First Principles Study of the Elastic Properties and Phonon Dispersion of Niobium Tin

Abigael NYANGARISA NYANDIKA[1], Phillip OTIENO NYAWERE[1] and Kebenei J. SELLA[1]

[1]Department of Physical and Biological Sciences, Kabarak University, P.O. Box Private Bag – 20157 Kabarak, Nakuru, Kenya.

Corresponding Author: anyandika@kabarak.ac.ke

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ABSTRACT

The paper reports the Elastic and dynamical properties of Niobium Tin. The calculations were performed with the generalized gradient approximation functional of density functional theory with the Perdew–Burke–Ernzerhof exchange–correlation energy through virtual crystal approximation.The mechanical and dynamical properties were investigated using first principles density functional theory within the generalized gradient approximations using Quantum Espresso code which is an open source code and pseudopotentials were extracted from QE database.The code QUANTUM ESPRESSSO which is open source was used with its pseudopotential database. The elastic constants, bulk moduli, Young's moduli and shear moduli, Poisson ratio, Pugh's ratio and anisotropic ratio were also evaluated. The study on the elastic constants was done at zero pressure and it clearly indicated that the compound is stable mechanically and the phonon dispersion study also indicated that the compound is stable dynamically. The elastic constants also led to the conclusion that Niobium Tin is brittle.

Key Words: Dynamical properties, Elastic properties, Density Functional Theory

INTRODUCTION

Superconducting magnets have been on demand due to their high magnetic fields and high currents. In high field magnets, especially in Magnetic Resonance Imaging, (MRI) and International Thermonuclear Experimental Reactor, (ITER), and transmission cables, mechanical loading during cooldown due to thermal contractions of the material is very large. Niobium Tin is a major component used in the MRI and ITER. Niobium Tin is an excellent material for such applications but is majorly affected by mechanical loading. Studies show that most strains lead to a low performance of Nb_3Sn.The effect of hydrostatic pressure and uniaxial strain are two of such studies that have been done on Nb_3Sn and have shown the effect of low performance. (Marzi G *et al*, 2005) reports that the Nb_3Sn wires inserted into stainless steel conduits get affected by compressive stresses due to the different thermal contraction coefficients of the different materials.

The superconducting environment and many other associated material properties greatly affect the performance of the superconductor towards realizing efficiency. Elastic behavior of materials is one such property that affects superconductivity and is a sure measure of how deformation of materials relate to external stress (Rivlin, 1997). The elastic behavior is more important in determining how best materials can change due to internal and external effects that affect the structural geometry and atomic orientation. This change is much dependent on the chemical composition, the structure of the crystal lattice, and the deforming stress. This work has therefore investigated the elastic and dynamical properties of Nb_3Sn to understand relationship with applications.

The study of phonons helps in understanding of materials' properties such as electrical and thermal conductivity. It enables vibration energy quantization. A phonon refers to lattice vibration in a crystal, where the particles vibrate at the same frequency. From the calculation of phonon dispersion, one can be able to calculate the critical temperature (T_C) of the material in question. A dispersion relation refers to the relationship between the frequency of vibration and the wave vector. Rack A *et al*, (2018) reported that there is irreversible critical current degradation upon mechanical loading. They stated that the mechanical degradation due to mechanical loading is a limiting factor in most of the Niobium Tin superconductors.

Chiesa L. , (2009) reported that a stainless steel conduit causes additional strain upon the cable during cool down because of differences in the thermal coefficients of expansion of the different materials. This strain has to be taken into consideration during the designing of the desired magnet. The Cable in Conduit Conductor (CICC) design is currently the standard cable design for very large magnets but it has various mechanical weaknesses since each single strand is not completely supported and thus experiences large loads during operation that can degrade its performance. The rest of this paper is arranged such that the methodology used is discussed, followed by discussions on the mechanical and elastic results.

METHODOLOGY

In this study, all the calculations were performed with QUANTUM ESPRESSO code, which gives room for self-consistent DFT calculations within a plane-wave pseudopotential approach. During the present calculations, Perdew– Burke–Ernzerhof (PBE) exchange–correlation procedure was applied to the generalized gradient approximation (GGA) functional for the terms of electron–electron interaction after geometry optimization of the surveyed crystal structures. Optimization of cell dimensions, the k-points, and the kinetic energy cut-off values were properly done through graphing and accurate values were obtained at the convergence of the ground state energy at minimum convergence threshold in the calculation.

Calculations of Young's modulus, Bulk modulus, Shear Modulus and Poisson ratios (all in Voigt Reuss-Hill approximations), Elastic constants and average Debye temperature were done using Thermo_PW code interfaced with Quantum Espresso (Corso, 2018). In the calculations, the wave functions kinetic energy cut-off points were all set at 35 Ry and energy cut off rho set at 400 Ry. A smearing width of 0.03 Ry and convergence threshold of 1.0E-11 Ry with a mixing beta of 0.3 was applied. The K-points separation of 10x10x10 was used for the compound.

