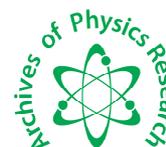




Scholars Research Library

Archives of Physics Research, 2014, 5 (3):66-75
(<http://scholarsresearchlibrary.com/archive.html>)



Scholars Research
Library

ISSN : 0976-0970

CODEN (USA): APRRC7

Structure and Stability of Gold Nanostructures

Dinesh Kumar^{1*}, Veena Verma², Keya Dharamvir³, H.S.Bhatti¹

¹Department of Physics, Punjabi University, Patiala (Punjab)

²Department of Physics, Govt. College Naya Nangal Distt. Ropar (Punjab)

³Department of Physics, Panjab University, Chandigarh

ABSTRACT

Using Gupta potential gold nanostructures have been studied. Gold nanowire icosahedron structure is found to be most stable structure. The value of cohesive energy, Young's modulus and shear modulus has been computed and all the values (except poisson ratio) are more than that of bulk gold. Another striking observation about gold nanostructures is that Young's modulus increases with tube radius whereas shear modulus decreases.

Keywords: Cohesive energy (U), Young's Modulus (Y), Shear Modulus (G), Poisson's ratio (ν)

INTRODUCTION

Intense interest has, over the last decade, been focused on metal nanoparticles due to their potential for advanced applications in a variety of fields such as catalysis, sensors, diagnostics, imaging, therapeutics, etc. The assembly of nanoparticles into well-defined two-dimensional and three-dimensional super lattices has attracted considerable attention especially of metal nanoparticles for applications in optoelectronic devices. Metal nanowires have become one of the significant research topics in recent years because of their potential applications as general building blocks in logic and memory circuits, nano-actuators, very-high-frequency (VHF) nano-electromechanical systems (NEMSs), structural reinforcement in composite materials, and sensors to detect airborne biological and chemical toxins.

Nano crystals have quite different physical properties from their corresponding bulk materials mainly because of their large surface-to-volume ratio. Among noble metals, gold nano particles have already shown their promise for a wide range of applications such as nanolithography [1], catalysts [2], nano bioelectronic devices [3], and ion detection [4]. Thus knowledge of the structure and stability of gold nano crystals is of great importance. Mechanical properties of metal nano-wires are very important for design and fabrication of nano-electromechanical systems. Understanding the mechanical properties of nanostructures is essential for the atomic-scale manipulation and modification of materials, whose behaviour is qualitatively different at the nano scale than at larger dimensions. Harris and others [5] have synthesized micron-sized colloidal crystals comprised of gold nanospheres directly from colloid by application of a laser. An array of colloidal crystals can be created by translation of the glass substrate under the laser beam. Extracellular synthesis of gold nanoparticles using *Pseudomonas denitrificans* and comprehending its stability has been studied by Mewada et.al. [6]

Huang and others [7] have reported the fabrication of novel gold nano dog-bones (GDBs) using a simple seed mediated growth (SMG) method. The GDBs were determined by x-ray diffraction (XRD) to be single-crystalline with a face-centered cubic (fcc) structure. While bulk gold has an fcc crystal structure, the competition between bulk and surface energies in nanometer-sized gold crystallites can result in several different competing structures [8, 9]. Bulk gold ($Z=79$, Xe $4f^{14} 5d^{10} 6s^1$) has nearest a neighbour distance equal to 2.884\AA [10] and cohesive energy 3.81 eV/A (electron volt per atom).

The Gupta potential is a many body potential developed on the basis of second moment approximation of the tight binding or linear combination of atomic orbital (LCAO) scheme. This is a very ‘chemical’ point of view as it is related in a natural way to yield metallic character of cohesive energy. The range of interaction has been extended up to fifth neighbor shell and the potential parameters have been adjusted to reproduce cohesive energy, atomic volume, and elastic constants of the real systems at $T=0\text{ K}$, though ensuring the stability of the appropriate crystal structure. The potential reproduces the lattice dynamical (phonon dispersion curves) and high temperature properties like specific heat, linear thermal coefficient, Gruneisen constant, latent heat enthalpy etc [11].

