COMMENT

The lattice contraction of nanometre-sized Sn and Bi particles produced by an electrohydrodynamic technique

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Abstract.   The observed lattice contraction of nanoparticles is attributed to both the surface bond that contracts with coordination number reduction of surface atoms, and the surface-to-volume ratio that increases with decreasing particle size. Surface bond contraction varies with materials and crystalline orientations while the surface-to-volume ratio depends on particle shape and size.

The lattice constant of a crystal is of great importance in determining the intensity of atomic interaction as well as the crystal field of the entire solid. The contraction of the lattice constant will increase the crystal field and hence the forbidden band gap. Recently, Yu *et al* [1] found that the values of lattice constants of Sn and Bi nanoparticles contract with the decrease of particle size. The contraction of the *c*-lattice is more significant than that of the *a*-lattice. The lattice variation in nanoparticles was attributed by Yu *et al* to the supersaturation of the vacant lattice sites in the nanoparticles. The interesting results of Yu *et al* and similar findings by others cited therein challenge for an approach to correlate the lattice contraction with the particle size. In this note, an additional mechanism is presented, in which the surface-bond contraction dominates the lattice contraction in nanoparticles.

In 1927, Goldschmidt [2] specified that the ionic radius of an atom contracts by 4% , 6% and 12% with the reduction of the atomic coordination number (CN) from 12 to 8, 6, and 4. Similarly, Pauling [3] formulated that the metallic radius of a metal atom also contracts with reduction of the CN. For Cu for instance, the radius reduces from 0.128 to 0.117 nm when Cu changes its CN from 12 to 1, or a single bond. Obviously, CN-reduction only takes place near or at the surface. The effect of surface-bond contraction plays an important role in oxygen chemisorption [4, 5] and the band-gap enlargement of nanoclusters [6].

For a spherical particle with radius R there are k atoms arranged along the R. The surface-to-volume ratio of a particular ith layer is

$$\gamma_i = \frac{N_i}{N} = \frac{4\pi[(k-(i-1))d]^2 d_i}{\frac{4}{3}\pi(kd)^3} = \frac{3}{k}\left(1 - \frac{i-1}{k}\right)^2 \qquad (R = kd) \qquad (1)$$

N_i is the total number of atoms in the ith shell of the sphere and N is the total number of atoms of the entire particle; d_i is the diameter of the atom in the ith layer and d is the average atomic diameter. The i counts from the outermost layer to the centre of the particle.

Generally, for a nanoscale particle

$$\gamma_i = \frac{n}{k}\left(1 - \frac{i-1}{k}\right)^{n-1} \qquad (R = kd) \qquad (2)$$

where $n = 1, 2, 3$ corresponds to the nanoscale plate, rod and spherical dot. Figure 1 shows the size and shape dependence of surface-to-volume ratio of the nanoscale rod, plate and spherical dot.
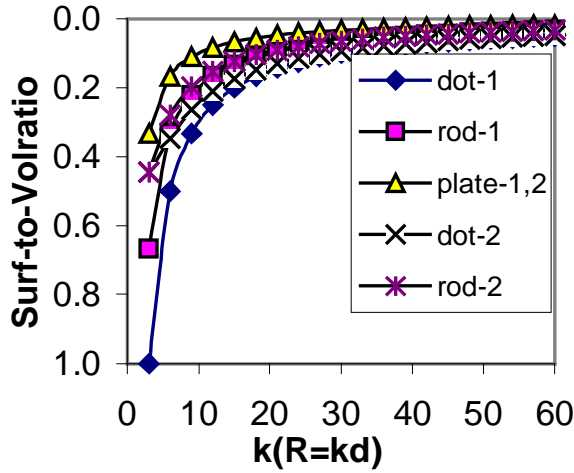
Figure 1. Particle size (k) and shape dependence of the surface-to-volume ratio, γ_1 and γ_2, of nanoscale dots, rods and plates.

