# Theoretical Study Of Energy Gap Of Metals And Linear Deformation

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**Abstract:** The effects of deformation on the energy gap of different elemental metals were computed and studied based on envelop function formalism. The electron density parameters of deformed metals under the application of different strains were obtained for different metals. The poison ratio relating the transversal compression to elongation in the direction of applied deformation for different elemental metals were computed using elastic moduli for homogeneous isotropic material and used in this work. The results obtained revealed that there is a good agreement between the computed and experimental value. The experimental value used in this work is theoretically obtained by applying the experimental value of Fermi energy obtained from solid state physics by Charles Kittel to the model obtained for the energy gap of metals in this work. Metals in the region of high density limit have high energy gap which decreases towards the region of the low density limit. There is high electron concentration in the region of high density limit than the low density limit. This seems to suggest that metals in this region have high conductivity in nature. The energy gap of all the metals investigated decreases as deformation increases. These seems to suggest that as deformation increases the strength of interaction between the electron decreases which forces the energy gap of the metals to decrease as deformation increases. The trend exhibited by metals in this work revealed that the energy gap of metals is greatly affected by deformation.

## 1.0       Introduction

Metals achieve structural stability by letting their valence electrons roam freely through the crystal lattice. These valence electrons are the equivalents of the molecules of an ordinary gas (Pillai, 2010). Electrons are the subatomic particles that carry a negative charge, and also surround the nucleus of an atom. When electrons move together in the same direction, they form an electric current (Aswani, 2001). Energy gap is an energy range in a solid where no electrons states can exist (Pillai, 2010). The energy band structure plays a crucial role in the theory of electron conductivity in the solid state and explains why materials can be classified as insulators, conductors and semiconductors (Ashcroft and Mermin, 1976). The energy band structure present in a semiconductor is a crucial ingredient in understanding how semiconductor devices work (Animalu, 1977). The band into which the ground state level splits is termed the valence band (Rudden and Wilson, 1995). The Band gap theory, combined with the Pauli Exclusion Principle, and some thermal physics, explains many of the basic conduction properties of crystals (Kittel, 1976). Energy band gap is usually referred to as the energy difference between the conduction band and the valence band. The conduction band is the outermost energy band where the free electrons lie and below that there is the valence band (Animalu, 1977). An electron residing in the valence band cannot jump to the conduction band unless it is provided the amount of energy needed for the electron to cross the energy barrier between the bands (Kaldis, 1979).

When electron acquire an energy equal to or greater than the band gap energy, it can go to the conduction band, become a free electron which is the main reason behind the high conductivity of metals (Kakani and Kakani, 2004). In the construction of energy band of solids, it is customary to omit the inner bands since they have little effect on the main electronic properties of solid. This is entirely analogous to the free atom in which the valence electrons are of primary importance (Theraja and Theraja, 2000). The importance of energy band theories for a crystalline solid is due to the fact that many important physical and optical properties of a solid can be readily explained using its energy band structure (Vijaya and Rangerajan, 2003). In insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap (Animalu, 1977). In solid-state physics, the electronic band structure of a solid describes the range of energies that an electron within the solid may have and ranges of energy that it may not have (Kachava, 1992).

Most solid substances are insulators, and in terms of the band theory of solids, there is a large forbidden gap between the energies of the valence electrons and the energy at which the electrons can move freely through the material (Pillai, 2010). The power of band theory lies in its application to specific problem in solid state physics, such as in the quantum theory of conduction and the operation of semiconductor devices (Guy, 1976). In most cases theoretical calculations of the energy band structures for semiconductor materials are guided by the experimental data from the optical absorption, photoluminescence, and photoemission experiments in which the fundamental absorption process is closely related to the density of states and the transitions from the initial to the final states of the energy bands Kittel, (1976). The envelop-function approach is most widely used due to its simplicity. With several refinements, this method become quite effective in dealing with many problems such as band mixing, the effects of external fields, impurities, and exciton states (Elliott, 1997). Deformation is the change in shape or size of solid (Backofen, 1972). A solid body is deform when a stress is applied to it, all solid materials exhibit nearly Hookean behaviour for small enough strain or stress *(*Borg,1990)*.* When a material is subjected to external forces its behaviour depends not only on the magnitudes of the forces and the inherent strength of the material itself but also on the way the forces are applied and combined. These particular combinations of forces may cause the material to deform elastically or plastically. The amount of deformation depends on knowing the intensity of the forces at all points throughout the material (Hugh Ford and Alexander, 1977). Metals can be deformed by compressive, tensile and torsion force. During deformation, atoms at the surface and interior of metals changes together with their atomic distance depending on the metallic surface area that is subjected to different deformation. The contact potential difference on the metal surface also changes during deformation (Borg, 1990). Consequently, a lot of efforts have been made to study the effect of deformation on some properties of metals theoretically and experimentally. Salah Daoud et al (2014) calculated the near neighbor distance (bond length) and the average energy gap using the pseudopotential plane wave method, in the frame work of the density functional theory (DFT) within the local density approximation (LDA) and the Hartungen-Goedecker-Hutter (HGH) scheme for pseudopotential of Boron-Bismuth compound in its structure zincblende phase and predicted the refractive index and some optoelectronic and thermal properties of boron-bismuth compound by means of some empirical formulas. The results obtained are analyzed and compared with the available theoretical data of the

