understand the material's true behaviors [6]. Mechanical properties are key indicators of Structural stability.

2. MATERIAL PROPERTIES

Any material has its own absolute characteristics and intrinsic behaviors. Understanding these characteristics and behaviors will help one to manipulate a material in a manner that is in line with the vision of material design [7]. This paper entails a study of the Structural and Mechanical properties of cubic ScF₃. A brief explanation on why it is important to study structural and mechanical properties of a material is given below.

2.1 Structural Properties

For structural properties, the focus is mainly on the lattice constant, which refers to the dimensions of a unit cell. Our sample is cubic and hence $a = b = c$. Knowledge on lattice constant is important in scenarios such as the growth of thin layers of materials on other materials. A mismatch in lattice constants promotes strains in a layer, thereby preventing epitaxial growth of thicker layers without defects [8]. Bond lengths and the bond angles are also key structural properties of a material. Bond length is inversely related to bond strength and the bond dissociation energy, all other things being constant, a stronger bond will be shorter. In a bond between two identical atoms, half the bond distance is equal to the covalent radius [8]. The bond angle is responsible for the three-dimensional arrangement of atoms that constitute a molecule. It determines several properties of a substance including its reactivity, polarity, phase of matter, color, magnetism, and biological activity [9].

2.2 Mechanical Properties

The elastic properties of solids are important because they relate to different basic solid-state properties like brittleness, ductility and anisotropy. The elastic constants give the connection between the mechanical and dynamic properties regarding the kind of forces existing in solids. They give much emphasis on the stability and stiffness of a material. Determination of elastic constants is key in predicting the mechanical behaviour in solid-state physics. A Cubic crystal has three independent elastic constants, C_{11} , C_{12} and C_{44} which are obtained by fitting the total energies of a strained crystal to a fourth-order polynomial strain. The bulk modulus B is the measure of resistance to volume change upon pressure application. Shear modulus G is the measure of resistance to reversible deformation upon shear stress.

The bulk modulus, B and the Shear modulus G , are estimated from the Voigt-Reuss-Hill approximation. The Shear modulus has a strong correlation to hardness of a material. The ratio $\frac{B}{G}$ is used in determining the brittle and ductile behaviour of materials in solid science [10].

When $\frac{B}{G} \leq 1.75$, then a material has a brittle characteristic and a material is ductile when $\frac{B}{G} > 1.75$.

Young's modulus E is the ratio of linear stress to linear strain. It indicates stiffness. Poisson's ratio ν estimates stability of a crystal against shear. Poisson's ratio ranges from -1 to 0.5. For ductile materials $\nu = \frac{1}{3}$ while $\nu < \frac{1}{3}$ for brittle materials [11]. Both Young's Modulus E and the Poisson's ratio ν are related to the Bulk modulus B and the Shear Modulus G by the two equations below.

$$E = \frac{9BG}{3B + G} \quad (1)$$

$$\nu = \frac{3B - 2G}{2(3B + G)} \quad (2)$$

The Zener anisotropy ratio (A) is a measure of the degree of anisotropy in solids [12]. $A = 1$ for isotropic materials. When A is smaller or greater to one, it is used to measure the degree of elastic anisotropy. The factor A can be computed with the following equation.

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (3)$$

3. COMPUTATIONAL METHODOLOGY

The unit cell of ScF₃ has atoms arranged in a simple cubic (sc) structure. The structure of the simple cubic lattice under study is shown in figure 1 below.

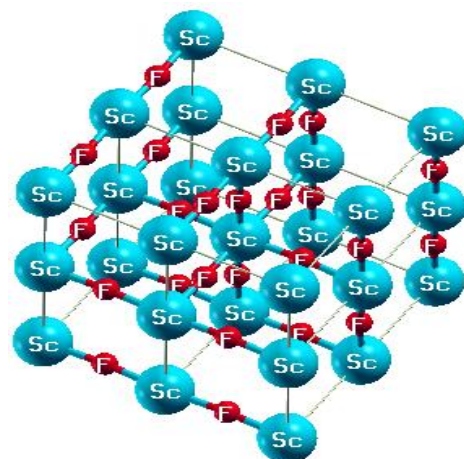


Fig. 1. (Color online) A simple cubic crystal structure for ScF₃. Small maroon balls and the large blue balls represent the F and Sc atoms respectively.

