Effect Of Linear Deformation On Electronic Heat Capacity Of Metals

Adesakin G. E.

Department of Physics, Ekiti State University, Ado-Ekiti, Nigeria
G-mail of corresponding author: adesakingbenga@gmail.com

Abstract: The effects of deformation on electronic heat capacity of different elemental metals were computed and studied based on Einstein model 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 base on 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 values of electronic heat capacity of metals. This shows that Einstein model can be used in the theoretical prediction of heat capacity of metals. The result obtained revealed that the electronic heat capacity of metals are more concentrated in the high density region than the low density region. This seems to suggest that the electronic heat capacity of metals depend on the electronic concentration. Also, the experimental value of electronic heat capacity is higher than the computed value, this could be due to some factors that the electronic heat capacity of metals depend upon that the model does not take into consideration. The result obtained shows that the electronic heat capacity of metals increases as the temperature increases. The electronic heat capacity of all the metals increases with an increase in deformation (strain). This could be due to the fact that as deformation increases, the collision between the interacting electron increases which forces the mean atomic velocity, amplitude of atomic vibration and electron thermal excitation to increase and there by result in the increase in the electronic heat capacity of the metals as deformation increases.

Keywords: Deformation, Einstein model, Debye temperature, heat capacity, poison ratio. electron density parameter

Introduction

Solid consists of a sufficiently large collection of atoms that exhibit the characteristic behavior of bulk material, the atom may lose some of its tightly bound electrons leaving the core electrons, such entity is known as ions (Rogalski and Palmer, 2000). Solid as an ensemble of independent quantum harmonic oscillators vibrating at a frequency which depends on the strength of the restoring force acting on the atom (Kittel, 1976). At a finite temperature, the atoms that form a crystalline lattice vibrate about their equilibrium positions with amplitude that depends on the temperature, these vibrations can be analyzed in terms of collective modes of motion of the ions. When an atom vibrates, the force on adjacent atoms changes causing them to vibrate (and vice-versa) (Efthimios, 2003). Crystal lattice dynamics can be discussed in the frame of the adiabatic approximation by solving Hamiltonian operator for the motion of the ions about their equilibrium position which defines the lattice spatial distribution. Lattice vibrations can be described in terms of waves propagating along a linear chain, such that the amplitude of the vibration for the atom is equal in the Debye approximation, a linear lattice can sustain long wavelength elastic waves which propagate without dispersion (Rogalski and Palmer, 2000). Fermi-Dirac statistics gives satisfactory calculation of the electronic contribution to the specific heat of metals and the Debye theory expression is obtained from the total internal energy of the valence electron gas at any temperature (Animalu, 1977). Electronic specific heat is the contribution to total specific heat due to transitions of electrons to state of higher energy. Debye temperature is one important factor in the discussion of many physical properties such as elastic constants, electrical conductivity and x-ray diffraction. The thermal properties of solid depend on energy change of the atoms and free electrons (Pillai, 2010). The specific heat at constant volume is the change in internal energy with temperature. (Elliot, 1997). We can also think about the number of degrees of freedom as the number of ways to absorb energy. The theorem of equipartition of energy (classical mechanics) states that in thermal equilibrium the same average energy is associated with each independent degree of freedom. The equality of kinetic and potential energy in harmonic approximation is addressed by the virial theorem of classical mechanics (Kittel, 1976). Contributions to the heat capacity can be considered classically only if \(E_n \sim h\nu \ll k_B T\). Energy levels with \(E_n \geq k_B T\) contribute little to the heat capacity. For a quantum harmonic oscillator the Einstein-Bose statistics must be applied and the statistical
distribution of energy in the vibrational states gives the average energy (Madelung, 1995). In the Einstein model for the thermal heat capacity one considers only phonons at one frequency, an approximation for optical phonons. Heat capacity of gas, solid or liquid tends to increase with temperature, due to the increasing number of excited degrees of freedom, requiring more energy to cause the same temperature rise. In discussing specific heats, there is one big difference between the one-dimensional case and the three-dimensional case. In the one-dimensional case, the dispersion relation is known exactly (for nearest-neighbor interactions) and from it the density of states can be exactly computed. In the three-dimensional case, the dispersion relation is not known, and so the dispersion relation of a classical isotropic elastic continuum is used instead. From this dispersion relation, a density of states is derived. Generally, this density of states curve does not compare very well with the density of states used in the Debye approximation. The reason the error is not serious is that the specific heat uses only an integral over the density of states (Patterson and Bailey, 2010). Deformation is the change in the shape or size of an object during stress or strain. The study of the elastic behaviour of a solid is very important in the fundamental and technical researches. In technology, it tells us about the strength of the materials. In fundamental research, it is of interest because of the insight it provides into the nature of the binding forces in solids. The relevant elastic constants also relate themselves to thermal properties like Debye temperature. The elastic properties of a homogenous crystal are generally anisotropic. In a cubic crystal, the relationship between stress and strain depends on the orientation of the crystal axes relative to stress system (Kachhava, 1992). Because of the anisotropy of a crystal, the atoms of any crystal can be deformed in a variety of ways that can be decomposed into three types of independent deformations viz, uniform compression associated with the bulk modulus or compressibility and two shears in both of which the volume is unchanged (Animalu, 1977). Mathematically, any lattice deformation can be characterized by a second-rank tensor \( \varepsilon_{ij} \), called a strain tensor which has three independent components in a system with cubic symmetry (Animalu, 1977). Consequently, a lot of efforts have been made to study the effect of deformation on some properties of metals theoretically and experimentally. 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 and Osiele (2012) computed the surface energy and surface stress of deformed metals based on the structureless pseudopotential formalism. The results obtained revealed that deformation causes a reduction of surface energy and this reduction is more pronounced in simple and alkaline metals. Tensile stress is present in most metallic surfaces whose surface stress were computed, although a few metals possess compressive stress on their surfaces. In the presence of deformation, the surface stress of some metals decreases, while deformation causes an increase in the surface stress of some metals. Adeshakin et al. (2012), developed a model based on the structureless pseudopotential to compute the correlation, binding and cohesive energy of deformed and undeformed metals. The computed binding and cohesive energy of metals were compared with available experimental values. The results obtained showed that correlation energy increases with increase in electron density parameter. The computed binding energy and cohesive energy of metals were in good agreement with experimental values. The results obtained also showed that deformation causes a decrease in the binding energy of metals and it does not cause a significant change in the cohesive energy of metals, although transition metals have high values of cohesive energy compared to alkaline and simple metals. Adeshakin et al. (2015) investigated the linear deformation and 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. In this work, Einstein model is extended to the study of the electronic heat capacity of deformed elemental metals consisting of monovalent, divalent, trivalent and polyvalent metals, and the result obtained were compared with available experimental values and results obtained using other method of calculation. This will provide an insight into how the electronic heat capacity of metals varies with deformation. The metals used in this study were chosen based on the
availability of experimental data, their industrial and technological applications and the availability of some physical constants of metals that is required for computation.