2. Structure of Armchair (or Zigzag) AuNTs:

We considered two different nano structures of gold: armchair AuNTs and icosahedral gold nanowire (AuNW). The former structures are hollow tubes, and only the ones with small diameters are expected to be stable while the latter has pentagonal cross-section locally, and has a single-atom chain running through the axis of the wire. For generation of the coordinates of armchair (n, n) nano tube of gold, we considered the two dimensional triangular lattice of gold atoms as shown in figure 1. The primitive vectors are shown as a_1 and a_2 and nearest neighbour distance is taken as bond length b of gold. First of all we generated the 2-d gold sheet in two different ways, the square sheet and the triangular sheet as shown in figure 1.

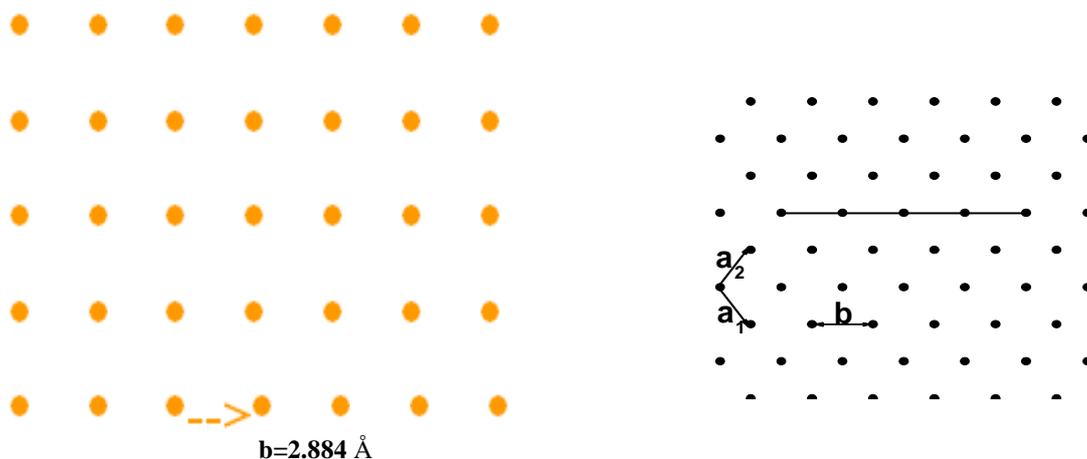


Figure 1. 2-d square (a) and triangular lattice (b) of gold

Using the above lattice AuNTs of different diameters are generated.

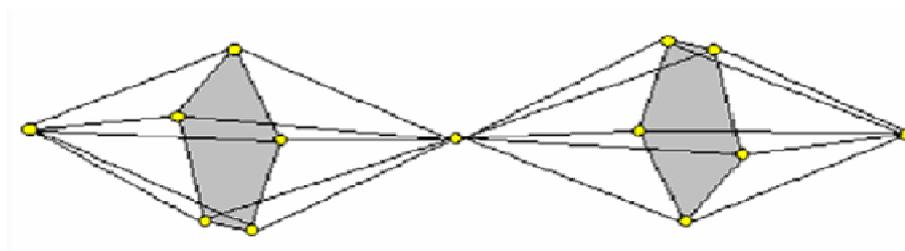


Figure 2. Gold nanowire Icosa structure

Gold Nanowire Icosa Structure

We also tried our hands on icosahedron structure of gold nanowire as shown in figure 2. Unit cell of this structure consists of two regular pentagons one above the other, one of pentagons rotated through 180 ° and one gold atom in between. So there are total 13 atoms and 20 triangles. It seems to be a stable structure with cohesive energy as -2.0381 eV/A..

3. The Gupta Potential

To model the gold clusters we used Gupta Potential .The potential energy between two atoms is given by:

$$E = E_{pair} + E_{embed} \quad (1)$$

$$= \sum_{i<j} \phi(r_{ij}) + \sum_I F(\rho_I) r_{ij}$$

where $\phi(r)$ is a short range pair potential and $F(\rho)$ is a many body embedding or glue function

$$\rho_I = \sum_j \rho(r_{ij}) \quad (1a)$$

$\rho(r)$ is a atomic density function.

$$\phi(r) = \sum_j 2A * \exp[-p(\frac{r}{r_o} - 1)] \quad (1b)$$

$$F(\rho) = -\xi * \sqrt{\rho} \sum_j [\exp\{-2q(\frac{r}{r_o} - 1)\}] \quad (1c)$$

the parameters of Gupta potential are:[11]

A=0.2061 eV, p=10.229 , q=4.036 , ξ =1.790 eV and r_o =2.884 Å

the parameters p and q describe the short range repulsive interaction and the hopping probability of the d-electrons to a neighboring site.

