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Effects of grain size and thermodynamic energy on the lattice parameters of metallic nanomaterials

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ABSTRACT

A thermodynamic method based on surface thermodynamics and atomic bond energy was developed to accurately investigate the lattice distortion rates of metallic nanomaterials. The results indicated that the lattice distortion rates of nanomaterials follow an inverse proportional relationship with the size, in good agreement with the experimental results. In this method, the anisotropy of the lattice distortion was a considerable issue. We found that the surface tension and Young's modulus of the nanocrystals, compared with those of the bulk materials, change because of the lattice distortion and exhibit a linear relationship at the nanoscale. By defining a shape factor (ξ), the lattice distortion rates of nanoparticles, nanowires, and nanofilms were calculated. This method provides a new approach for the evaluation of the lattice distortion rates in nanomaterials.

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1. Introduction

As a bridge spanning between the atomic level and its bulk counterpart, the lattice parameters of metallic nanomaterials have become an active area of research in material science [1]. Recent experimental observations show that the lattice parameters of metallic nanomaterials are size dependent. For most metallic materials, the lattice parameters decrease with decreasing the size [2]; however, some reports highlight the opposite behavior, describing an increase of the lattice parameters when the size is reduced. A typical example is provided by Palkar et al. [3], who reported a lattice expansion as the particle size of CuO decreased. However, Borgohain et al. [4] reported the opposite result, and the only difference between the two studies resided in the adopted synthesis procedure [5].

Meanwhile, researchers have proposed several models to investigate the lattice distortion. Sun et al. [6] and Wolfer et al. [7] proposed a surface-atom-bond contraction model. Obviously, this method, which is based on atomic bonds, is considered the most basic and intuitive, but is also considerably complicated. Wagner et al. [8] and Qin et al. [9] developed a model based on grain boundaries and vacancies to explain the lattice expansion as the particle size decreases. The results were confirmed by electron microscopy observations, which indicated that vacancies often

lead to a lattice expansion. Yu et al. [10] and Jiang et al. [11–13] proposed some models based on surface tension, surface stress, and elastic modulus. In fact, Young's modulus and atomic bond energy are associated. Nanda et al. [14] postulated that a nanoparticle can be described as a liquid drop. However, this method implies that the surface tension and elastic modulus do not decrease with the size, and it is indeed possible to come to incorrect conclusions for nanoscale materials [15].

Furthermore, Yu et al. [10] observed that the contraction of the c-lattice is more significant than that of the a-lattice. To resolve this problem, Nanda et al. [14] examined different crystal structures based on the internal and external pressures. In addition, Jiang and Qi [11–13] studied different shapes and crystal surfaces.

Moreover, Findik et al. [16–21] and Lei et al. [22] considered the spinodal decomposition and discrete dynamical model to study the thermodynamic energy of metal materials, achieving some interesting results. Currently, a thorough research study on the surface-atom-bond contraction model based on surface tension, surface stress, and elastic modulus has not yet been proposed. In this work, we try to establish the relationship between the lattice distortion and the size of the nanocrystal to investigate their intrinsic properties by using the surface thermodynamic method.

2. Relationship between lattice distortion rate and nanosize

From surface thermodynamics considerations, the surface atom bond energy is different from that of the atoms located inside the

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crystal. This unbalanced energy may cause the surface-atom-bond contraction. For a spherical particle, the Laplace equation is used to calculate the pressure [10]:

$$\Delta P = \frac{2\sigma}{R} \tag{1}$$

where ΔP is the difference in pressure inside and outside the spherical particle, and σ and R are the surface tension and the radius of the spherical particle, respectively.

Furthermore, a relationship between the difference in pressure, spherical particle volume, and bulk modulus is given by [14,21]

$$\Delta P = -K \cdot \frac{\Delta V}{V} = -\frac{3K\Delta a}{a} \tag{2}$$

where ΔV is the volume change of the spherical particle caused by the surface tension; V is the total volume of the spherical particle; K is the bulk modulus, which refers to the compressibility of the material ($K = Y/[3(1 - 2\mu)]$, where Y is Young's modulus and μ is Poisson's ratio); a is a lattice parameter.

Following Eqs. (1) and (2), the lattice distortion rate ($\Delta a/a$) is given by

$$\frac{\Delta a}{a} = -\frac{2\sigma}{3K} \cdot \frac{1}{R}. \tag{3}$$

For bulk crystal materials, $\Delta a/a$ and the grain radius exhibit an inverse proportional relationship because of the surface tension σ and the fact that the bulk modulus is considered as a constant. However, the surface tension and Young's modulus are size dependent for nanoscale crystal materials [23].

According to the broken-bond rule, the surface energy W is equal to [24]

$$W = \frac{1}{2} \cdot Z \cdot N \cdot E_{atom} \cdot A \tag{4}$$

where Z is the change of the coordination number of the lattice, N is the lattice area, E_{atom} is the atomic binding energy of the bulk material, and A is the increase of the surface area. From Eq. (4), the surface tension σ can be expressed as

$$\sigma = \frac{1}{2} \cdot Z \cdot N \cdot E_{atom} \tag{5}$$

Thus, according to Eq. (5), the surface tension σ and atomic binding energy E_{atom} have a proportional relationship [10].