All the calculations of full energies, optimized geometries and elastic constants were carried out using the

QUANTUM ESPRESSO [13] computer code and were performed in the framework of Density Functional Theory (DFT). We did our calculations with five (5) exchange – correlations (XC); the Perdew-Burke-Ernzerhof (PBE) [14], the Perdew-Wang-91 functional (PW91) [15], the Wu-Cohen functional (WC) [16], the enhanced Perdew-Burke-Ernzerhof functional for solids (PBEsol) [17] and the Perdew-Zunger functional (PZ) [18]. We picked these exchange-correlations since they are computationally efficient and no adjustable parameter was required. The core–valence electron interaction was described by Projector Augmented Wave (PAW) pseudo-potentials from the 0.3.1 version of the library of Dal Corso *et al* [19]. The crystal structure of ScF₃ was relaxed at 0K and at an ambient pressure. After convergence tests, a cut-off energy of 60 Ry for the plane wave basis was chosen. The Monkhorst-Pack scheme [20] and the Brillouin zone integration was performed at 8x8x8 k-point meshes. Post-processing of data in this paper was done using the Thermo-pw software [21].

We obtained our results by fitting the energy-volume data to the Murnaghan equation of state [22]. The energy-volume data were obtained as follows; the volume of the simple cubic structure of ScF₃ was deformed by a single parameter ε such that the lattice spacing was defined as $\alpha = a_0 = (1 + \varepsilon)$ where a_0 was the theoretical equilibrium parameter that was extracted from Materials project database. We then fitted to the Murnaghan equation of state a series of total energy values for 21 sets of volumes with ε ranging from -0.05 to +0.05 in steps of +0.005.

4. RESULTS AND DISCUSSION

4.1. Structural Properties of ScF₃

Figure 2 shows the curves obtained from Murnaghan equation of state and plotted as total energy with respect to the equilibrium volume for the various exchange correlations. There is a clear resemblance in the energy-volume curves, with similar shape but different minima.

Table 1: Indicating the calculated values of the lattice parameter a_0 , Bulk modulus B_0 , the first pressure derivative of the Bulk Modulus B'_0 , the Volume per atom \AA^3 , minimum energy E_0 , the Bond length \AA , the bond angles, the Gravimetric Densities and unit cell masses of cubic ScF₃ using different exchange correlations (XC)

Exchange Correlation XC	Reference	a_0 (\AA)	B_0 (GPa)	B'_0	Volume per atom (\AA^3)	E_0 (Ry)	Bond length Sc-F (\AA)	Bond angle F-Sc-F	Density g/cm^3	Mass Of Unit cell (a.m.u)
PBE	This work	4.07	88.23	4.37	16.85	-335.75	2.11	89.99 ⁰	2.44	98.95
PBEsol	This work	4.03	95.79	4.40	16.36	-332.16	2.11	90.00 ⁰	2.52	98.95
PW91	This work	4.06	90.20	4.21	16.73	-336.65	2.11	89.98 ⁰	2.45	98.95
PZ	This work	3.98	105.50	4.40	15.76	-328.89	2.11	89.99 ⁰	2.61	98.95
WC	This work	4.03	94.48	4.37	16.36	-334.20	2.11	89.99 ⁰	2.52	98.95
EXPERIMENT	[23]	4.03	88.80	-	16.36	-	-	-	-	-
PBE	[24]	4.03	-	-	16.36	-	-	-	-	-
HF-DFT PBE0	[24]	4.05	-	-	16.61	-	-	-	-	-
LCAO method	[24]	4.03	-	-	16.36	-	-	-	-	-

Comparative studies suggest that ground state properties of materials are highly depended on the choice of XC functional, see table 1 above. We deduce that, there exist an inverse relationship between compressibility of a material and its lattice parameter. The smaller the lattice parameter a_0 , the smaller the volume and hence a large bulk modulus. This implies that compact materials have a high resistance to deformation [25]. PBE and PZ produced two extreme values i.e, high and low respectively, while the other XC functionals varied dismally from the experimental value. We noted that bond angles were well predicted by the 5 XC functionals, confirming that the ground state structure was cubic. We observed that our results were in agreement with previous reported DFT results. Gravimetric density (g/cm^3) is a derived quantity that relies on the predicted volume of the material since the mass of specific isotope under consideration does not depend on simulation technique. Due to over-binding notoriety of PZ functional, the predicted density was huge in comparison with other exchange-correlations functionals.

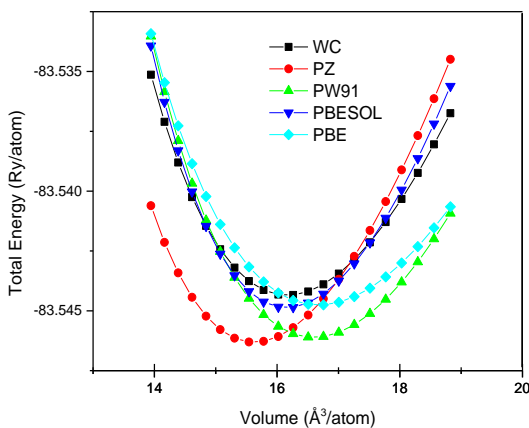


Fig. 2. (Color online) Total energy versus volume per atom for ScF₃ using different exchange correlations

4.2. Mechanical Properties of ScF₃

The calculated elastic constants are reported in the [table 2](#) below together with some other available data. The data indicated that Cubic ScF₃ was mechanically stable since it satisfied the stability criteria of cubic crystals where by $C_{44} > 0$, $C_{11} > |C_{12}|$ and $C_{11} + 2C_{12} > 0$. We also calculated the

$\frac{B}{G}$ ratio and it was noticed that ScF₃ was a ductile material at ambient conditions. The calculated anisotropic ratio also showed that ScF₃ was elastically anisotropic since it was found to be less than one. The Poisson's ratio calculated also confirmed that ScF₃ was ductile.