literature. Ahmad and Mohib-ul Hag (2014) develop a simple relation between the optical electronegativity, energy gap, refractive index and electronic polarizability for tenary chalcopyrite semiconductors. He obtained the energy gap from electronegativity while the refractive index and the electronic polarizability were obtained from the energy gap by proposing a linear relation between them. The calculated values are in agreement with the experimental values and the result obtained by their earlier researchers. Kiejna and Pogosov (1999) performed an experimental investigation on the effect of deformation on some electronic properties of metals by taking the direct measurement of deformed metal using Kelvin method. They observed that the contact potential difference of the metals increase when compressed and decreases when tensed. Pogosov and Shtepa, (2006), calculated the surface stress and the contact potential difference of elastically deformed metals based on structureless pseudopotential model using self-consistent Kohn Sham method. The results of surface stress obtained were in agreement with experimental results, and also confirmed that the contact potential difference obtained for the deformed metallic surfaces by Kelvin method correspond to change in surface potential. Adeshakin *et. al* (2015) investigated the effect of linear deformation on the electronic properties of metals based on the modified structureless pseudopotential model to compute and study the effects of deformation on the electron density parameter, Fermi energy, Fermi wave vector and chemical potential of different metals. The results obtained revealed that increase in deformation causes an increase in electron gas parameter, and decrease in Fermi wave vector, Fermi energy and chemical potential of metals. Adesakin, (2016) develop a model to compute the electrical conductivity of different elemental metals based on pseudopotential formalism. The results obtained revealed that there is a good agreement between the computed and experimental value of the electrical conductivity of metals. There is high concentration of electron in the high density region than the low density region. The electrical conductivity of metals decreases as deformation (strains) increases for all the metals investigated. The effect of deformation is more pronounced on the electrical conductivity of noble and transition metals than in alkaline metals. Adesakin 2017 computed the effects of deformation on the bulk modulus and compressibility of different elemental metals based on pseudopotential formalism. The results obtained revealed that there is a good agreement between the computed and experimental value of the bulk modulus and compressibility of metals. There is high concentration of electron in the high density region than in the low density region for the bulk modulus

and compressibility of metals these seems to suggest that the bulk modulus and compressibility of metals depend on the density of valence electron in metals. The bulk modulus of all the metals investigated decreases as deformation increases while the Compressibility increases with an increase in deformation for all the metals investigated. In this work, the energy gap of undeformed and deformed elemental metals were computed based on envelop function formalism. The results obtained for the energy gap of undeformed metal were compared with the theoretical experimental value to validate the model used in this work. How the energy gap of metals varies with deformation is also computed and studied. The metals used in this work were selected based on the availability of experimental data, their industrial and technological applications and availability of some physical constants of metals that is required for computation.

## 2.0 Theoretical Consideration

Due to the thermal dependence of the electron flow, we can use Maxwell-Boltzmann statistics to describe the $I - V$ characteristics of the diode. We find

$$I = I_0(eV/kT - 1) \qquad (1)$$

where $I_0$ is the current through the diode when there is no bias applied to it (also known as the reverse saturation current), I is the applied current, V is the applied voltage, e is elementary charge, k is the Boltzmann constant, and T is the temperature at which the system in thermal equilibrium.