RESULTS

The study of elastic properties of solids helps in analyzing some of their vital properties such as anisotropy, ductility and brittleness. The elastic constants are used to show how dynamic and mechanical properties are connected in regard to the type of forces present in the solids. Much emphasis is put on the stiffness and stability of the material. The elastic constants also play a major role in predicting the mechanical nature of solid materials.

A crystal has independent elastic constants depending on the symmetry and for cubic structure there are three such constants, C_{11}, C_{12} and C_{44}. These constants are obtained by fixing the full energies of a strained crystal to a fourth-order polynomial strain (Pugh, 1954). The bulk modulus is used to measure the ability to resist deformation upon the application of pressure. A greater value of bulk moduli results into a greater capacity to resist deformation (Cherkaev & Gibiansky,1993). Shear modulus measures the resistance to shear deformation on shear pressure.

The three elastic constant for a cubic crystal structure describe the mechanical hardness of the cubic crystal and they are required to determine the stability of a given material. C_{11}, C_{12} and C_{44} elastic constants are obtained from the total energy calculations and they signify the single-crystal elastic characters, whereas Voigt–Reuss–Hill approach is a convenient scheme for the elastic constants of materials. The elastic constants in Voigt notation (C_{ij}) determine the response of a material crystal to external forces. A given crystal cannot be termed stable unless it obeys some certain conditions. These constants then play a huge role in determining a material's strength.

According to Born stability, cubic elastic constants C_{11}, C_{12} and C_{44} must prove the following conditions; $C_{11}-C_{12}>0$, $C_{44}>0$, $C_{11}+2C_{12}>0$ for structural stability and $C_{12}<B<C_{11}$ for cubic stability. Poisson's ratio, (υ) represents the ratio between the transverse and longitudinal strain in the elastic loading direction of the regarding material. It also gives comprehensive knowledge about the bonding type in solids. Bulk modulus (B) implies much information about the bonding strength in materials and can be explained as the resistance of a given material to external deformations. Young's modulus (E) can be described as the resistance of materials under uniaxial

tensions and provides the materials stiffness degree, that is, the higher the value of E, the stiffer is the material.

The shear moduli G and bulk moduli B are given by equation 1 and 2 respectively; (Han et al., 2008).

$$B=\frac{1}{3}(C_{11}+2C_{12}) \quad \ldots\ldots 1$$

$$G=\frac{1}{2}(G_V+G_R) \quad \ldots\ldots 2$$

Where

$$G_V=\frac{1}{5}(3C_{44}+C_{11}-C_{12})$$

$$G_R=5C_{44}\ (C_{11}-C_{12})/(4C_{44}+3(C_{11}-C_{12}))$$

The Young's moduli E, Poisson's ratio υ and anisotropic coefficient A are obtained according to equation. (3), (4) and (5) respectively (Khon, 1965; Music & Schneider, 2006).

$$E=\frac{9BG}{3B+G} \quad \ldots\ldots 3$$

$$\upsilon=\frac{3B-2G}{2(3B+G)} \quad \ldots\ldots 4$$

$$A=\frac{2C_{44}}{C_{11}-C_{12}} \quad \ldots\ldots 5$$

Unit cell for Niobium Tin

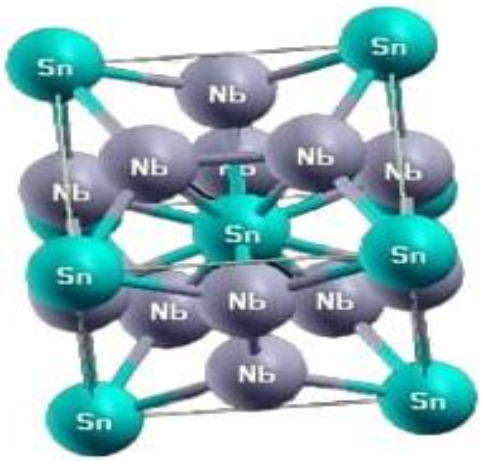

Figure 1:

A schematic representation of the host crystal Niobium Tin showing all the atomic positions.

