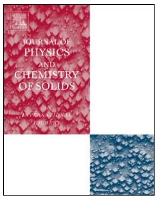
Journal of Physics and Chemistry of Solids 108 (2017) 1–8

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



Size dependent structural stability of Mo, Ru, Y and Sc nanoparticles

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ARTICLE INFO

Keywords:
Size effect
Phase transition
Nanoparticles
Gibbs free energy
Phase diagram

ABSTRACTS

The Gibbs free energy model was generalized to predict the phase stability of Mo, Ru, Y and Sc at all size range from nanometer to bulk size. The size-, shape- and temperature-dependent phase diagrams of Mo, Ru, Y and Sc were firstly computed to explain the corresponding experimental observations, including the latest one on Ru nanoparticles. Especially, we re-confirmed and summarized that there exists a general law for the stable phases of metal nanoparticles: for body-centered-cubic (BCC) metals (eg. Mo), there exists face-centered-cubic (FCC) phase at small size; for a kind of hexagonal-close-packed (HCP) metals (eg. Ru), they can transform into FCC at small size; for the other kind of HCP metals (eg. Sc or Y), they can change to BCC at high temperature (Y at 1754 K, and Sc at 1588 K) but to FCC at small size. This work establishes a map of the evolution of the structures from macro to nanoscale.

1. Introduction

Nanoparticles have attracted the attention of researchers in different fields. Due to large surface-to-volume ratio and high fraction of undercoordinated atoms at surface [1], nanoparticles show unique properties depending on the particle size and shape [2–5], such as melting temperature [6,7], cohesive energy [8,9] and order-disorder transition [10,11].

Structure transition is an important phenomenon in solids, while the transition at nanoscale is different from the bulk due to surface effect. Some stable phases present at nanoscale though does not exist in bulk materials. Kim et al.[8] prepared the stable face-centered-cubic (FCC) Mo nanoparticles in the size of 4 nm, although the FCC is unstable in bulk Mo. Kohei Kusada *et al.*[12] discovered the pure FCC Ru nanoparticles with the size of 2–5.5 nm by simple chemical reduction methods with different metal precursors. By annealing the FCC Ru nanoparticles up to 723 K, Kusada proved that the FCC Ru particles are stable when the size is smaller than a critical value. Though the FCC does not exist in the bulk phase diagram, the FCC Ru particles have been obtained because of the size effect. It is also reported that the phase transitions from hexagonal-close-packed (HCP) to body-centered-cubic (BCC) for Ti, Zr and Hf will take place by increasing the temperature or the pressure [13–15]. Manna et al. found that there exist structural transitions from HCP to FCC for Ti and Zr when the crystal size decreases to several nanometers during the high-energy ball milling process [16,17]. The transition from HCP to FCC for nanosized Hf was also observed in the high-energy ball milling experiments [18]. Similar phase transformations are also found in Nb [19], W [20] and V nanoparticles [21].

Researchers use Gibbs free energy to study the structural transitions of nanomaterials. Jiang et al.[22] used the size dependent surface free energy and elastic energy to compute the Gibbs free energy differences. Barnard et al.[23] developed a model for predicting the phase transitions of nanoparticles by considering the contributions from the surfaces, edges and corners to Gibbs free energy. Xiong and Qi et al.[24,25] generalized the Debye model of the Helmholtz free energy (HFE) for bulk materials to calculate the Gibbs free energy (GFE) of nanoparticles.

In this work, the Gibbs free energy of nanoparticles is formulized to describe the phase transitions of Mo nanoparticle (BCC is stable in bulk Mo) and Ru nanoparticle (HCP is stable in bulk Ru). Furthermore, the Gibbs free energies of Y and Sc are also calculated and their phase transitions at nanoscale are predicted.

2. Model

According to Debye Model, the Helmholtz free energy can be written as [24].

$$F = E_c + E_D - TS_D \tag{1}$$

where E_c is the cohesive energy. E_D and S_D is the lattice vibrational energy and vibration entropy, respectively. In Debye model, E_D and S_D can be expressed as

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http://dx.doi.org/10.1016/j.jpcs.2017.04.010
Received 14 January 2017; Received in revised form 30 March 2017; Accepted 18 April 2017

$$E_D = 3k_BTB\left(\frac{\Theta}{T}\right)+E_0 \tag{2}$$

$$S_D = 4k_B\left[B\left(\frac{\Theta}{T}\right) - \frac{3}{4}\ln\left(1 - e^{-\frac{\Theta}{T}}\right)\right] \tag{3}$$

where k_B and Θ are Boltzmann constant and Debye temperature, respectively. $E_0=9k_B\Theta/8$ is the energy of zero-point lattice vibrations. $B(\frac{\Theta}{T}) = 3(T/\Theta)^3\int_0^{\Theta/T}(x^3/(\exp x - 1))dx$ is the Debye function. The Helmholtz free energy for bulk material can be written as

$$F_b = E_b + 3k_BT\ln\left(1 - \exp\left(\frac{-\Theta}{T}\right)\right) - k_BTB\left(\frac{\Theta}{T}\right) \tag{4}$$

Different from bulk material, nanoparticles have different values in lattice vibrational energy, entropy, cohesive energy and Debye temperature due to the dangling bonds existing on the surface. According to the core-shell model, the total atoms of a nanoparticle are classified as surface and inner atoms. Then the Helmholtz free energy for the nanoparticle can be expressed as [24].