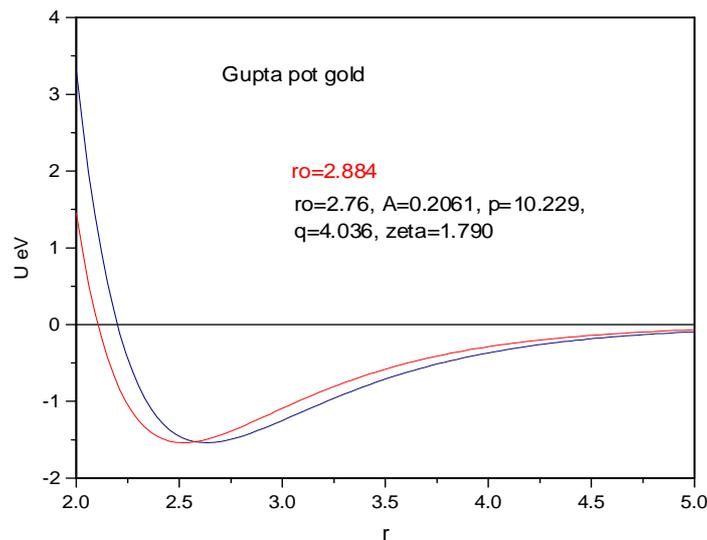


Figure 3. Gupta potential for gold, red curve ($r_o = 2.884$ Å) and navy curve ($r_o = 2.76$ Å)

The average nearest-neighbor distances, calculated by DFT-LDA [12] compare very well with those obtained through a scalar relativistic all-electron density functional method [13] for the ordered structures with $n = 38, 55$. For example, for Au 38, the calculated average nearest-neighbor distance of 2.77 Å is in excellent agreement with the value of 2.78 Å reported in Ref. [13]. So the Gupta potential curve is also plotted for $r_0 = 2.76$ Å

4. Generation of Coordinates of AuNTs:

First of all we generated the coordinates of gold atoms for triangular 2-d lattices and icosahedron structure. Figure 1 (b) represents a triangular lattice of gold atoms. When 2-d lattice of gold is folded to form AuNT of a particular diameter depending on the no of atoms on the circumference and the chirality of the AuNT. To generate a $(m, 0)$ AuNT, gold sheet of figure 1 (b) is rolled into a cylinder of radius given by

$$R = \frac{0.5 * b}{\sin \alpha} \quad (2)$$

where $b = 2.884$ Å (Au-Au nearest neighbor distance)

$$\text{and } \sin \alpha = \frac{\pi}{m}$$

Although this distance is called 'radius', it is actually the center-to-atom distance. For this reason area of cross-section of the wire is not equal to πR^2 , especially for a small diameter. This fact will be relevant when Young's modulus will be calculated. For a triangular lattice, unlike the hexagonal one, which is used for the carbon nanotubes, there is no difference between zigzag and armchair directions[14].

A zigzag AuNT is generated from 2-d triangular lattice keeping b same and second line of atoms is generated at a distance of 2.5 Å ($\sqrt{3} * b / 2$).

4.1 Minimization of Energy

First we generate the coordinates of gold atoms on a AuNT. The nearest neighbours of each atom are found within a range of 3.0 Å and energy per atom is calculated using the potential in equation 1. The total energy of the tube is given by

$$U = \sum_{ij} V (r_{ij}) \quad (3)$$

Next, the coordinates of each atom are modified in very small steps and energy is compared with previous energy. The modified coordinate is accepted if this energy is smaller than the previous one, otherwise we continue with the previous value of the coordinate. This is done successively for all the $3 N_a$ coordinates ($N_a =$ total number of Au atoms in the tube); and such a cycle is repeated several times till the energy of the tube is minimized. This is the process of relaxation under the given potential. Cohesive energy of AuNTs are given in table I. Out of all the three types of AuNT studied, Icosa AuNT appears to be the most stable. Using Gupta potential we computed the cohesive energy for icosahedron gold NW and AuNTs for triangular lattice and value of cohesive energy obtained by us for icosahedron NW (25 atoms) is -2.0381 eV/Å . Our values seem to agree well with [15]. They have reported the energy of the disordered structure for Au75 as 272.3771 and the energies for the icosahedral configurations of gold as Au38: 235.9173, Au55: 252.5177, and Au75: 272.2021.