A. *Elastic Constants*

Parameter	Present	Other work (WIEN2K CODE)
C_{11} (GPa)	286.8593	284.23
C_{12} (GPa)	110.0611	107.70
C44 (GPa)	60.4042	67.07

B. *Bulk, Shear, Young's modulus, Poisson ratio, Anistropy ratio, Pugh's index, Debye temperature*

Property	Present			Other(WIEN2K CODE)
	Voigt	Reus	Voigt -Reus-Hill	(sundareswari *et al*, 2010)
Bulk Modulus (B)	168.9938GPa	168.9938GPa	168.9938GPa	166.54GPa
Young's Modulus (E)	250.5612GPa	240.6400GPa	245.6051GPa	195.34GPa
Shear Modulus (G)	107.7014GPa	87.5678GPa	97.6346GPa	74.87GPa
Poisson Ratio (v)	0.2561	02593	0.2577	0.27
Anisotropy Ratio (A)	-	-	0.6833	0.76
Pugh's Index (G/B)	-	-	0.577	0.45
Debye Temperature, Θ_D(K)	-	-	289.136K	281.83

Bulk modulus for Niobium Tin is 166.54 GPa. This gives the measure of how the material withstands changes in volume when compressed from all sides. The capacity of a material to resist deformation is directly proportional to its bulk modulus. Shear modulus for Niobium Tin is 74.87 GPa. This is a numerical value that measures the ability of materials to resist transverse deformation. A larger value of shear modulus indicates that the solid is highly rigid and may require greater force to be deformed.

The calculated Young's modulus of 195.34 GPa indicates the tensile elasticity of a material. That is, a measure of the ability of a material to withstand variations in length when subjected to compression or lengthwise tension. It is obtained when longitudinal stress is divided by strain, which indicates how stiff a material is. The larger the ratio, the stiffer the material.

Pugh's' ratio is a limit for ductile and brittle behavior of materials. If G/B is 0.571 and higher, the material is brittle otherwise the material becomes ductile. Considering this, the results in Table 2 show that the Pugh's ratio is 0.577 indicating that the material is brittle. Poisson's ratio is given by calculating the ratio of the lateral strain to that of the longitudinal strain in the direction of the stretching force. Applying Pugh's criterion, a ratio is below 0.26 indicates that the material is brittle while a ratio above 2.6 indicates that the material is ductile. It can therefore be concluded that Niobium Tin is brittle since it has a Poisson's ratio of 0.2577. When Poisson's ratio is in the range 0.25–0.5, it implies that the forces in the compound are central.

The elastic anisotropy, A of crystals is important for engineering applications since it is correlated with the possibility of producing micro cracks in materials. For a completely isotropic system, the value is 1, otherwise values of A which are less than or greater than 1 indicates

anisotropy. The calculated shear anisotropic factor for Niobium Tin is 0.6833. which indicates that the material is elastically anisotropic.

C. Debye Temperature

The Debye temperature is an important parameter that correlates with many physical properties of solids such as specific heat capacity, elastic constants and superconducting temperature (Ravindran *et al*, 1998). One of the standard methods to calculate the Debye temperature can be estimated from the averaged sound velocity (Zhang *et al*., 2007). The average sound velocity V_M is approximately given by;

$$Vm = \left(\left[\frac{1}{3}\left(\frac{2}{v_t^3}+\frac{1}{v_l^3}\right)\right]\right)^{-1/3} \quad \text{.....6}$$

Where V_t and V_l are the longitudinal and transverse sound velocities respectively, which can be obtained from bulk modulus B and shear modulus G (Wang & Ye, 2003).

$$V_t = \left(\frac{3B+4G}{3\rho}\right)^{1/2} \quad \text{.....7}$$

$$V_t = \left(\frac{G}{\rho}\right)^{1/2} \quad \text{.....8}$$

The values of Debye temperature are estimated using;

$$\Theta_D = \left(\frac{h}{K_B}\left[\frac{3nN_{AP}}{4\pi M}\right]\right)^{-1/3} V_M \quad \text{.....9}$$

Where V_M is the average sound velocity, h, k_B and N_A are planks constant, Boltzmann constant and Avogadro number respectively. ρ is the density, M is the molecular weight and n is the number of atoms in the unit cell.

The Debye temperature is a parameter that is associated with the highest allowed mode of vibration. The Debye temperature in this study was 289.136K and the average Debye sound velocity was calculated to be 2056.003m/s. A Debye temperature of above 400 K indicates that the crystal's thermal conductivity is high while a value to below 400K shows low thermal conductivity. Since the compound that was studied had a Debye temperature of below 400 K, we concluded that Niobium Tin has lower thermal conductivity. For temperatures below the Debye temperature, the heat capacity of the compound increases with the temperature and for temperatures above the Debye temperature, the heat capacity of the crystal remains constant , it no longer depends on temperature. The Debye temperature and the heat capacity are directly proportional.

