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Calculations of Electronic Structure and Elastic Properties of Nb_3Sn and V_3X (Ga, Si) Compounds Using First Principles DFT Study

K.R. Ojo[1,2], R.I. Adeniji[1,4], P. O. Adebambo[1], J.A. Akinlami[1], A.A.A. Agboola[3], and G.A. Adebayo[1].

[1]Department of Physics, Federal University of Agriculture, PMB 2240 Abeokuta, Nigeria

[2]Department of Physics, Federal College of Education, Osiele, P.M.B. 2096, Abeokuta. Nigeria

[3]Department of Mathematics, Federal University of Agriculture, PMB 2240 Abeokuta, Nigeria

[4]Department of Physics, Federal College of Education (Tech), Akoka, Nigeria

Abstract

The electronic structure and elastic properties of some A 15 superconducting compounds (Nb_3Sn, V_3Ga and V_3Si) were investigated using the density functional theory within the generalized gradient approximations as expressed in 'ESPRESSO'. The crystal structures of the compounds understudy were determined. The band structures at T=0 exhibit transitions of electrons from valence band to conduction band at M and slightly at R along the high symmetry points in Nb_3Sn, V_3Ga and V_3Si and in V_3Ga there is no electrons from -6.0eV to -5.0eV which revealed that they are metallic compounds. The elastic properties were investigated at T=0, the values of Elastic anisotropy, Young's modulus (GPa), Poisson ratio and shear modulus (GPa) for the compounds revealed that the compounds are stable and ductile and that V3Ga is more stable than V3Si and Nb3Sn respectively. The results obtained were in agreement with the previous theoretical research on A 15 superconducting compounds. Therefore we conclude that the three compounds were metals, stable and ductile. This make them to be useful in hospital for magnetic Resonance Imaging, Particle accelerators for manipulation of charged particle beams, generation of strong DC magnetic fields and power transmission.

Keywords: Elastic properties; A15 compounds; GGA; First-principles.

INTRODUCTION

Karmerlingh Onnes in 1911 discovered Superconductivity, that is, a material that is cooled below its critical temperature Tc and conducts DC electric current with zero resistance and refer to such materials as superconductors. He therefore, called the phenomenon superconductivity [16]. This property of conducting electric current at zero resistance makes the superconductor useful in hospitals for Magnetic Resonance Imaging (MRI), particle accelerators, generation of strong DC magnetic fields, and power transmission [2][12].

There are up to fifty A15 compounds, those with highest critical temperature are found among Nb and V based compounds. The A15 compounds are usually of the type A_3B and of high superconducting transition temperature [4]. In the unit cell of A15 structure compound, there are six atoms of the transition metal A and two atoms of the non transition element B. The transition element of A are in groups IV, V, VI, and non transition element of B are from group III [3]. The size of the A15 compounds determines its stability. The A15 compounds belong to the space group Pm3n and have eight atoms in their primitive cubic cell. The cubic unit cell of A15 compounds contains six A atoms at 0.25 0.00 0.50, 0.50 0.25 0.00, 0.00 0.50 0.25, 0.00 0.50 0.75, 0.50 0.75 0.00 and 0.75 0.00 0.50 and two B atoms at 0 0 0 and 0.5 0.5 0.5 [5].

Bendjemil calculated the electronic structure, magnetic and Fermi surface of heavy-fermions superconductors compounds based on Nb_3Si [1]. Sundareswari, Ramasubramanian and Rajagopalan calculated the elastic and thermodynamical properties of A15 Nb_3X (X = Al, Ga, In, Sn and Sb) compounds using the first principle DFT study [6]. In this work, the main attention was on the electronics structure and elastic constants.

However, to the best of our knowledge, for comparison purpose, we are yet to lay hands on any experimental or theoretical work available on V_3Ga and some elastic properties of V_3Si. Very recently, the lattice constant and some elastic properties of V_3Si such as elastic constants and Shear Modulus were reported [17].