2.0 Theoretical Consideration

Considering a hypothetical crystal in the shape of a rectangular parallelepiped. In the undeformed state all of its faces are equivalent. Assume that deformation is a measured quantity and a metallic crystal to be considered as assembled from a number of simple crystallites. Express the average electron density in a metal as a function of deformation. Express the average electron density in a metal as a function of deformation for this purpose, consider a cubic cell of the side length \( a_o \) and volume (Kiejna and Pogosov, 1999).

\[
\Omega_o = a_o^3 = \frac{4}{3} \pi r_o^3
\]

(1)

where \( r_o \) is the radius of the Wigner-Seitz cell given as \( r_o = \frac{1}{3} r_s \), where \( r_s \) is the electron density parameter of undeformed metal defined as the radius of sphere containing one electron on average and a measure of the average distance between electrons. \( r_s \) is defined as

\[
r_s = \left( \frac{3}{4 \pi n} \right)^{1/3}
\]

(2)

where \( n \) is the electronic density of undeformed crystal. For a cubic cell deformed by applying an elongative force along the x-axis, the volume of the deformed cell is

\[
\Omega_d = a_x a_y a_z = \frac{4}{3} \pi ab^2
\]

(3)

where \( a_x, a_y, a_z \) are the sides of the deformed cubic cell. If the uniaxial strain is \( u_{xx} \), then

\[
a_x = a_0 \left[ 1 + u_{xx} \right]
\]

\[
a_y = a_0 \left[ 1 + u_{yy} \right]
\]

\[
a_z = a_0 \left[ 1 + u_{zz} \right] = a_0 \left[ 1 - \nu u_{xx} \right]
\]

(4)

where \( \nu \) is the polycrystalline Poisson ratio that relates the transversal compression to the elongation in the direction of the applied deformation that is \( u_{yy} = u_{zz} = -\nu u_{xx} \).

