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Impact of Shape, Size and Crystal Structure on Vacancy Related Properties of Gold Nanoparticles

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Abstract

It is necessary to consider defects to explain the electron movement, thermal transport and mechanical properties of materials. In the present study, a simple quantitative model for cohesive energy of nanoparticles is extended to determine the size, shape and crystal structure effect on vacancy formation energy, vacancy entropy, and vibrational frequency in free surface Au nanoparticles. Vacancy entropy variation with size has been studied for spherical, regular octahedral, regular hexahedral and regular tetrahedral Au nanoparticles (NP's). The computed results depict the drop in entropy with respect to size is maximum in regular tetrahedral NP's and least in spherical Au NP's. It is found from model results that vibrational frequency decrease with decrease in diameter of the nanoparticles and reduction is different for different shapes as surface atoms to volume ratio changes. The consistency of present obtained results with the results from other theoretical models supports the present formulation and predicts well the effect of size and shape on the physio-chemical properties in nanomaterials.

Keywords: Melting temperature; vacancy formation energy; vacancy entropy; size; shape parameter

INTRODUCTION

The study of physio-chemical properties of nanomaterials is the subject of interest worldwide from past few decades because of the fascinating behavior seen with size reduction to the nanometer scale. Nanomaterials possess unique and interesting properties in comparison to their bulk form as they possess a greater number of surface atoms in comparison to bulk which modify their physio-chemical properties. It is found that quantum effects begin to dominate in nanomaterials with decrease in size [1-3].

There are significant deviations in thermodynamic properties at nanoscale as surface area to volume ratio increases leading to decrease in melting temperature and cohesive energy of the material [4-7]. Debye temperature, Debye frequency, vacancy entropy and enthalpy also get affected due to decrease in size of the material to nanoscale.

Vacancies are Schottky or point defects in materials that have strong effect on thermodynamic, electrical and thermal properties of material. Vacancy is characterized by energy of formation of vacancy and entropy. As Energy required for Vacancy creation and vacancy entropy varies with size and shape of the material, so it is pertinent to take into account the shape parameter and size effect to estimate these properties. Previous studies reveal that it is quite difficult to determine experimentally the formation energy of vacancy in material [8-10]. During past few decades, various models such as surface area difference model, Guisbiers model, and pair potential method etc. have been used to predict the Energy required for Vacancy creation and vacancy entropy in nanomaterials [11-14]. In this article, a theoretical model formulated by Qi et

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al [15]. is extended to obtain expressions that predict the size, shape and crystal structure impact on vacancy related properties in the nanoparticles. The model theory is explained in section 2 and the results are discussed in section 3.

MATHEMATICAL FORMULATION

Cohesive Energy and Melting Temperature

Qi and Wang [15] expressed the cohesive energy of the solid nanomaterial E_{cN} as follows:

$$E_{cN} = E_o\left(1 - \frac{3N}{4n}\right) \tag{1}$$

Where E_o the cohesive energy in bulk material, n denotes the total atoms and N denotes the total number of surface atoms in nanomaterial.

To consider the effect of shape in nanomaterials, shape parameter α is defined as follows for spherical atoms with atomic diameter d and diameter of the nanomaterial as D[15, 16]:

$$\alpha = \frac{Surface\ area\ of\ nonspherical\ nanoparticle(S')}{Surface\ area\ of\ spherical\ nanoparticle\ (S)} \tag{2}$$

To consider the effect of crystal structure on the nanomaterial, packing fraction term P_F is included in the calculation of $\frac{N}{n}$ as follows:

$$\frac{N}{n} = \frac{Surface\ area\ of\ nanoparticle \Big/ Surface\ area\ of\ an\ atom}{(Volume\ of\ nanoparticle)X(packing\ fraction\ P_F) \Big/ volume\ of\ an\ atom}$$

$$\frac{N}{n} = \alpha\frac{4d}{DP_F} \tag{3}$$

Melting temperature and cohesive energy in bulk solid are related as follows [17]:

$$T_{mB} = \frac{0.032}{k_B}E_0 \tag{4}$$

where k_B is Boltzmann constant.