RESULTS

6.1 Cohesive Energy

The value of cohesive energy obtained by us for icosahedron NW (25 atoms) is -2.0381 eV/Å .the value of each atom of Icosa structure is same expect for middle that is 7th atom in each unit cell. In a dimer the 7th, 13th and 19th atoms have slightly less (-1.5 eV) cohesive energy whereas all other atoms have energy of the order of -2.2 eV. As shown in table 1, the cohesive energy per atom for zigzag AuNTs decreases as the radius increases and our values seem to agree well with [15].

The AuNW was compressed and the structure was relaxed by changing the X, Y coordinates slightly in smaller and smaller steps but no buckling has been observed, this structure is very stable one.

Table I: Cohesive energy, Y, ν and G for various AuNTs

AuNT	R (Å)	No of atoms	U (eV/A)	Y (GPa)	ν	G (GPa)
Bulk gold	-	-	-3.81 [10]	78[13] 130.9[16] 110 [15]	0.44[13] 0.28[16]	27[13]
Icosa NW	2.453	25	-2.0381	131.9	0.19	188
(4,0)AuNT	2.039	32	-2.0643	117.4	0.35	254.8
(5,0)AuNT	2.453	40	-2.0565	142	0.37	229.1
(6,0)AuNT	2.884	48	-2.0520	156	0.41	186.1
(7,0)AuNT	3.323	56	-2.0499	165	0.35	173.2

6.2 Young's Modulus

By applying the pressure along the tube/nanowire axis, Young's modulus has been calculated. The estimation of elastic moduli requires the knowledge of the wall thickness of the tubes if we consider it to be a hollow cylinder. We have adopted the conventional thickness of 2.884 Å, equal to the adjacent atomic separation in gold atoms. After getting the final position coordinates of all the atoms on the surface of AuNW and AuNTs of given chirality's (n,m) and length, we then consider the same tube / nanowire under longitudinal stress. This stress is simulated by keeping the mutual distance between the end rings fixed at slightly larger (elongation) or smaller (compression) than normal. The coordinates of the rest of the atoms of the tube are varied till minimum energy is obtained. The force which produces a certain extension, say $l - l_0$ (or Δl), is obtained by the first derivative at l , since

$$F = -\frac{\partial U}{\partial l} \quad (4)$$

The standard expression for Young's modulus is,

$$Y = \frac{F/a}{\Delta l/l_0} \quad (4a)$$

where l_0 is the length of the tube and a is the cross sectional area. Since, around the minimum,

$$U = k(\Delta l)^2, \quad (4b)$$

where k is a constant $\left(k = \frac{1}{2} \frac{\partial^2 U}{\partial l^2} \Big|_0\right)$, we obtain,

$$Y = \left(\frac{l}{a} \frac{\partial^2 U}{\partial l^2}\right)_0 \quad (4c)$$

The cohesive energy is plotted against length of AuNW and other AuNTs as shown in figure 4 and 5. For hollow AuNTs the thickness of cylinder is taken as 2.74Å as size of (Au ion is 1.37 Å) for calculating Young's modulus. the computed values of Young's moduli are listed in table 1 for both AuNW and other AuNTs.