Also, $I_0$ and energy gap Eg are related by

$$\ln (I_0) = \ln (BT^{2/3}) - (Eg/hk) (1/T) \qquad (2)$$

so we simplify Eq. (2) as

$$\ln (I_0) = (-Eg/hk) (1/T) \qquad (3)$$

The probability P (E) that an electron gains sufficient thermal energy at an absolute temperature T such that it will be found occupying a particular energy level E, is given by the Fermi-Dirac distribution:

$$P (E) = 1/(1 + \exp (E - E_F)/k_BT) \qquad (4)$$

where $k_B$ is the Boltzmann constant, $k_BT$ is the thermal energy and $E_F$ is the Fermi energy or Fermi level.

The total number of electrons in the conduction band and the total number of holes in the valence band is obtained as

$$n = \frac{\pi}{2}\left(\frac{8m_e}{h^2}\right)^{3/2} \int_{E_C}^{\infty} E^{1/2} \, exp\left(\frac{E_F-E}{k_BT}\right) dE \qquad (5)$$

and

$$p = \frac{\pi}{2}\left(\frac{8m_p}{h^2}\right)^{3/2} \int_{-\infty}^{E_v} (E_v - E)^{1/2} \, exp\left(\frac{E-E_F}{k_BT}\right) dE \qquad (6)$$

Where $E_c$ is the energy in the conduction band, $E_v$ is the energy in the valence band, $m_e$ is the electron mass, $m_p$ is the mass of hole, $E_F$ is the Fermi energy, E is the energy, $k_B$ is the Boltzmann constant, T is the temperature and h is the Planck's constant.

For a metal under the action of a deforming force, the average electron density in such a metal as a function of deformation is expressed as (Pogosov and Shtepa, 2006).

$$n = n_o[1 - (1 - 2v)u_{xx}] + 0u_{xx}^2 \qquad (7)$$

where $v$ is the Poisson ratio relating compression to elongation in the direction of applied deformation, $u_{xx}$ is the applied deformation or strain and $n_0$ is the average electron density in the bulk of undeformed metal and is given as $n_0 = 3/4\pi r_s^3$ and $r_s$ is the electron density parameter of undeformed metal. For a metal under the action of a strain or deforming force, the electron density parameter of the metal is

$$r_s[1 + (1 - 2v)U_{xx}]^{1/3} \qquad (8)$$

The behaviour of electrons in the deformed metal is governed by the Schrodinger time independent equation

$$\frac{\hbar^2}{2m}\nabla^2\Psi + E\Psi = 0 \qquad (9)$$

The normalized solution of equation (9) has the form

$$\Psi = \left(\frac{8}{\Omega}\right)^{1/2} \sin\left(\frac{n_x\pi}{a_x}\right)\sin\left(\frac{n_y\pi}{a_y}\right)\sin\left(\frac{n_z\pi}{a_z}\right) \qquad (10)$$

The eigenvalues are given by

$$\gamma = \frac{2mE}{\hbar^2} = \pi^2\left(\frac{n_x^2}{a_x^2} + \frac{n_y^2}{a_y^2} + \frac{n_z^2}{a_z^2}\right) \qquad (11)$$

or by

$$\gamma = k_x^2 + k_y^2 + k_z^2 = |k|^2$$

where $k_x$, $k_y$, $k_z$ are the components of the wave vector k. In computing the quantities that requires summation over the wave vector, k the summation over k is replaced by integration according to the transformation.

$$\sum_k \rightarrow \frac{2\Omega^3}{(2\pi)^3}\int d^3k$$

The factor of two appearing in the denorminator comes from the spin, According to Pauli Exclusion Principle; two one-electron states with opposite spins can be assigned to every k-point. In the ground state, each of the states up to the maximum, $k_{max}$ is occupied

by two electrons filling a sphere in k-space of radius $k_{max}$ called Fermi sphere. For the system of N free electrons in the volume, $\Omega$, the average electronic density $n_{ave}$ in terms of $k_f$ is

$$n_{ave} = \frac{N}{\Omega} = \frac{k_f}{3\pi^2} \tag{12}$$

The energy of the highest occupied state at absolute zero temperature is called the Fermi energy expressed as

$$E_f = \frac{\hbar^2 k_f^2}{2m} = \frac{\hbar}{2m} \left(3\pi n_{ave}\right)^{2/3} \tag{13}$$

The electron gas parameter, $r_{su}$ of the deformed metal is defined as

$$\frac{4\pi}{3} r_{su}^3 = \frac{\Omega}{N}$$

The Fermi wave vector $k_f$ and the Fermi energy $E_f$ of deformed metals in terms of the electron gas parameter, $r_{su}$ is obtained as

$$k_f = \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_{su}} \tag{14}$$

and

$$E_f = \frac{me^4}{2\hbar^2} \left(\frac{9\pi}{4}\right)^{2/3} \left(\frac{1}{r_{su}^2}\right) \tag{15}$$