METHODS OF CALCULATION

Total energy and functional

The quantum mechanics is used in getting all possible information from the system through the system wave function ψ. Therefore,

$$H\psi = E\psi \quad (1)$$

where H is the Hamiltonian and E is the eigenvalue of the system

However, using W. Kohn and L.J. Sham theory which state that ‘in Density functional theory the e-e interaction can be written as one-electron effective term’ [7]:

$$\sum_{j} \frac{e^2}{|r_i - r_j|} = \int \frac{\rho_e(r')}{|r_i - r'|} dr' + dr' + V_{xc}\left(\rho_e(r_i)\right) \quad (2)$$

Where $$E[n] = F[n] + \int V_{ext}\, n(r) d^3r \quad (3)$$

V_{ext} is as a result of electrons interaction with nuclei and other fields. Universal functional which is independent of external potential and is given by:

$$F[n] = T[n] + U[n] \quad (4)$$

Kohn and Sham in 1965 were able to show that by replacing original many-body problem with an independent electron problem which can be solved self-consistently, the unknown functional E[n] can be recast into the form:

$$F[n] = T_s[n] + \int \frac{n(r)n(r')}{rr'} d^3r d^3r' + E_{xc}[n] \quad (5)$$

The non-interacting independent-particle kinetic energy $T_S[n(r)]$ is therefore, given by

$$T_s[n] = \sum \int \psi_i(r) \nabla^2 \psi_i(r) d^3r \quad (6)$$

Elastic Constants

The elastic constant of a material is the ratio of the stress to the strain. To calculate the elastic constant, the tensile stress and shear components will first be determined. Both stress and strain have three tensile and three shear components then the linear elastic constants form 6 X 6 matrix.

$$\sigma_i = C_{ij} E_i \quad (7)$$

for small stress σ and strain E [5].

For cubic crystal, there are three generally accepted elastic stability criteria namely [9][6] $C_{11} + C_{12} > 0$, $C_{44} > 0$, $C_{11} - C_{12} > 0$, where C_{ij} are the conventional elastic constants in Voigt notation. For a cubic system, C_{11}, C_{12}, and C_{44} comprise the complete set of three independent elastic constants. The elastic constants can be obtained by calculating the total energy as a function of the volume-conserving strains that break the cubic symmetry [6].

Shear Modulus (G), Young's Modulus (E), Bulk Modulus (B), Poisson's ratio (ν) and elastic anisotropy ratio (A) of a cubic system can be derived from C_{11}, C_{12}, and C_{44} which are given by

$$G = \frac{1}{2}(G_V + G_R) \quad (8)$$

Where

$$G_V = \frac{1}{5}(3C_{44} + C_{11} - C_{12}) \quad (9)$$

$$G_R = \frac{5C_{44}(C_{11}-C_{12})}{4C_{44}+3(C_{11}-C_{12})} \quad (10)$$

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

$$E = \frac{9GB}{G+3B} \quad (12)$$

The elastic constants (C_{ij}) also determine the stability of the cubic structure [8][9] when all the necessary conditions such as

$$C_{11} + 2C_{12} > 0 \quad (13)$$

$$C_{44} > 0 \quad (14)$$

$$C_{11} - C_{12} > 0 \quad (15)$$

are satisfied.

COMPUTATIONAL DETAILS

The computational method used is Density functional theory as implemented in the QUANTUM ESPRESSO software distribution [18,19,20], within the local density approximation, a plane wave expansion up to 60 Ry for the kinetic energy cut-off for Nb_3Sn, 45 Ry for the kinetic energy cut-off for V_3Ga and 50 Ry for the kinetic energy cut-off for V_3Si. The method to determine elastic constants consisted of applying a given strain and calculating the stress, since the unit cell was kept fixed and only the interval coordinates were optimized. Both stress and strain have three tensile and three shear components, giving six in total. The linear elastic constants form 6 X 6 matrix such that

$$\sigma_i = C_{ij}E_i$$

for small stress σ and strain E. For cubic crystal, there are three generally accepted elastic stability criteria, namely $C_{11} + C_{12} > 0$, $C_{44} > 0$, $C_{11} - C_{12} > 0$, where C_{ij} are the conventional elastic constants in Voigt notation. For a cubic system, C_{11}, C_{12}, and C_{44} comprise the complete set of three independent elastic constants which can be obtained by calculating the total energy as a function of the volume-conserving strains that break the cubic symmetry.

The calculations were performed using the QUANTUM ESPRESSO software distribution [18,19,20]. The fundamental eigenvalues were calculated using Kohn-Sham approach [7]. The pseudopotential approximation and the plane-wave approach were used for investigating the interactions valence electrons and core electrons [10]. The exchange-correlation energy was calculated at the generalized gradient approximation level using the Perdew, Burke and Ernzerhof (PBE) formalism [5,21,22,23,24].