For Au bulk, $Y = 78 \text{ GPa [13]}$
 $= 130.91 \text{ GPa [16]}$,
 $= 60-110 \text{ GPa [17]}$

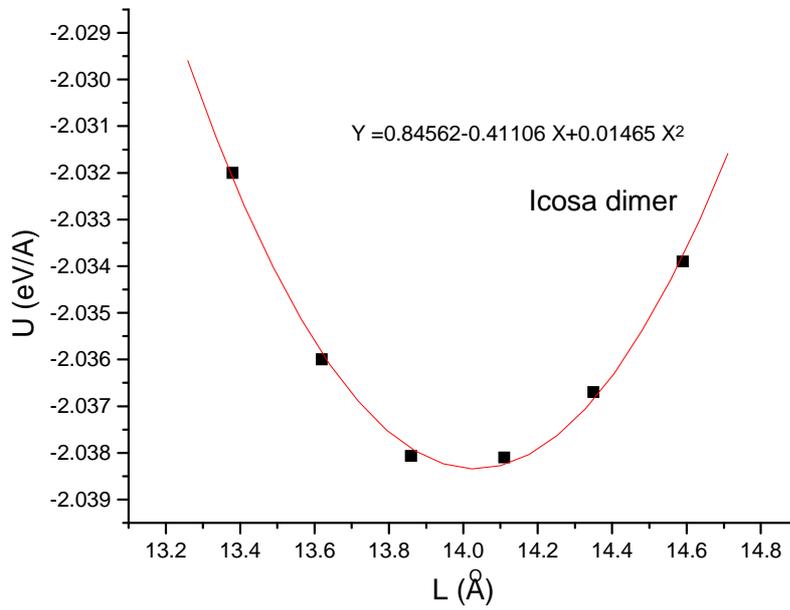


Figure 4. U in eV/A versus length of Dimer of AuNW

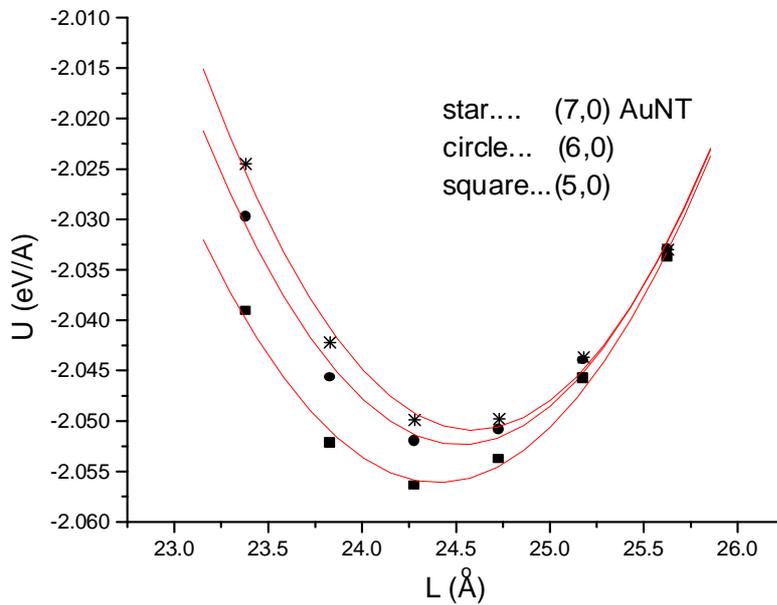


Figure 5. U versus length of AuNT triangular lattice

6.3 Poisson Ratio

Another mechanical property of interest is the Poisson ratio, ν , which is given by the variation of the radius of SWNT resulting from applying the axial strain on the tube.

$$\nu = \frac{\text{lateral strain}}{\text{longitudinal strain}} = \frac{\Delta r / r_o}{\Delta l / l_o} = \frac{r_s - r_o}{r_o} \frac{l_o}{\epsilon} \quad (5)$$

$$\text{where } \epsilon = \frac{\Delta l}{l_o} = \text{axial strain}$$

r_s is the radius of the strained tube and r_o is the radius of the unstrained tube. We have calculated ν for the tubes under study values are tabulated in Table 1. The value of poisson ratio is found to be