$$F_n = NE_n+(N - n)(E_D-TS_D) + n(E^s_D-TS^s_D) \tag{5}$$

where N and n are the total and the surface atom number, respectively. The inner atoms are regarded as the same as bulk atoms. Due to the lower coordination, the outmost atomic layer is considered as the shell, which exhibits different vibrational amplitude (x) and frequency (ω). Sun [1] reported the relationship of x and ω between surface atoms and bulk atoms as

$$\frac{x_s}{x_b} = 1.43 \tag{6}$$

$$\frac{\omega_s}{\omega_b} = 0.404 \tag{7}$$

By regarding the lattice vibration as a spring oscillator, the vibrational energy of surface atoms (E^s_{vib}) and the entropy (S^s_{vib}) of surface atoms are expressed as

$$E^s_D = \left(\frac{x_s}{x_b}\right)^2 E_D \tag{8}$$

$$S^s_D = S_D+\Delta S_D \tag{9}$$

where the energy of zero-point lattice vibration energy is neglected in Eq. (8). For ΔS_D, the vibrational frequency change can be written as $\Delta S_D=3k_B\ln\left(\frac{\omega_b}{\omega_s}\right)$ in terms of the statistic mechanics. Accordingly, the vibrational energy of surface atoms (E^s_{vib}) and entropy of surface atoms (S^s_{vib}) are

$$E^s_D = 6k_BTB\left(\frac{\Theta}{T}\right) \tag{10}$$

$$S^s_D = 4k_B\left[B\left(\frac{\Theta}{T}\right)-\frac{3}{4}\ln\left(1 - e^{-\frac{\Theta}{T}}\right)\right]+2.7k_B \tag{11}$$

Then the Helmholtz free energy of nanoparticle is

$$F_n = NE_n+(N - n)(E_D-TS_D)+n(E^s_D-TS^s_D) = NE_n+3Nk_B T\ln\left(1 - e^{-\frac{\Theta}{T}}\right)-Nk_BTB\left(\frac{\Theta}{T}\right)+nk_BT\left[3B\left(\frac{\Theta}{T}\right)-2.7\right] \tag{12}$$

The number of the surface atoms can be computed as $n = \pi\alpha f_i^{-2/3}N^{2/3}$ and the total number of nanoparticle atoms $N = f_i\frac{d^3}{D^3}$ [26], where d and D are the diameter of atoms and nanoparticles, respectively. The f_i is the packing faction related to crystal structures (f_i=0.74 for FCC and HCP structures and f_i=0.68 for BCC structure). The shape factor [27] α is used to describe the shape difference between the spherical and other shape nanoparticles ($\alpha = 1$ for spherical nanocrystal to $\alpha = 1.49$ for tetrahedral nanoparticle). Thus $\frac{n}{N} = \frac{\alpha\pi d}{f_iD}$, and then we can get the Helmholtz free energy for a nanoparticle

$$F_n = N_AE_n+3RT\ln\left(1 - e^{-\frac{\Theta}{T}}\right)-RTB\left(\frac{\Theta}{T}\right)+\frac{\alpha\pi d}{f_iD}RT\left[3B\left(\frac{\Theta}{T}\right) - 2.7\right] \tag{13}$$

where $R=k_BN_A$ with N_A is the Avogadro constant. The size, structure and shape dependent cohesive energy of nanoparticles can be written as [28].

$$E_n = E_b\left(1 - \alpha\pi C^*\frac{d}{D}\right) \tag{14}$$

in which C is the structure related constant. E_b is the cohesive energy of bulk material. According to Lindemann melting criterion, the relationship of the melting temperature T_{nm} and the Debye temperature can be given as follows [29–31].

$$\frac{T_{nm}}{T_{bm}} = \left(\frac{\Theta}{\Theta_b}\right)^2 \tag{15}$$

where Θ_b and T_{bm} denote the Debye temperature and the melting temperature of bulk solid, respectively. For the melting temperature of nanoparticles considering relaxation can be written as [32].

$$T_{nm} = T_{bm}\left(1 - \frac{\alpha d}{D}\right) \tag{16}$$

then we have

$$\Theta = \Theta_b\left(1 - \frac{\alpha d}{D}\right)^{1/2} \tag{17}$$

The Gibbs free energy of solids can be written as

$$G = F + PV_m \tag{18}$$

where P and V_m are the pressure and volume, respectively. For bulk material, P can be neglected if there is no additional pressure. However the pressure cannot be ignored due to the large value in terms of Laplace-Young equation [33–35].

$$P = \frac{-4f}{D} \tag{19}$$

where f denotes the surface stress *f* can be computed approximately as [24].

$$f = 0.628\left(\frac{d^2S_mH_m}{\kappa RV_m}\right)^{1/2} \tag{20}$$

in which κ, S_m and H_m are the bulk values of compressibility, melting entropy and melting enthalpy, respectively. Then we can predict the Gibbs free energy of nanoparticles.

3. Results and discussions

The GFE of Mo, Ru, Y and Sc bulk materials with BCC, FCC and HCP structures were calculated to study their structural transition. Chung [36] reported the Voigt-Reuss-Hill (VRH) values to estimate the bulk modulus B and Poisson ratio ν [37–39], and then obtained the Debye temperature Θ as [40].

$$\Theta = k(\nu)\frac{\hbar}{k_B}(48\pi^5)^{1/6}\sqrt{\frac{r_0B}{M}} \tag{21}$$

where $k(\nu) = \left(\frac{1}{3}\left\{\left[\frac{1+\nu}{3(1-\nu)}\right]^{\frac{3}{2}} + 2\left[\frac{2(1+\nu)}{3(1-2\nu)}\right]^{\frac{3}{2}}\right\}\right)$ and M is the atomic weight. r_0 is the equilibrium W-S radius, defined by $\frac{4\pi r_0}{3}$=M/ρ. We obtained the Debye temperatures of Ru, Sc and Y with HCP structures in the same method. For FCC-Y, FCC-Ru and FCC-Sc, the elastic constants are calculated by first principle method (see Support