D. Phonon Dispersion

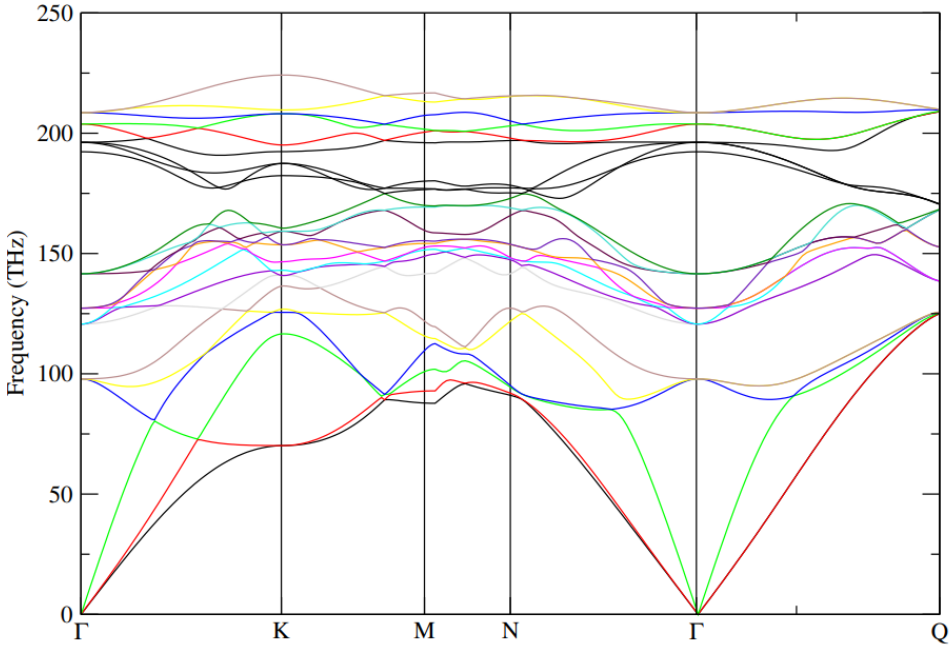

Figure 2 : *Phonon dispersion curve*

There are two branches in phonon dispersion relation: the lower mode wich is the acoustic mode and the upper mode which is the optical mode. The acoustic mode refers to the in-phase vibration mode while the optical mode refers to the out-of-phase vibration. The name optical phonons is derived from the fact that the phonons get excited by the infrared radiation in ionic crystals. The phonons were calculated using the Density Functional Perturbation Theory as implemented in PWSCF.

The graph shows phonon dispersion curve for Niobium Tin. The optical mode and the acoustic mode are clearly differentiated. In the phonon study, there are three modes that are associated with each mode number n, considering *x*, *y*, and *z*. The number of acoustic modes is usually three for crystals whose number of atoms is equal to or greater than two, and the optical modes are given by the formula 3N-3. Given that Niobium Tin has got 8 atoms in its unit cell, there are 24 modes of vibration, 21 being optical modes and 3 being acoustic modes. The acoustic modes converge at the gamma high symmetry point as shown in the graph.

Acoustic modes vibrate at a slower frequency and are always in the same phase with the unit cell. Optical modes vibrate at a higher frequency compared to acoustic modes .Two adjacent atoms vibrate in a direction opposite to each other in optical modes. In the acoustic mode, the two adjacent atoms will vibrate together in the same direction. Phonon dispersions are computed and the above information therefore confirms that the compound is dynamically stable.

A system is considered to be dynamically stable at equilibrium if the potential energy is always increasing for any combination of displacement of atoms. The phonons should therefore have non-negative and real frequencies for stability. Negative frequencies imply that the potential energy reduces; hence, the system is unstable. Phonon frequencies arise as a result of the displacement of atoms in a given crystal from the rest position, which in turn makes the forces rise. It is thus important to identify the number of normal modes that are neighboring a certain

phonon energy to give details necessary when studying thermal and electrical conductivity and also establishing the critical temperature of superconducting materials.

In summary, the results of the current study show a fair agreement with the existing data from Sundareswari *et al* (2010).

DISCUSSION

The study aimed at determining the dynamical and elastic properties of Niobium Tin.The phonon dispersion curve depicted dynamical stability of the compound.The elastic constant values calculated satisfy the four Born criterion conditions for elastic stability. The calculated shear anisotropic factor for Niobium Tin is 0.6833 which indicates that the material is elastically anisotropic. Niobium Tin is brittle since it has a Poisson's ratio of 0.2577. The Debye temperature in this study was 289.136K. The study was able to closely compare wih other existing data.

CONCLUSION

The results on the elastic constants and phonon dispersion of the Niobium Tin, studied from first principles have been reported. The reported elastic constants are C_{11} is 286.8593 GPa, C_{12} is 110.0611 GPa and C_{44} is 60.4042 GPa .The Debye temperature is 289.136K . From the study, it can be concluded that the compound is dynamically and mechanically stable. Niobium Tin is brittle but not a good thermal conductor deduced from its Debye temperature.

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