0.19 for Au nanowire
0.35 for AuNTs
0.44. [13], 0.28 [16] for bulk gold

6.4 Shear Modulus

A lateral force, in the form of a twist, is applied to the nanotube and nanowire of figure 2, keeping one of its ends fixed. The total torsion that has to be given to the AuNW has been distributed equally along its whole length and again the coordinates of the tube in minimum energy configuration are obtained. Based on the theory of elasticity, shear modulus at the macroscopic scale is given by

$$G = \frac{Tl_o}{\theta J(t)}, \quad (6)$$

where T , l_o , θ and $J(t)$ stand for the torque acting at the end of the AuNT / AuNW, the length, the total twist that is applied and the cross sectional polar moment of inertia of the AuNT or AuNW respectively. The polar inertia $J(t)$ is a function of wall thickness and for a AuNT with radius r_o and wall thickness t is given by

$$J(t) = \frac{\pi}{2} \left[\left(r_o + \frac{t}{2} \right)^4 - \left(r_o - \frac{t}{2} \right)^4 \right] \quad (6a)$$

and for AuNW polar inertia $J(t)$ is given by

$$J(t) = \frac{\pi}{2} [r^4] \quad (6b)$$

Here again taking Au nanowire as a solid cylinder of radius 4.11\AA ($2.453\text{\AA} + 1.66\text{\AA}$) where 1.66\AA is Vanderwaals radius. Using these equations, the shear moduli of Au nanowire and AuNTs have been obtained and the values are given in table 1. Our value for AuNW comes out to be 188 GPa where as for bulk gold it is 27 GPa [13] and 79.92 GPa [16].

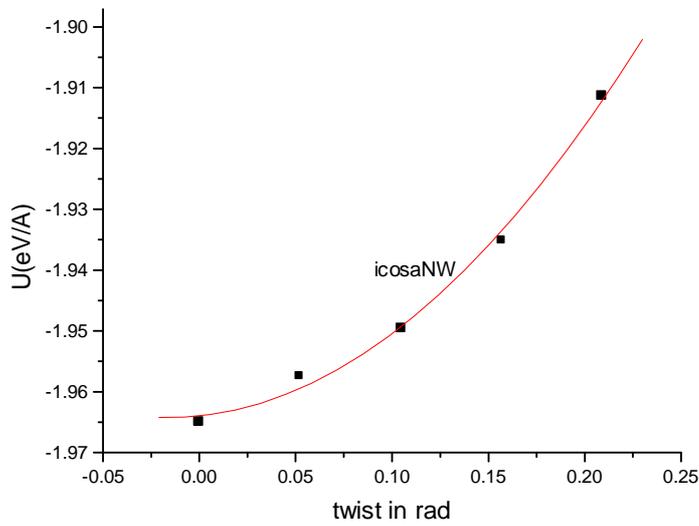


Figure 6. U (eV/A) versus twist in radian for AuNW.

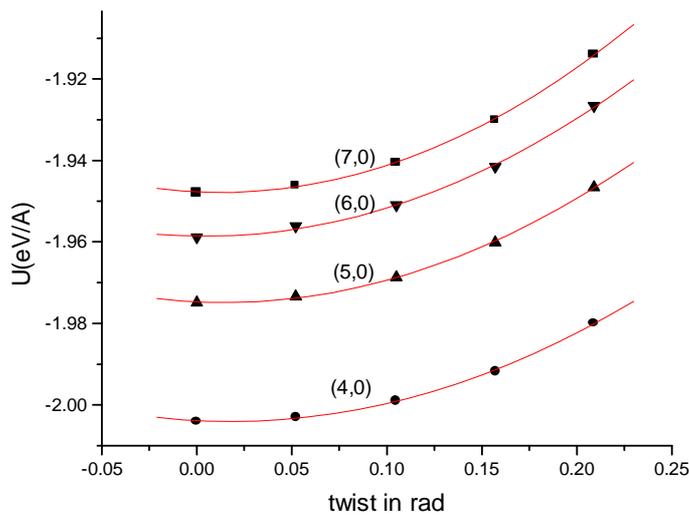


Figure 7. U (eV/A) versus twist in radian for AuNTs (triangular lattice)

The shear modulus for AuNTs of smaller radii is large and it decreases with increase in radius. The value of shear modulus is 188 (half = 94) Gpa for icosa structure of gold.