While the energy gap of deformed metals is obtained as

$$E_g = \left(\frac{1.9192}{r_s [1 + (1 - 2\upsilon) U_{xx}]^{1/3}}\right)^2 \tag{16}$$

where, $r_s$ is the electron density parameter of undeformed metal, $\upsilon$ is the Poisson ratio relating compression to elongation in the direction of applied deformation and $u_{xx}$ is the applied deformation or strain. In this work, the energy gap of undeformed metals were computed using envelop function approach for different elemental metals of different group and period, and how deformation affects energy gap of this metals is also studied.

### 3.0 Results and Discussion

Figure 1 shows the variation of energy gap with electron density parameter for some elemental metals belonging to different groups and period. Figure 1 revealed that energy gap of metals decreases as the electron density parameter increases. Figure 1 revealed that there is agreement between the experimental and computed value of energy gap. The experimental value used in this work is theoretically obtained by

applying the experimental value of Fermi energy obtained from solid state physics by Charles Kittel (1976) to the model obtained for the energy gap in this work. This agreement between the computed and experimental value could be due to the fact that the model take into consideration most of the factors that the energy gap of metals depend upon such as conduction and valence electron, excitation and vacancy formation energy and some Fermi and bulk properties of metals. The trend exhibited by metals in figure 1 also revealed that metals in the region of high density limit have high energy gap which decreases towards the region of the low density limit. This may be due to the dependence of the energy gap on the electronic excitation, electron mobility, electronic concentration and the density of states of the electrons in the metals. Also, the observed trend in figure 1 revealed that there is high electron concentration in the region of high density limit than the low density limit. This seems to suggest that metals in this region have high conductivity in nature.
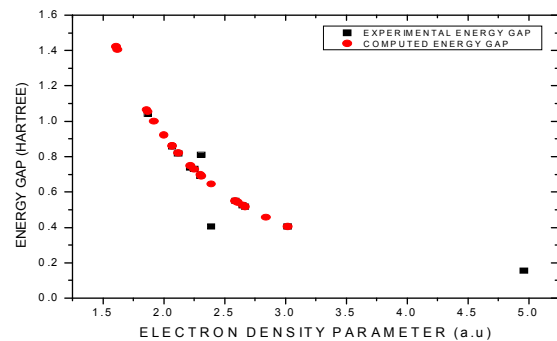


**Figure 1: Variation Of Energy Gap With Electron Density Parameter Of Metals**

Figure 2 shows the variation of energy gap with deformation for some monovalent, divalent, trivalent and polyvalent metals. Figure 2 revealed that the energy gap of all the metals investigated decreases as deformation increases. This decrease in energy gap of all the metals could be due to an increase in the scattering of phonon electron and decrease in the bond strength of the metals during deformation which forces the energy gap of all the metals to decrease as deformation increases. The trend exhibited by metals in figure 2 revealed that potassium has the lowest energy gap while molybdenum and tunasten were found to be having the highest energy gap among all the metals subjected to different deformation. These could be due to the fact that the valence level in the molybdenum and tunasten split at larger separation than potassium and the electron begin to move away from the parent nucleus due to external influence (deformation/strain).
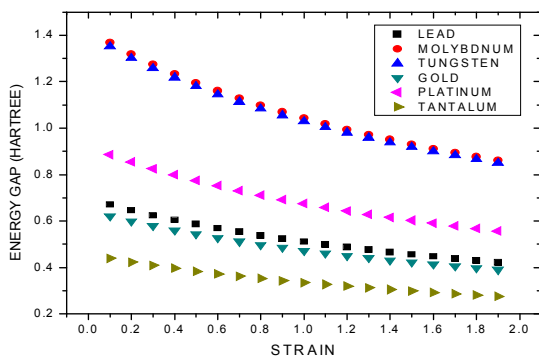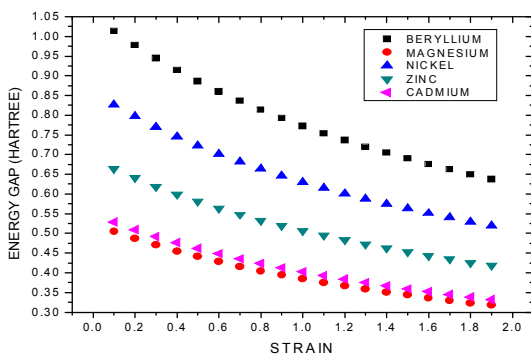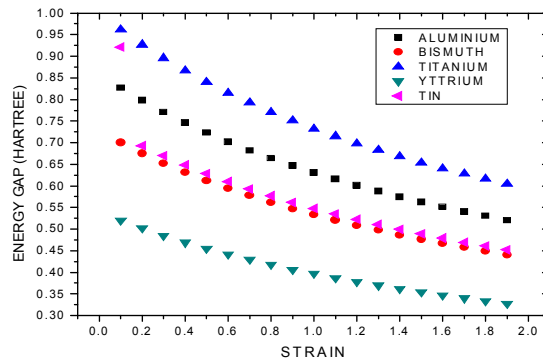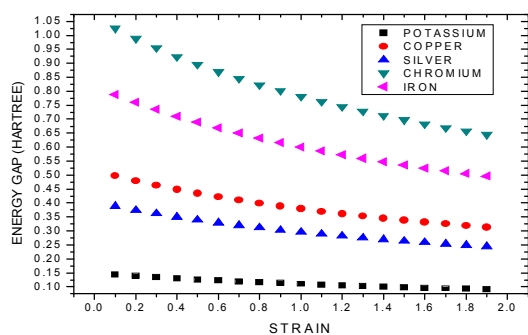
**Figure 2: Variation Of Energy Gap Of Some Metal With Strain**