The ratio of the unit volume of the deformed cubic cell to that of the undeformed cell is

\[
\frac{\Omega_d}{\Omega_o} = \frac{a_0 \left[ 1 + u_{xx} \right] a_0 \left[ 1 + u_{yy} \right] a_0 \left[ 1 + u_{zz} \right]}{a_0^3}
\]

(5)

\[
\frac{\Omega_d}{\Omega_o} = \left[ 1 + u_{xx} \right] \left[ 1 + u_{yy} + u_{zz} + u_{yy} u_{zz} \right]
\]

(6)

Neglecting higher order terms of the uniaxial strain, then (Kiejna and Pogosov, 1999)

\[
\frac{\Omega_d}{\Omega_o} - 1 = u_{xx} + u_{yy} + u_{zz}
\]

(7)

From equation (4), then for the deformed cube,

\[
a = r_0 (1 + u_{xx})
\]

\[
b = r_0 (1 - \nu u_{xx})
\]

In the same vane, the lattice spacing in the planes perpendicular to the y or z direction is

\[
d_y = d_o (1 - \nu u_{xx})
\]

where \( d_o \) is the interplanar spacing in an undeformed metal given as

\[
d_o = \frac{a}{\sqrt{h^2 + k^2 + l^2}}
\]

(8)

where \( h, k \) and \( l \) are the Miller indices of the plane.

The average electron density in the deformed metal is

\[
n_{av} = \frac{n_o \Omega_o}{\Omega} = \frac{n_o a_0^3}{a_0 \left( 1 + u_{xx} \right) (1 - \nu u_{xx})^2}
\]

\[
n_{av} = n_o \left[ 1 - (1 - 2\nu) u_{xx} \right] + 0 (u_{yy}^2)
\]

where \( n_o \) is the electronic density of undeformed metal.

The electron gas parameter of the deformed metal is obtained from its volume as

\[
\frac{4}{3} \pi r_{su}^3 = \frac{4}{3} \pi ab^2
\]

\[
r_{su}^3 = r_0 \left( 1 + u_{xx} \right) \left( 1 - \nu u_{xx} \right)^2
\]

\[
r_{su}^3 = r_0^3 \left[ 1 + u_{xx} - 2 \nu u_{xx} + u_{yy}^2 - u_{xx} - u_{xx} \right]
\]

Neglecting higher order terms in the strain or deformation, we have (Kiejna and Pogosov, 1999).

\[
r_{su} = r_0 (1 + u_{xx} (1 - 2\nu))^{1/3}
\]

(10)

The electron gas parameter of deformed metals, \( r_{su} \) gives the mean inter electronic distance in a deformed metal (Kiejna and Pogosov, 1999).

The number of states in the blackbody radiation with frequency between \( \nu \) and \( \nu + d\nu \) is

\[
g(\nu) d\nu = \frac{8\pi \nu^3}{c^2} d\nu
\]

(11)

Where \( g(\nu) d\nu \) gives the number of oscillatory modes in the frequency range \( d\nu \) corresponding to the
energy range \(dE\), \(V\) is the volume and \(c\) is the speed of light.