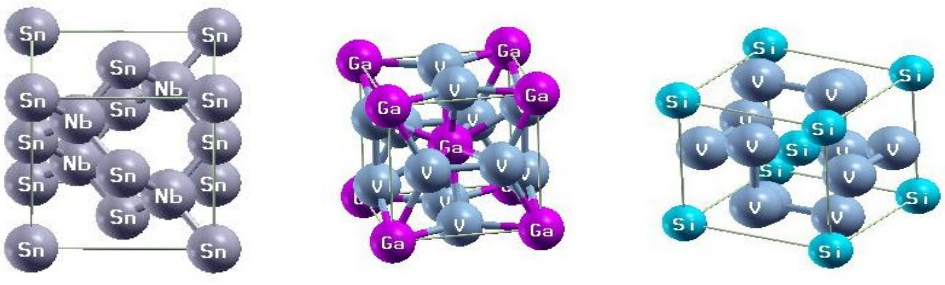
In order to obtain reliable results, a highly accurate computational method such as the THERMO-PW method is employed to calculate the elastic constants as implemented in the QUANTUM ESPRESSO code using the three accepted elastic stability for cubic crystal [8], [6]. The three criteria are $C_{11} + C_{12} > 0$, $C_{44} > 0$, $C_{11} - C_{12} > 0$, where C_{ij} are the conventional elastic constants in Voigt notation.

RESULTS AND DISCUSSION

Structural Properties

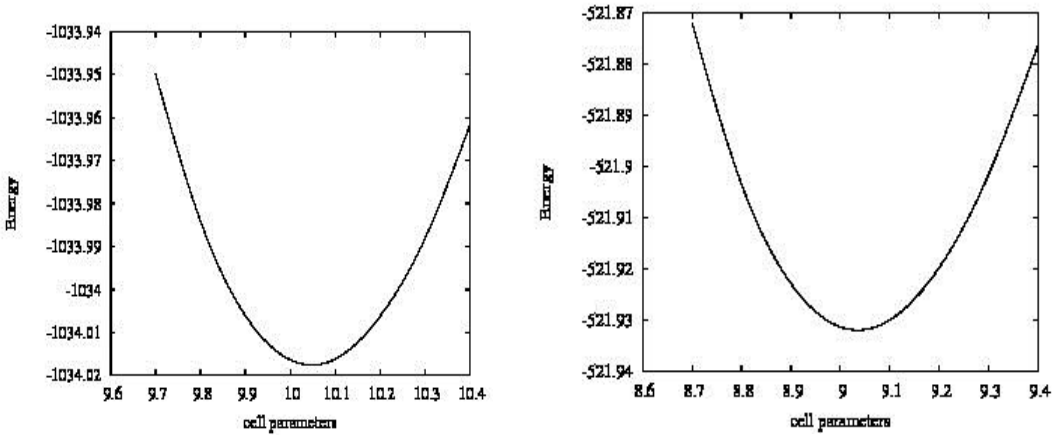
The Xcrysden tool [25] was used to visualize the crystal structures of Nb_3Sn, V_3Ga and V_3Si

In investigating the structural properties of Nb_3Sn, V_3Ga and V_3Si, the crystal structure was optimized with respect to lattice constants, and internal atomic positions are as shown in Figure 1a - c. The calculated lattice parameters of Nb_3Sn, V_3Ga and V_3Si are presented in Table 1 along with previously published computational and experimental data. The equilibrium lattice constant of Nb_3Sn, V_3Ga and V_3Si were calculated by minimizing various values of lattice parameters. For each value of lattice parameter, the total energy of compound was estimated. The total energies of Nb_3Sn, V_3Ga and V_3Si were plotted against the corresponding lattice parameters are as shown in figure 2a - c. Therefore, the lattice constants estimated for Nb_3Sn, V_3Ga and V_3Si are respectively 10.05atm, 9.03atm and 8.85atm

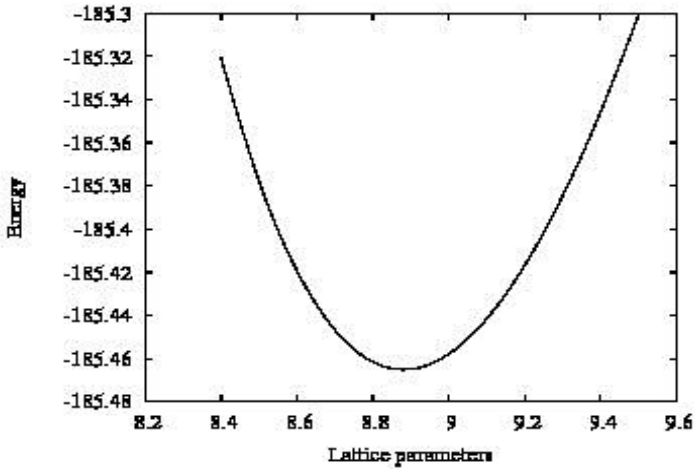


(a) (b) (c)

FIG. 1: Crystal Structures of (a) Nb_3Sn (a) V_3Ga (b) V_3Si.