Figure 2 also revealed that metals in the high density region has high energy gap while metals in the low density region has low energy gap for all the metals subjected to different deformation. These seems to suggest that as deformation increases the strength of interaction between the electron decreases which forces the energy gap of the metals to decrease as deformation increases. Furthermore, the trend exhibited by metals in figure 2 revealed that as deformation increases, there is an increase in the collision between the electron due to delocalization of the electron from their position which result in the decrease in some of the properties that the energy gap of metals depend upon. The trend exhibited by metals in these work revealed that the energy gap of metals is greatly affected by deformation.

Table 1 shows the Energy Gap of Deformed Metals (Hartree) (Table 1).

Table 2 shows the Calculated Energy Gap of Undeformed Metals and their Experimental values (Table 2).



**Table 1: Energy Gap of Deformed Metals (Hartree)**

| Metals | $r_s$ (a.u) | Strain | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | 1.2 | 1.4 | 1.6 | 1.8 |
| K | 4.96 | 0.1389 | 0.1299 | 0.1222 | 0.1156 | 0.1098 | 0.1047 | 0.1001 | 0.0960 | 0.0923 |
| Cu | 2.67 | 0.4794 | 0.4483 | 0.4218 | 0.3989 | 0.3789 | 0.3612 | 0.3455 | 0.3314 | 0.3186 |
| Ag | 3.02 | 0.3748 | 0.3504 | 0.3297 | 0.3117 | 0.2961 | 0.2823 | 0.2701 | 0.2590 | 0.2491 |
| Be | 1.87 | 0.9774 | 0.9139 | 0.8598 | 0.8132 | 0.7724 | 0.7364 | 0.7043 | 0.6756 | 0.6496 |
| Mg | 2.65 | 0.4867 | 0.4551 | 0.4282 | 0.4049 | 0.3846 | 0.3667 | 0.3507 | 0.3364 | 0.3235 |
| Cr | 1.86 | 0.9879 | 0.9238 | 0.8691 | 0.8219 | 0.7807 | 0.7443 | 0.7119 | 0.6829 | 0.6566 |
| Fe | 2.12 | 0.7605 | 0.7111 | 0.6690 | 0.6327 | 0.6010 | 0.5730 | 0.5480 | 0.5256 | 0.5054 |
| Ni | 2.07 | 0.7977 | 0.7458 | 0.7017 | 0.6636 | 0.6303 | 0.6010 | 0.5749 | 0.5513 | 0.5301 |
| Zn | 2.31 | 0.6405 | 0.5989 | 0.5635 | 0.5329 | 0.5062 | 0.4826 | 0.4616 | 0.4427 | 0.4257 |
| Cd | 2.59 | 0.5095 | 0.4764 | 0.4482 | 0.4239 | 0.4026 | 0.3839 | 0.3672 | 0.3522 | 0.3386 |
| Al | 2.07 | 0.7977 | 0.7458 | 0.7017 | 0.6636 | 0.6303 | 0.6010 | 0.5748 | 0.5513 | 0.5301 |
| Bi | 2.25 | 0.6751 | 0.6313 | 0.5939 | 0.5617 | 0.5335 | 0.5087 | 0.4865 | 0.4666 | 0.4487 |