For the elastic transverse waves and the longitudinal waves we have

\[
g_t(v)dv = \frac{8\pi NV}{v^2} v^2 dv
\]

(12)

And

\[
g_l(v)dv = \frac{4\pi NV}{v^2} v^2 dv
\]

(13)

Where \(v_t\) is the velocity of the transverse wave and \(v_l\) is the velocity of the longitudinal wave. The total number of vibrational modes in the frequency range \(dv\) is

\[
g(v)dv = g_t(v)dv + g_l(v)dv
\]

(14)

Substituting equation (12) and (13) into equation (14) we have

\[
g(v)dv = 4\pi V \left(\frac{1}{v_t^2} + \frac{2}{v_l^2}\right) v^2 dv
\]

(15)

In a continuous medium, there is no limit to the total number of vibrational modes. But in solids that has an atomic structure and contain \(N\) atoms, any vibrational mode must be described in terms of \(3N\) positional coordinates of the atoms. This therefore imposes a limit on the total number of independent modes of freedom which must be equal to \(3N\), where \(N\) is the number of atoms in a monatomic homogeneous solid. This imposes a limit on the maximum vibrational frequency. Using equation (15)

\[
3N = \int_0^{\infty} g(v)dv
\]

(16)

Putting equation (15) into equation (16) we have

\[
3N = 4\pi V \left(\frac{1}{v_t^2} + \frac{2}{v_l^2}\right) \int_0^{\infty} v^2 dv
\]

(17)

\[
3N = 4\pi V \left(\frac{1}{v_t^2} + \frac{2}{v_l^2}\right) V^3
\]

(18)

Therefore,

\[
\frac{3N}{v_o^3} = 4\pi V \left(\frac{1}{v_t^2} + \frac{2}{v_l^2}\right)
\]

(19)

By substituting equation (19) into equation (15) we have

\[
g(v)dv = \frac{3N}{v_o^3} v^2 dv
\]

(20)

Photons are associated with the vibrational modes of solids, in thermal equilibrium photons obey Bose-Einstein statistics.

\[
dn = \frac{3N}{v_o^3} \frac{v^2}{e^{v/v_o} - 1} dv
\]

(21)

Equation (21) is the number of photons of energy \(E = hv\) in the frequency range between \(v\) and \(v+dv\) and in thermal equilibrium with the solid lattice at temperature \(T\). The total vibrational energy of the solid in the frequency range \(dv\) is

\[
dU = Edn = \frac{3N\hbar}{v_o^3} \frac{v^3}{e^{v/v_o} - 1} dv
\]

(22)

The total vibrational energy of solid is obtained by integrating equation (23), then we have

\[
U = \int_0^{\infty} \frac{3N\hbar}{v_o^3} \frac{v^3}{e^{v/v_o} - 1} dv
\]

(23)

The heat capacity at constant volume is given by

\[
C_v = \frac{1}{N\alpha} \left(\frac{3N\hbar}{v_o^3} \int_0^{\infty} \frac{v^3}{e^{v/v_o} - 1} dv\right)
\]

(24)

Where, \(n\) is the number of mole, \(N_A\) is the Avogadro number, \(\hbar\) is the normalized Planck’s constant, \(K\) is the Boltzmann constant, \(T\) is the temperature and \(h\) is the Planck’s constant. In this work, the electronic heat capacity of deformed metals for monovalent, divalent, trivalent and polynuclear metals were computed using equation (24) and how deformation affects the electronic heat capacity of metals is also studied.