(a) (b)



(c)

FIG 2: The plot of minimization of Energy against the calculated lattice constants for different compositions: (a) Nb_3Sn, (b)V_3Ga (c) V_3Si

TABLE I: Equilibrium lattice constants of compounds Nb3Sn, V3Ga and V3Si

Compound	a(a.u)
Nb_3Sn	5.19[a], 5.29[b], 5.32[c]
V_3Ga	4.75[a]
V_3Si	4.97[a], 5.11[d]

[a]Present result

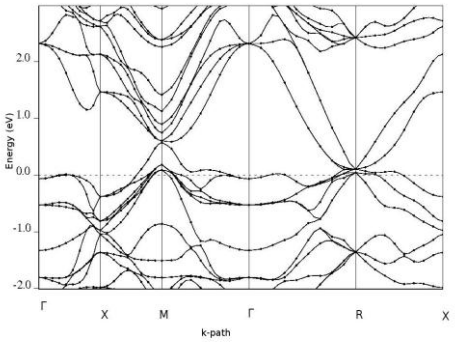
[b]Reference [15]

[c]Reference [6]

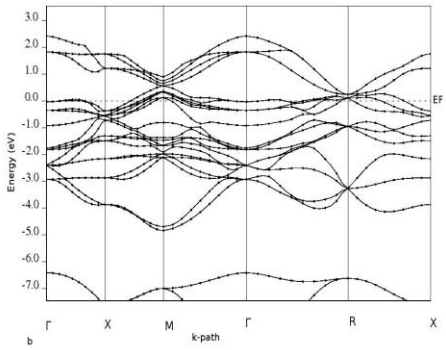
[d]Reference [17]

Band Structures

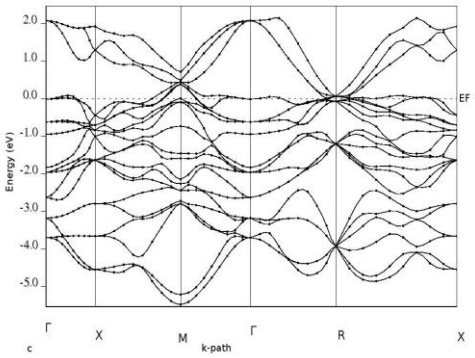
Figure 3(a) shows the band structures of Nb_3Sn, V_3Ga and V_3Si plotted along high symmetry points Gamma-X-M-Gamma-R-X at T=0. The band structures at T=0 exhibit transitions of electrons from valence band to conduction band at M and slightly at R along the high symmetry points in Nb_3Sn, V_3Ga and V_3Si and in V_3Ga there is no electrons from -6.0eV to -5.0eV which revealed that they are metallic compounds because of the absence of band gap.. This transition of electrons from valence band to conduction band which was observed along high symmetry points M and R is in agreement with the work of Bendjemil as shown in Figure 3(b). All the band structures reported at the given x-values have been calculated based on density functional theory within PBE-GGA approximation. For comparison, Bloch vector k was plotted along the high symmetry directions BZ Gamma-X-M-Gamma-R-X in the Bendjemil as presented in Figures 3 (a) - (c).



(a)



(b)



(c)

FIG 3: Band Structures of (a) Nb_3Sn (b) V_3Ga and (c) V_3Si

Elastic Properties

The calculated elastic constants of Nb_3Sn, V_3Ga and V_3Si are shown in Table II. The anisotropy factor A, Young's modulus Y, and Poisson's ratio ν were calculated from the elastic constants. The results are presented in Table III. To our knowledge, this is the first theoretical elastic constants results on V_3Ga, and some elastic constants of V_3Si such as anisotropy factor, Young Modulus and Poisson ratio will be calculated.

Shear modulus plays a dominant role in predicting the hardness rather than bulk modulus. The shear modulus in GPa decreases in the following order: V_3Ga (93.19), V_3Si (80.94) and Nb_3Sn (69.64). The shear modulus of V_3Ga is higher than those other materials under study. As a result, we said that V_3Ga is stronger than the other materials.