| Metals | $r_s$ (a.u) | Strain | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | 1.2 | 1.4 | 1.6 | 1.8 |
| Ti | 1.92 | 0.9272 | 0.8669 | 0.8156 | 0.7714 | 0.7327 | 0.6985 | 0.6681 | 0.6408 | 0.6162 |
| Y | 2.61 | 0.5017 | 0.4691 | 0.4414 | 0.4174 | 0.3965 | 0.3780 | 0.3616 | 0.3468 | 0.3335 |
| Sn | 2.22 | 0.6935 | 0.6484 | 0.6101 | 0.5770 | 0.5480 | 0.5225 | 0.4998 | 0.4793 | 0.4609 |
| Pb | 2.30 | 0.6461 | 0.6041 | 0.5684 | 0.5375 | 0.5106 | 0.4868 | 0.4656 | 0.4466 | 0.4294 |
| Mo | 1.61 | 1.3186 | 1.2329 | 1.1600 | 1.0970 | 1.0420 | 0.9934 | 0.9501 | 0.9114 | 0.8763 |
| W | 1.62 | 1.3024 | 1.2177 | 1.1457 | 1.0335 | 1.0292 | 0.9812 | 0.9385 | 0.9002 | 0.8655 |
| Au | 2.39 | 0.5984 | 0.5595 | 0.5264 | 0.4978 | 0.4729 | 0.4508 | 0.4312 | 0.4136 | 0.3977 |
| Pt | 2.00 | 0.8545 | 0.7990 | 0.7517 | 0.7109 | 0.6752 | 0.6438 | 0.6157 | 0.5906 | 0.5679 |
| Ta | 2.84 | 0.4238 | 0.3962 | 0.3728 | 0.3526 | 0.3349 | 0.3193 | 0.3054 | 0.2929 | 0.2816 |

**Table 2: Calculated Energy Gap of Undeformed Metals and their Experimental values**

| Metals | Electron Density Parameter $r_s$ (a.u) | Experimental Energy Gap (Hartree) | Computed Energy Gap (Hartree) |
|---|---|---|---|
| Potassium | 4.96 | 0.1558 | 0.1497 |
| Copper | 2.67 | 0.5145 | 0.5167 |
| Silver | 3.02 | 0.4028 | 0.4039 |
| Beryllium | 1.87 | 1.0393 | 1.0533 |
| Magnesium | 2.65 | 0.5241 | 0.5245 |
| Chromium | 1.86 | - | 1.0647 |
| Iron | 2.12 | 0.8158 | 0.8195 |
| Nickel | 2.07 | - | 0.8596 |
| Zinc | 2.31 | 0.8085 | 0.6903 |
| Cadmium | 2.59 | 0.5483 | 0.5491 |
| Aluminium | 2.07 | 0.8548 | 0.8596 |
| Bismuth | 2.25 | 0.7276 | 0.7276 |
| Titanium | 1.92 | - | 0.9992 |
| Yttrium | 2.61 | - | 0.5407 |
| Tin | 2.22 | 0.7372 | 0.7474 |
| Lead | 2.30 | 0.66887 | 0.6963 |
| Molybdnum | 1.61 | - | 1.4210 |
| Tunasten | 1.62 | - | 1.4035 |
| Gold | 2.39 | 0.4050 | 0.6448 |
| Platinum | 2.00 | - | 0.9208 |
| Tantalum | 2.84 | | 0.4567 |

## 4.0 Conclusion

In this work, a generalized model is developed and used to study the effect of linear deformation on energy gap of metals using the envelop function approach formalism. The energy gap of undeformed metals were in agreement with the experimental values which shows the validity of the formalism used in the work. The result obtained revealed that metals in the region of high density limit have high energy gap which decreases towards the region of the low density limit. There is high electron concentration in the region of high density limit than the low density limit. This seems to suggest that metals in this region have high conductivity in nature. The energy gap of all the metals investigated decreases as deformation increases this suggest that as deformation increases the strength of interaction between the interacting electron decreases which forces the energy gap of the metals to decrease as deformation increases. These revealed that energy gap of metals is strongly affected by deformation.

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