In view of equation (3), the melting temperature in nanomaterials T_{mN} is expressed as follows

$$T_{mN} = \frac{0.032}{k_B}E_{cN} \tag{5}$$

Considering eq. (4) and eq. (5), the relation between melting temperatures of nanomaterial T_{mN} and bulk T_{mB} is as follows:

$$T_{mN} = T_{mB}\left(1 - \frac{3N}{4n}\right) \tag{6}$$

Debye Temperature

In view of Lindemann criterion of melting [18, 19]; the Debye temperature θ_D and melting temperature T_m are related as follows:

$$\theta_D \propto (T_m)^{1/2} \tag{7}$$

If $\theta_{DN}; \theta_{DB}$ denote Debye temperatures of nanomaterial and its bulk counterpart, the relation between them is as follows:

$$\theta_{DN} = \theta_{DB}\left(1 - \frac{3N}{4n}\right)^{1/2} \tag{8}$$

Vacancy Formation Energy and Vibrational Frequency

Melting temperature and energy used in formation of vacancy are linearly related as both the properties are linked with electrons which follow Fermi-Dirac statistics [5, 11, 20,21]. Therefore, energy of vacancy formation in nanomaterial E_{vN} to bulk E_{vB} iswritten as follows:

$$E_{vN} = E_{vB}\left(1 - \frac{3N}{4n}\right) \tag{9}$$

As Debye frequency and Debye temperature are directly proportional; the relative vibrational frequency relation $\frac{\omega_{vN}}{\omega_{vB}}$is written as follows [14,22]:

$$\frac{\theta_{DN}}{\theta_{DB}} = \frac{\omega_{vN}}{\omega_{vB}} = \left(1 - \frac{3N}{4n}\right)^{1/2} \tag{10}$$

Vacancy Entropy

Bulk vacancy entropy S_{vB} is directly related to melting temperature T_{mB} as follows [23]:

$$S_{vB} = \frac{3}{2} k_B \, ln\left(\frac{T_{mB}}{c}\right) \tag{11}$$

Vacancy entropy S_{vN} is related to melting temperature of nanomaterial T_{mN} as follows [23]:

$$S_{vN} = \frac{3}{2} k_B \, ln\left(\frac{T_{mN}}{c}\right) \tag{12}$$

Where k_B; c are constants.

In view of equations (11) and (12), vacancy entropies of nano and bulk are related as follows:

$$S_{vN} = S_{vB} + \frac{3}{2} k_B \, ln\left(\frac{T_{mN}}{T_{mB}}\right) \tag{13}$$

In view of eq. (6) and eq. (9), considering linear relation between energy of formation of vacancy and vacancy entropy, vacancy entropy in nanomaterials can be expressed as [24]:

$$S_{vN} = S_{vB}\left(1 - \frac{3N}{4n}\right) \tag{14}$$

RESULTS AND DISCUSSION

In the present article, the effect of vacancies or defects on the thermophysical properties of Au nanoparticles (NP's) is discussed. The phenomenological model formulated by Qi et al. [15] is used and is extended to predict the impact of size, shape and crystal structure on vacancy related properties in the Au nanoparticles. As the crystal structure of Au is face centered cubic (FCC), so packing fraction is taken as 0.74 [22]. The model calculations require the value of atomic diameter D taken from reference [7]. The shape parameter for spherical and non-spherical NP's is taken from reference [16]. The input values of energy of formation of vacancy and vacancy entropy for bulk material is considered from references [25, 26].

Formation energy of vacancy and vacancy entropy remain same for bulk material but these parameters vary with size in NP's. Using eq. (3) in eq. (9), vacancy formation energyE_{vN} is determined. It is found that energy of formation of vacancy in nanoparticles reduces as its size reduces. Figure 1 shows the reduction in E_{vN} of Au spherical nanoparticles as size of the nanoparticles reduce to nano size. As melting temperature of material is linearly related to vacancy formation energy E_{vN} of the material experimentally [10], it is clear that E_{vN} decreases with decrease in diameter to nanoscale. The present predicted results for Au (spherical) NP's are observed in agreement with the results obtained from Guisbiers model [14]. Equation (11) relates the entropy to melting temperature [23]. Figure 2 shows the vacancy entropy change in Au NP's with change in size of the particle. The calculated results obtained using eq. (14) shows the drop in entropy with size reduction to nano regime. It is found that

the predicted results obtained using eq. (14) is consistent with the previous theoretical results [14]. It is found that variation trend in vacancy entropy of nanoparticles with size is similar to that in previous results [24]. Figure 3 show the vacancy entropy change with respect to size in Au spherical NP's, regular tetrahedral, regular octahedral and regular hexahedral NP's. The computed results show that the drop in entropy with respect to size is maximum in regular tetrahedral NP's as they possess a greater number of surface atoms in comparison to other while drop in entropy is least in spherical Au NP's. The figure plotted depicts the effect of shape and size on vacancy entropy of Au nanoparticles.