Table 2: Mechanical properties and elastic constants for cubic ScF₃

	PBE	PBEsol	PW91	WC	PZ	EXPT	
C ₁₁ (GPa)	231.65	252.60	235.29	250.29	280.15	230.00	
C ₁₂ (GPa)	17.21	18.18	17.53	16.41	18.52	17.30	
C ₄₄ (GPa)	18.49	18.27	18.61	18.47	17.74	18.00	
Debye Temp (θ_D) in kelvins	484.13	486.75	486.25	488.33	488.24	505.00	
Voigt Approximation	B (GPa)	88.24	95.79	90.20	94.48	105.53	
	E (GPa)	134.37	144.22	136.54	144.14	157.44	
	G (GPa)	53.91	57.73	54.72	57.85	62.91	
	ν	0.25	0.25	0.25	0.25	0.25	
Reuss Approximation	B (GPa)	88.23	95.79	90.20	94.48	105.53	
	E (GPa)	75.09	75.48	75.75	76.07	74.92	
	G (GPa)	24.45	27.57	27.84	27.85	27.11	
	ν	0.36	0.37	0.36	0.37	0.38	
Voigt- Reuss-Hill Approximation	B (GPa)	88.23	95.79	90.20	94.48	105.53	88.80
	E (GPa)	104.73	109.85	106.15	110.11	116.17	99.00
	G (GPa)	40.78	42.65	41.28	42.85	45.01	38.00
	ν	0.28	0.29	0.29	0.29	0.29	0.300
Debye Velocity (m/s)	4168.30	4145.80	4179.80	4160.83	4155.46		
A	0.17	0.16	0.17	0.16	0.14	0.17	
$\frac{B}{G}$	2.19	2.25	2.18	2.23	2.34	2.34	
REFERENCE	This work	This work	This work	This work	This work	[26]	

Our calculated values of the three elastic constants widely varied from experimental values depending on the choice of the exchange correlation functional. This arose due to the varied volumes and equilibrium energies as discussed in [section 4.1](#). From [equation 4](#) below, it can be noted that the tensor of elastic constants is derived from the second order derivative of E and this explains the deviations in the three elastic constants.

$$C_{ijkl} = \frac{1}{V_0} \left(\frac{\partial^2 E}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right)_{\epsilon=0} \quad (4)$$

It's equally important to note that, the variation in the volume of a material, will automatically lead to varied mechanical properties. A good agreement was observed in PBE while PZ had a deviation of about 50 GPa in C₁₁ from that of the experimental value. However, for C₁₂ and C₄₄, all the 5 exchange correlations predicted almost similar values. This was fortuitous and should be taken as such.

Apart from elastic constants, other derived quantities are tabulated in [table 2](#). For instance, the Debye temperature calculated by the 5 exchange correlations was underestimated in comparison to experimental value. We

noticed that the Voigt, Reuss and Voigt-Reuss-Hill (VRH) approximations predicted not similar values of E, G and ν . It's known that Voigt and Reuss values represent the upper and lower bounds respectively, while the Voigt-Reuss-Hill approximation is perceived as the averaged approximation. In the case of shear modulus G, the VRH value was 40.78GPa when using PBE functional. The Voigt and Reuss values using the same functional were 53.91GPa and 24.45GPa respectively. This clearly indicated that VRH was an averaged value.

5. CONCLUSION

The Structural and Mechanical properties of thermomiotic ScF₃ have been investigated by the first-principles calculations. From the results, its clear that ScF₃ is a ductile material under ambient conditions. The elastic constants, bulk modulus, Young's modulus and shear modulus were equally calculated. All the 5 exchange correlations produced results comparable to the existing experimental data and other DFT calculations. The errors obtained lied within the agreeable experimental error. It should be noted that determining hardness of a material with only one parameter is rather misleading. The Bulk Modulus B and

Shear Modulus G are very important parameters in Mechanics. The Bulk Modulus allows one estimate rigidity, while the Shear Modulus determines the ductility of a material. In this paper, it is strongly evident that Cubic ScF_3 is relatively soft, readily machinable and thus damage tolerant.

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