We may define the surface bond contraction factor $q_i = d_i/d_0$, and $i = 1, 2, 3$ has been proven sufficient in considering the surface bond contraction. For $i > 3$, $q_i = 1$. Therefore, the average lattice constant in a nanoparticle is,

$$\overline{d} = \frac{\sum N_i q_i d_0 + [N - \sum N_i]d_0}{N} = d_0 \sum [\gamma_i(q_i - 1)] + 1 \qquad (3)$$

and consequently,

$$\frac{\Delta d}{d_0} = \frac{\overline{d} - d_0}{d_0} = \sum \gamma_i(q_i - 1) = \sum \gamma_i q_i. \qquad (4)$$

The relative change of the lattice constant of a particle depends on both the surface-to-volume ratio γ_i and the CN-determined bond contraction, q_i', of surface atoms.

By adjusting the contraction factors, the lattice contraction [1] of Sn and Bi is simulated as given in figure 2. Acceptable agreement is achieved within the error. The possible errors in experiment may come from the shape and sizes of the particles. As can be seen from equation (2) and figure 1, the surface-to-volume ratio of a rod is 2/3 times that of a dot. Besides, the fact that the c-lattice contracts more significantly than that of the a-lattice may be indicative that the CN varies with crystal orientation.

Briefly, the observed lattice contraction is dominated by the surface bond contraction that involves two factors. One is the surface-to-volume ratio and the other is the reduced CN of surface atoms. The supersatuation of the lattice vacancies, as suggested by Yu *et al*, may modify the absolute values but no the trends as the lattice vacancies also shorten the bond length of the atoms surrounding the vacancies due to the lowered CN. However, correlation needs to be established between the vacancy density and particle size. It is anticipated that the lattice contraction will be significant when the particle size is smaller than 10 nm and that this phenomenon is independent of processing conditions or any particular element. The contraction factors may vary with material and crystal orientation. For instance, the lattice contracts by 2.4% of 5 nm Ni particles [7], one to two orders higher than the Sn and Bi particles.
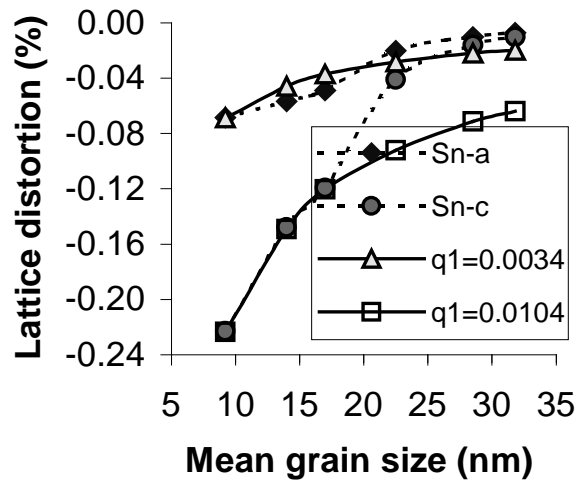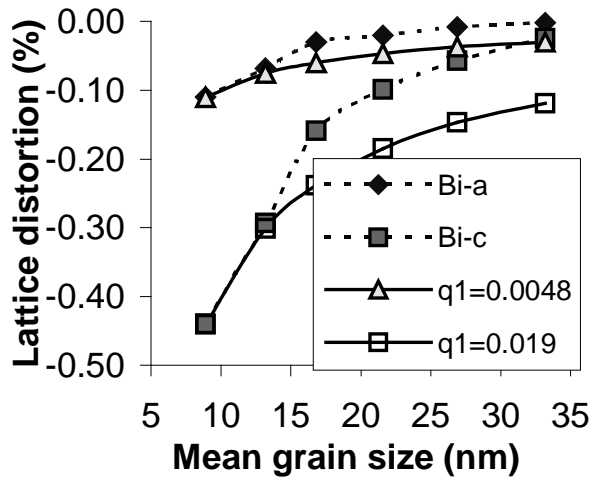
Figure 2. Simulation of the experimental observations (broken lines) of Yu *et al* [1]. Agreement is acceptable within error by introducing different bond contraction parameters, as indicated. Atomic radii of 0.162 and 0.170 nm were used for Sn and Bi, respectively.

References

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