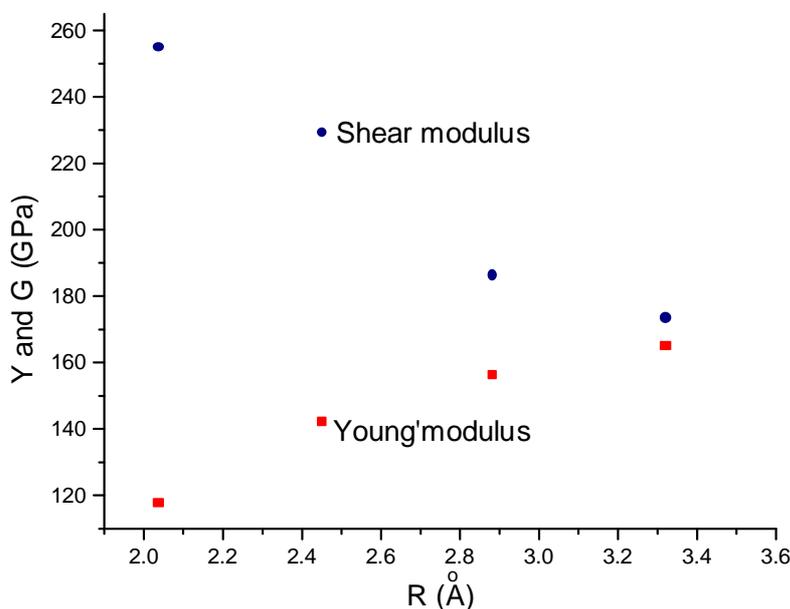


Figure 8. Variation of Y and G with radius of AuNT

CONCLUSION

In conclusion, using Gupta potential isolated gold nanoclusters have been studied and we have found essentially equal structural stability for AuNTs and AuNW icosahedron structure. Various moduli of gold nanostructures have been computed and results are encouraging. Therefore, we expect further experimental and theoretical efforts in the near future, to confirm the above predictions and provide a complete characterization of gold nanoclusters. The possible existence of novel physical and chemical properties of small gold and other metal nanoparticles provide motivation for further theoretical and experimental studies on these systems since they would be useful in the fabrication of new materials based on these nanostructures.

REFERENCES

- [1] J. Zheng, Z. Chen, and Z. Liu, *Langmuir* **2000**, 16, 9673-9676.
- [2] A. T. Bell, *Science* **2003**, 299, 1688-1691.
- [3] Y. Xiao, F. Patolsky, E. Katz, J. F. Hainfeld, and I. Willner, *Science* **2003**, 299, 1877-1881.
- [4] S. O. Obare, R. E. Hollowell, and C. J. Murphy, *Langmuir* **2002**, 18, 10407-10410.
- [5] N. Harris, M. J. Ford, M. B. Cortie and A. M. McDonagh, *Nanotech.* **2007**, 18, 36, 365301.
- [6] A Mewada, G Oza, S Pandey and M Sharon Scholars Research Library *J. Microbiol. Biotech. Res.*, **2012**, 2 ,4, 493-499
- [7] Chien-Jung Huang, Pin-Hsiang Chiu, Yeong-Her Wang, Teen-Hang Meen and Cheng-Fu Yang, *Nanotech.* **2007**, 18, 39, 395603.
- [8] S. Iijima and T. Ichihashi, *Phys. Rev. Lett.* **1986**, 56, 616-619.
- [9] C. L. Cleveland, W. D. Luedtke, and U. Landman, *Phys. Rev. B* **1999**, 60, 5065-5077.
- [10] C. Kittel, *Introduction to Solid State Physics*, seventh edition, Wiley Eastern Limited Reprint **2008**, 57.
- [11] R.P. Gupta, *Phys. Rev. B* **1981**, 23, 6265-6270
- [12] I. L. Garzón, K. Michaelian, M. R. Beltrán, A. Posada-Amarillas, P. Ordejón, E. Artacho, *Phys. Rev. Lett.* **1998**, 81, 8, 1600-1603
- [13] I. L. Garzon, K. Michaelian, M.R. Beltran, A. Posada-Amarillas, P. Ordejon D. Sánchez-Portal, and J. M. Soler *Eur. Phys. J.D* **1999**, 9, 211-215

- [14] D Kumar, V Verma, K Dharamvir and H.S.Bhatti *International Journal of Physics and Research* **2013**,3,2, 33-44
- [15] Bin Wu, Andreas Heidelberg and John J. Boland *Nature Materials* **2005**, 4,7, 525-529
- [16] <http://en.wikipedia.org/wiki/Gold>
- [17] Almaz Optics, Inc, USA.