3.0 Results And Discussion

Figure 1 shows the variation of the electronic heat capacity with electron density parameter for different elemental metals containing group one, group two, group three, noble and transition metals. The experimental values used in these work is obtained from solid state physics by pillai 2010. The experimental value of the electronic heat capacity seems not to exhibit a particular trend unlike the computed value that seems to exhibit a linear trend. Figure 1 shows that at \(1.2 < \alpha < 3.0\) a.u, the computed electronics heat capacity of some metals is in good agreement with experimental value, although the experimental values is higher than the computed values for most of the metals. The discrepancy between the computed and experimental value of the electronic heat capacity could be due to the fact that there are some factors which the electronic heat capacity depend upon that the model does not take into consideration such as packing density, vibration of atoms around their equilibrium position, degree of freedom, atomic lattice and the crystalline architecture of the metals. The trend exhibited by metals in figure 1 revealed that almost all the metals have their electronic heat capacity concentrated in the high density region. This seems to suggest that the electronic heat capacity of metals strongly depend on the electronic concentration. Figure, 2 shows the variation of electronic heat capacity with temperature.
for different elemental metals containing monovalent, divalent, trivalent and polyvalent metals. Figure 2 revealed that the electronic heat capacity of metals increases as temperature increases. This could be due to the fact that the electrons in metals scattered more frequently by lattice vibrations which forces the electronic heat capacity to increase as the temperature increases. The trend exhibited by metals in figure 2 can also be due to the fact that as the temperature increases, the degree of freedom among the interacting electron also increases which result in the increase in the electronic heat capacity of the metals. Figure 2 revealed that potassium has the highest electronic heat capacity among all the metals whose electronic heat capacity were computed for different temperature this could be due to the high valence electron density and free conduction electron in them. Figure 3 shows the variation of electronic heat capacity with strain for different elemental metals of different group. Figure 3 revealed that the electronic heat capacity of all the metals increases with an increase in deformation (strain). This could be due to the fact that as deformation increases, the collision between the interacting electron increases which forces the mean atomic velocity, amplitude of atomic vibration and electron thermal excitation to increase and there by result in the increase in the electronic heat capacity of the metals as deformation increases. The trend exhibited by metals in figure 3 also revealed that metals in the high density region have low electronic heat capacity while metals in the low density region has high electronic heat capacity for all the metals subjected to different deformation. This seems to suggest that in the high density region the rate at which the electron scattered and the temperature between the interacting atoms during deformation is low compared to the metals in the low density region. The trend exhibit by metals in figure 3 could also be due to the fact that metals in the high density region has low degree of freedom while metals in low density region has high degree of freedom. Figure 3 also revealed that potassium has the highest deformed electronic heat capacity while molybdenum and tungsten has the lowest deformed electronic heat capacity among all the metals subjected to different deformation. This could be due to the high electronic concentration and high valence electron density in the alkaline metals that makes it to be highly affected by deformation. The trend exhibited by different metals in figure 3 shows that the electronic heat capacity of metals is highly affected by deformation.
lower the valence electron density in metals the lower metals the higher the electronic heat capacity and the suggest that the higher the valence electron density in metals are more concentrated in the high density value of the electronic heat capacity of undeformed can be used in the theoretical prediction of heat experimental valu.
The results obtained for the electronic heat capacity of undeformed metals were in good agreement with the experimental results obtained for the electronic heat capacity of undeformed metals. The computed and experimental value of the electronic heat capacity of undeformed metals are more concentrated in the high density region than the low density region. This seems to suggest that the higher the valence electron density in metals the higher the electronic heat capacity and the lower the valence electron density in metals the lower the electronic heat capacity of the metal. The electronic heat capacity of metals increases as temperature increases. This could be due to the fact that as the temperature increases the electrons in metals scattered more frequently due to lattice vibrations which forces the electronic heat capacity to increase as the temperature increases. The electronic heat capacity of all the metals increases with an increase in deformation (strain). This could be due to the fact that as deformation increases, the collision between the interacting electron increases which forces the mean atomic velocity, amplitude of atomic vibration and electron thermal excitation to increase and there by result in the increase in the electronic heat capacity of the metals as deformation increases.

**Conclusion**
In this work, a generalized approach for computing and studying the effect of linear deformation on electronic heat capacity of metals based on the Einstein model formalism is presented. The results obtained for the electronic heat capacity of undeformed metals were in good agreement with the experimental values which shows that Einstein model can be used in the theoretical prediction of heat capacity of metals. The computed and experimental value of the electronic heat capacity of undeformed metals are more concentrated in the high density region than the low density region. This seems to suggest that the higher the valence electron density in metals the higher the electronic heat capacity and the lower the valence electron density in metals the lower the electronic heat capacity of the metal.

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</table>
Table 2: Electronic Heat Capacity of undeformed Metals. The experimental values were obtained from Introduction to solid state Physics by Kittel (1976) and Ashcroft and Mermin (1976).

<table>
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<tr>
<th>Metals</th>
<th>Symbol</th>
<th>Electron Parameter $r_e$(a.u)</th>
<th>Density</th>
<th>Calculated Electronics Heat Capacity (J/kg-K)</th>
<th>Experimental Electronics Heat Capacity (J/kg-K)</th>
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References

5. Efthimios Kaxiras (2003): Atomic and Electronic Structure of Solids. Published by the press syndicate of the University of Cambridge UK.

3/13/2018