The electrical, thermal and optical properties of nanomaterials get strongly affected by large surface area to volume ratio of nanomaterials due to phonon scattering and in turn affect the optical properties of material. Debye frequency as well as Einstein frequency is directly related to Debye temperature [22, 27]. Eq. (10) explains the drop in Debye temperature with size reduction led to reduction in vibrational frequency.

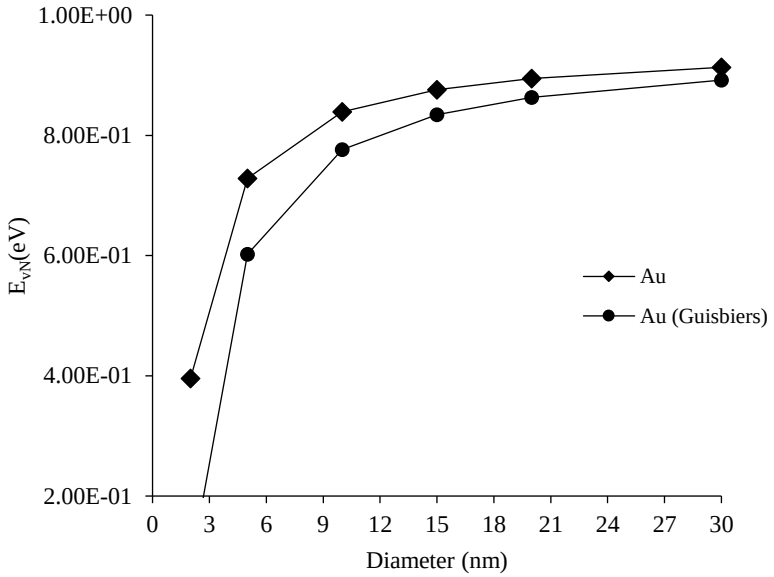

Figure 1. Vacancy formation energy versus size in Au spherical NP's.

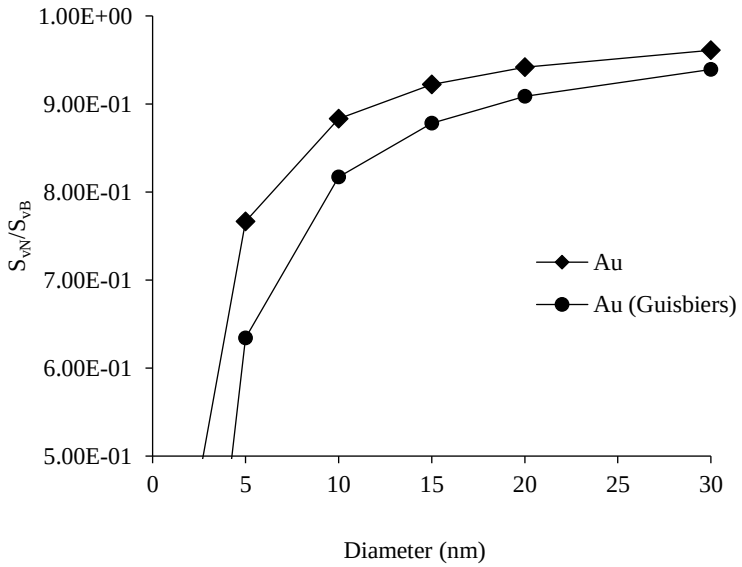

Figure 2. Relative vacancy entropy versus size in Au spherical NP's.