On the other hand, the atomic binding energy E_{atom} is proportional to the cohesive energy E. In addition, it was demonstrated that the cohesive energy is size dependent, and that the surface tension is proportional to the cohesive energy E in nanoscale systems [13]. Therefore:

$$\frac{\sigma_{nano}}{\sigma_{bulk}} = \frac{E_{nano}}{E_{bulk}}. \tag{6}$$

Furthermore, some reports indicate that Young's modulus Y, the atomic bond energy, and cohesive energy are associated [15]. Consequently:

$$\frac{Y_{nano}}{Y_{bulk}} = \frac{E_{nano}}{E_{bulk}} = \frac{\sigma_{nano}}{\sigma_{bulk}}. \tag{7}$$

Combining Eq. (3) and Eq. (7),

$$\left(\frac{\Delta a}{a}\right)_{nanoscale} = -\frac{2(1 - 2\mu)\sigma_{bulk}}{Y_{bulk}} \cdot \frac{1}{R}. \tag{8}$$

In Eq. (8), Poisson's ratio μ, surface tension σ_{bulk}, and Young's modulus Y_{bulk} are all constant. As a result, there is an inverse proportional relationship between the lattice distortion rate of the nanoscale crystal materials and the grain radius.

3. Results and discussion

3.1. Lattice distortion of nanoscale metals

Fig. 1 shows the variation of the lattice distortions rates with the radius of Ag, Al, Au, Cu, Pd, and Pt spherical nanoparticles. The solid line is given by Eq. (8). The data used for the calculation are listed in Table 1 [25–27]. The reported experimental data for Ag [28,29], Al [29,30], Au [29,31], Cu [32], Pt [32], and Pd [33,34] are represented by the corresponding symbols. We found that the lattice parameters of the metallic Au, Cu, Al, Pt, Pd, and Ag nanocrystals are size dependent. According to Eq. (8), the lattice distortion rate of the Au nanoparticles was approximately 0.08% for a particle radius of 6 nm. The value of $\Delta a/a$ gradually increased to 0.50% as the radius decreased to approximately 1 nm, exhibiting a sharp increase as the particle radius continued to decrease. The value of $\Delta a/a$ was around 2.50% when the radius reached the value of 0.2 nm. The reported experimental data are shown in Fig. 1a for comparison. The results indicated that the values obtained from Eq. (8) were in good agreement with the experimental data.

The lattice distortion rates of the Al, Au, Cu, Pd, and Pt nanoparticles exhibited the same relationship with the nanoparticle size, as shown in Fig. 1b–f. All the results from Eq. (8) agreed well with the corresponding experimental results.

Fig. 2 shows the variation of the lattice distortions rates $\Delta a/a$ and $\Delta c/c$ with the size for Sn and Bi nanoparticles. Notably, Sn element has a tetragonal crystal structure and a ratio of $c/a = 3.28237$ ($c > a$). From Eq. (5) we found that the coordination number of the lattice (Z) and the atomic binding energy of the bulk material (E_{atom}) are constant, but the lattice area is different. Therefore $\Delta a/a$ is smaller than $\Delta c/c$ and $\Delta c/c = K \cdot \Delta a/a$ is reasonable. The results show that the lattice distortion $\Delta c/c$ is greater than $\Delta a/a$ consistently with the experimental results, as shown in Fig. 2a. Elemental Bi has a rhombohedral crystal structure and a ratio of $c/a = 3.86741$ ($c > a$). Its behavior is also consistent with Eq. (8). The lattice distortion rates along the a and c directions agree well with the experimental results, as shown in Fig. 2b.

All the results have theoretically and experimentally demonstrated that Eq. (8) can accurately describe the lattice distortion in nanoscale crystals. The lattice distortion rates follow an inverse proportional relationship with the radius of the nanoscale materials.

3.2. Surface tension and Young's modulus of nanoscale metals

The cohesive energy $E(r)$ of the materials can be given by [11]

$$E(r) = \left(\frac{p \cdot q}{p - q}\right) \cdot E_{atom} \cdot \left[\left(\frac{a}{r}\right)^p \cdot \frac{1}{p} - \left(\frac{a}{r}\right)^q \cdot \frac{1}{q}\right] \tag{9}$$

where p and q are constant, a is lattice parameter, and r is the distance between the atoms.

For metals, $p = 12$ and $q = 6$. From Eq. (9), we have:

$$\frac{dE(r)}{dr}\Big|_{r=r_0} = 0 \quad \text{and} \quad -\frac{d^2E(r)}{dr^2}\Big|_{r=r_0} = E \cdot \frac{72}{r_0^2} \tag{10}$$

where r_0 is the equilibrium distance between the atoms. Eq. (2) can be rewritten as

$$K = -V \cdot \frac{dP}{dV} = -V\frac{\partial}{\partial r}\left[-\frac{\partial E(r)}{\partial r} \cdot \frac{dr}{dV}\right] \cdot \frac{dr}{dV}. \tag{11}$$

From Eqs. (10) and (11), based on the model of Sun and Jiang [6,11], we have

$$K = c \cdot \frac{E_{atom}}{r_0^3} \tag{12}$$