Higher Young's modulus (Y) for a given material, means that the material is stiffer. From the results of Y obtained from computation, we can say that V_3Ga is a stiffer material than the others, V_3Si and Nb_3Sn because Young's modulus in GPa is relatively higher for V_3Ga (93.19) as shown in Table III. The ductile/brittle nature of the materials under study depends on the following: Cauchy pressure $C_{12} - C_{44}$, Pugh's index of ductility on $\frac{G}{B}$ and on Poisson's ratio (ν) [13]. According to Pettifor (1962), for metallic bonding, $C_{12} - C_{44}$ is positive, and the material is ductile; whereas for directional bonding, the Cauchy pressure is negative and therefore, the material is brittle [15]. The three compounds under study Nb_3Sn, V_3Ga and V_3Si can be said to be ductile since their $C_{12} - C_{44}$ values are more positive ranging from 40.00 to 42.12 (Table II). According to Pugh's criterion in 1994, material is brittle or (ductile) if the $\frac{G}{B}$ ratio is greater or (lesser) than 0.57. The $\frac{G}{B}$ ratio of Nb_3Sn, V_3Ga, and V_3Si ranges between 0.43 to 0.46 which make them ductile in nature. The third condition for being brittle/ductile in nature is derived from Pugh's criterion, and that is when Poisson ratio ν is less than 0.26, the material is brittle otherwise it is ductile (Table III). Applying this third condition, it is observed that the three compounds Nb_3Sn, V_3Ga, and V_3Si Poisson's ratio (ν) range from 0.30 to 0.31, which shows that the three materials are ductile.

The ratio of the bulk modulus (B) to C_{44} may be interpreted as a measure of plasticity [14]. If the values of $\frac{B}{C_{44}}$ are large, it indicates that the material possesses excellent lubricating properties. Since the values of the ratio $\frac{B}{C_{44}}$ of Nb_3Sn, V_3Ga, and V_3Si were found to be much less with the maximum of 3.20 and minimum of 2.70. Therefore, all the three compounds are not good lubricants. Another important parameter in determining the structural stability is the elastic anisotropy (A). For a completely isotropic system, A=1. Deviation from unity measures the degree of anisotropy. The degree of anisotropy of the study compounds is Nb_3Sn (0.67), V_3Ga (0.77), and V_3Si (0.70).Therefore, we can say that the materials are stable compounds.

TABLE II: Calculated Elastics constants of Nb_3Sn, V_3Ga and V_3Si.

Compounds	C_{11}(GPa)	C_{12}(GPa)	C_{44}	B(GPa)	$C_{11} - C_{12}$
Nb_3Sn	278.13[a]	101.48 [a]	59.36 [a]	160.36 [a]	42.12 [a]
Nb_3Sn (Theory)	284.23 [b]	107.70 [b]	67.07 [b]	166.54 [b]	40.63[b]
V_3Ga	294.62[a]	120.99 [a]	66.90 [a]	213.96 [a]	54.09 [a]
V_3Si	311.00 [a]	110.00 [a]	70.00 [a]	177.00 [a]	40.00 [a]
V_3Si (Theory)	321.00 [c]	112.00 [c]	72.00 [c]	181.00 [c]	

[a]Present result

[b]Reference [6]

[c]Reference [17]

TABLE III: Calculated Anisotropy factor A, Shear modulus (G), Young's modulus (Y), Poisson's ratio (ν), $\frac{G}{B}$ and $\frac{B}{C_{44}}$

Compounds	A	Y(GPa)	(ν)	G(GPa)	$\frac{G}{B}$	$\frac{B}{C_{44}}$
Nb_3Sn	0.67[a]	182.50 [a]	0.31[a]	69.64[a]	0.43[a]	2.70[a]
Nb_3Sn (Theory)	0.76[b]	195.34[b]	0.27[b]	74.87[b]	0.45[b]	2.48[b]
V_3Ga	0.77[a]	244.13[a]	0.31[a]	93.19[a]	0.43[a]	3.20[a]
V_3Si	0.70[a]	210.70[a]	0.30[a]	80.94[a]	0.46[a]	2.53[a]
V_3Si (Theory)	-	-	-	84.00[c]		

[a]Present result

[b]Reference [6]

[c]Reference [17]

CONCLUSION

In conclusion, we have studied elastic and electronic properties of some A15 compounds Nb_3Sn, V_3Ga and V_3Si by using the first-principles density functional theory. In particular, the elastic constants of each of the compounds understudied and some other structural and electronic properties have determined. From the elastic constants, shear modulus, young modulus, and Poisson's ratio are obtained. Also, this work is in close agreement with few available results. The results of the elastic constants obtained show the ductile nature of Nb_3Sn, V_3Ga and V_3Si.

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