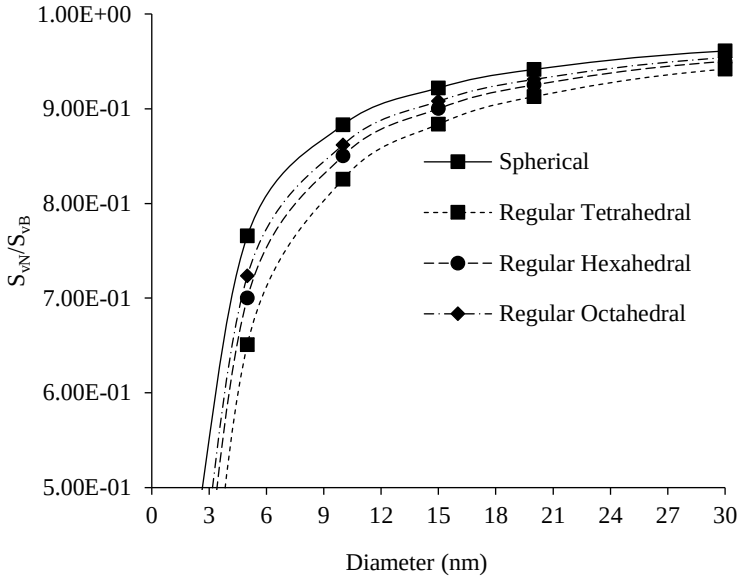

Figure 3. Relative vacancy entropy versus size in Au NP's of different shapes.

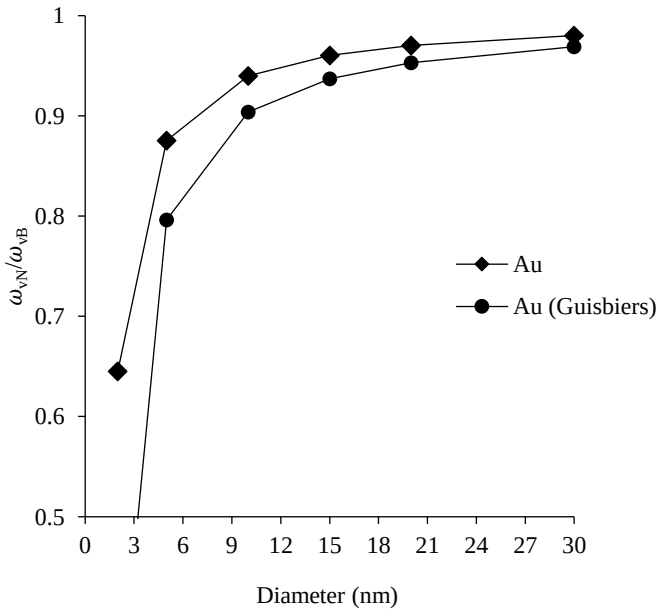

Figure 4. Relative vibrational frequency versus diameter in Au spherical NP's.

The relative change $\frac{\omega_{vN}}{\omega_{vB}}$ in Au spherical nanoparticles with diameter is studied using eq. (10). The results of variation of $\frac{\omega_{vN}}{\omega_{vB}}$ with size are depicted in Figure 4 with the Guisbiers models results [14]. It is noted that variation trend matches with the previous studies.

Breaking of chemical bonds results in the formation of vacancies. As number of broken bonds increases with size reduction of the material, vacancies get formed easily in material. Increase in the concentration of vacancies at nano regime results in decrease in vacancy formation energy, vacancy entropy. Vacancies results in increase in electrical resistivity and thereby affects the scattering of electrons [28]. This results in less efficient thermal and electron transport in nanomaterials.

CONCLUSION

In the present paper, the influence of size, shape and crystal packing fraction on the vacancy formation energy, vacancy entropy and vibrational frequency of gold nanoparticles is studied using a simple model. Vacancies are created in solid due to the breaking of bonds and results in increase in resistivity. It is noted that concentration of vacancies increases in nanoparticles with size reduction to nano regime.

REFERENCES

1. Richman EK, Hutchison JE. The nanomaterial characterization bottleneck. ACS Nano. 2009; 3(9): 2441-6p. doi: 10.1021/nn901112p.
2. Yeo YH, Oh TS. Thermoelectric properties of *p*-type $(Bi,Sb)_2Te_3$ nanocomposites dispersed with multiwall carbon nanotubes. Mater. Res. Bull. 2014; 58:54-5p. doi: 10.1016/j.materresbull.2014.04.046.
3. Roduner E. Size matters: why nanomaterials are different. Chem. Soc. Rev. 2006; 35(7): 583-10p. doi:10.1039/B502142C.
4. Goyal M, Gupta BRK. Shape and size dependent thermophysical properties of nanocrystals. Chinese J. Physics. 2018; 56 (1):282-10p.
5. Safaei A. Cohesive energy and physical properties of nanocrystals. Philosophical magazine. 2011; 91: 1509-31p.doi:10.1080/14786435.2010.548836.
6. Jiang Q, Zhang SH, Li JC. Grain size-dependent diffusion activation energy in nanomaterials. Solid stat. Commun. 2004; 130 (9): 581-5p. doi: 10.1016/j.ssc.2004.03.033
7. Goyal M, Goyal V. Effect of size and temperature on vacancy concentration in nanomaterials, Pramana J. Phys, 2021; 95 (3): 99. 10.1007/s12043-021-02127-8
8. Agullo-Lopez F, Catlow CRA, Townsed PD. Point defects in materials (Academic Press, London 1988: 445 p.
9. Muller M, Albe K. Concentration of thermal vacancies in metallic nanoparticles. Acta Materialia. 2007; 55 (9): 3237-8p.
10. Gladkikh NT, Kryshtal OP. On the size dependence of the vacancy formation energy. Funct. Mater. 1999;6 (5): 823-5p.
11. Qi W. Size- and coherence-dependent thermodynamic properties of metallic nanowires and nanofilms. Modern Physics Letters B. 2006; 9 (20): 1943-9p. Doi:10.1142/S0217984906012092.
12. Ouyang G, Zhu WG, Yang GW, Zhu ZM. Vacancy Formation Energy in Metallic Nanoparticles under High Temperature and High Pressure. J. Phys. Chem. C. 2010; 114 (11): 4929-5p. DOI: 10.1021/jp100583n.
13. Qi WH, Wang MP, Zhou M, Hu WY. Surface-area-difference model for thermodynamic properties of metallic nanocrystals. J. Phys. D. Appl. Phys. 2005; 38 (9): 1429.doi:10.1088/0022-3727/38/9/016.
14. Guisbiers G. Schottky Defects in Nanoparticles. The J. of Physical Chemistry C. 2011; 115 (6): 2616-6p. doi:10.1021/jp108041q.
15. Qi WH, Wang MP. Size and shape dependent melting temperature of metallic nanoparticles. Material chem. & Phys. 2004; 88(2-3): 280-5p. doi: 10.1016/j.matchemphys.2004.04.026
16. Qi WH, Wang MP, Liu QH. Shape factor of nonspherical nanoparticles. Journal of material science. 2005; 40: 2737-3p.doi:10.1007/s10853-005-2119-0.
17. Shanker J, Kumar M. Studies on Melting of Alkali Halides. Phys. Status. Solidi. B. 1990; 158 (1990) 11.doi:10.1002/pssb.2221580102.
18. Lindemann F A. The calculation of molecular vibration frequencies. Phys. Z. 1910; 11: 609-4p.
19. Dash JG. History of the search for continuous melting. Rev. Mod. Phys.1999; 71:1737. doi:10.1103/RevModPhys.71.1737
20. Guisbiers G, Buchaillot L. Universal size/shape-dependent law for characteristic temperatures. Phys. Lett. A. 2009; 374 (2): 305-4p. doi: 10.1016/j.physleta.2009.10.054
21. Guisbiers G. Size-dependent Materials Properties Toward a Universal Equation. Nano Res. Lett. 2010; 5 :1132. https://dx.doi.org/10.1007%2Fs11671-010-9614-1

22. Kittel C. Introduction to Solid State Physics, 7 th Edition, John Wiley & sons, New York, 1996.
23. Regel AR, Glazov VM. Entropy of melting of semiconductors. Semiconductors. 1995; 29: 405.
24. Skordas ES. On a universal relation for defect data in solids. Phys. B. 2010; 405 (20): 4320-3p. DOI: 10.1016/j.physb.2010.07.034.
25. Bollmann W, Uvarov NF, Hairetdinov EF. Estimation of point defect parameters of solids on the basis of a defect formation model of melting (II). Vacancy formation enthalpy in relation to the heat of fusion and the increase of volume due to melting. Crystal Res. Technol. 1989; 24 (1989) 421.doi:10.1002/crat.2170240418.
26. Wautelet M. Estimation of the variation of the melting temperature with the size of small particles, on the basis of a surface-phonon instability model. J. Phys. D.: Appl. Phys. 1991; 24 (3): 343. doi:10.1088/0022-3727/24/3/017.
27. Yang CC, Li S. Investigation of cohesive energy effects on size-dependent physical and chemical properties of nanocrystals. Phys. Rev. B. 2007; 75 (16):165413. doi:10.1103/PhysRevB.75.165413.
28. Kraftmakher Y. Equilibrium vacancies and thermophysical properties of metals. Phys. Rep. 1998; 299(2-3): 79-110 p.doi:10.1016/S0370-1573(97)00082-3

