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COMMENT

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

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Abstract

The size dependence of lattice contraction can be understood by assuming the nanoparticles to be a liquid drop and that there exists a pressure difference (Δp) between the inside and outside of the liquid drop. The analysis of the experimental data of Yu *et al* on the lattice contraction reveals that the isothermal compressibility is different for different orientations of the lattice plane, which is in good agreement with earlier reported data.

Recently, Yu *et al* [1] observed lattice contraction in Sn and Bi nanoparticles and that the contraction of the *c*-lattice is more significant than that of the *a*-lattice. It is important to note that the structure of Sn is tetragonal and that of Bi is rhombohedral. According to Yu *et al* [1] the lattice variation in nanoparticles was attributed to the supersaturation of the vacant lattice sites in the nanoparticles. On the other hand Sun [2] has argued that the supersaturation of lattice vacancies does not explain the particle size dependence of the lattice parameter. He has shown that surface-bond contraction associated with the co-ordination number reduction of surface atoms as well as the large surface-to-volume ratio for small particles explain the lattice contraction in nanoparticles. However, there is no solid basis for the surface bond contraction to depend on the crystal orientation. In this comment, we show that the lattice contraction associated with decreasing crystalline size can be understood by considering the particle as a liquid drop [3]. The thermodynamical relation for a liquid drop in equilibrium is

$$\Delta p \, dV = \gamma \, dF$$

where $\gamma \, dF$ is the surface energy (γ is the surface tension coefficient, dF is the surface area) and $\Delta p \, dV$ is the work (Δp is the difference in pressure inside and outside the particle). The pressure difference Δp inside a spherical particle with diameter d is given by

$$\Delta p = 4\gamma/d.$$

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If the small particles are crystalline and cubic in structure with lattice constant a , then the relative lattice contraction is given by

$$\frac{\Delta a}{a} = \frac{4}{3} \frac{\gamma \kappa}{d} \quad (1)$$

where κ is the compressibility of the material related to Δp and $V_0 (= a^3)$ as $\kappa = \Delta V_0 / (V_0 \Delta p)$. This relation can also be applied to the particles with tetragonal and rhombohedral structure. In this context it is worth pointing out that the volume of the unit cell decreases with increasing external pressure applied to it [4]. On the other hand the volume of the unit cell decreases as the particle size is reduced [1]. This strengthens the applicability of the liquid drop model to nanoparticles.

Table 1. Different parameters obtained by analysing the experimental data (figure 1).

Material	Axis	Slope (nm)	Intercept	d_0 (nm)	$10^{11} \kappa$ ($\text{m}^2 \text{N}^{-1}$)	Ratio (c/a)
Sn	a-	$0.876\,2925 \pm 0.156$	$-0.017\,378\,56 \pm 0.0099$	50.42	1.005	3.282 37
	c-	$2.876\,315 \pm 0.287$	$-0.074\,517\,06 \pm 0.018$	38.6	3.3	
Bi	a-	$1.350\,577 \pm 0.084$	$-0.040\,983\,62 \pm 0.0056$	2.95	2.022	3.867 41
	c-	$5.223\,236 \pm 0.3$	$-0.135\,7154 \pm 0.0195$	38.5	7.82	

It can be noted that the lattice contraction is proportional to Δp , which is expected to depend not only on the size but also on the shape of the particles. In case of a pancake-like particle with diameter d and height l , the pressure difference Δp is given by

$$\Delta p = \gamma \left(\frac{4}{3} \right) \left[\frac{2}{d} + \frac{1}{l} \right]$$

and, hence, the relative lattice contraction will be

$$\frac{\Delta a}{a} = \kappa \gamma \left(\frac{4}{9} \right) \left[\frac{2}{d} + \frac{1}{l} \right]. \quad (2)$$

In the case of a thin wire with diameter d and height l ($\gg d$), the relative lattice contraction will be

$$\frac{\Delta a}{a} = \frac{8}{9} \frac{\kappa \gamma}{d} \quad (3)$$

whereas, in the case of a thin film $d \gg l$ and the relative lattice contraction will be

$$\frac{\Delta a}{a} = \frac{4}{9} \frac{\kappa \gamma}{l}. \quad (4)$$

The height l is referred to as the length in the case of a wire and thickness in the case of a thin film. From equations (1), (3) and (4), it is easy to note that

$$\left. \frac{\Delta a}{a} \right|_{\text{sphere}} : \left. \frac{\Delta a}{a} \right|_{\text{wire}} : \left. \frac{\Delta a}{a} \right|_{\text{film}} = 3 : 2 : 1. \quad (5)$$

This implies that the lattice contraction is significant for a spherical particle.

In order to test the above formulation, we analyse the lattice distortion data of Yu *et al* [1] for Sn and Bi particles. The lattice distortion is plotted as a function of the inverse of the particle size (figure 1) and fitted to straight lines, which reveal that the relative lattice distortion decreases almost linearly with the inverse of d . The intercepts and the slopes of the straight lines are given in table 1. From the slopes and the intercepts, we estimate the size (d_0) for

which the relative lattice distortion is zero and is given in table 1. The average size (d_0) for Sn and Bi is ~ 45 and ~ 35 nm, respectively. Further, from the slopes (table 1), it can be noted that the contraction of the c -lattice is almost four times that of the a -lattice for Bi and almost three times for Sn. It has been reported for Au and Pt [4] that the surface tension does not change appreciably with the orientation of crystal plane which leads to a conclusion that the different contraction of a - and c -lattices, is mainly due to the difference in the thermal compressibility. In this context it is worth pointing out that the anisotropy in the thermal expansion coefficients is four for Bi [5, 6] and three for Sn [6] particularly at low temperatures. Overall, it can be concluded that the effect of temperature on lattice parameter is similar to the effect of particle size. We have also estimated the volume compressibility κ from the slopes and it is presented in table 1. We take $\gamma = 0.654 \text{ J m}^{-2}$ for Sn and 0.501 J m^{-2} for Bi [7].

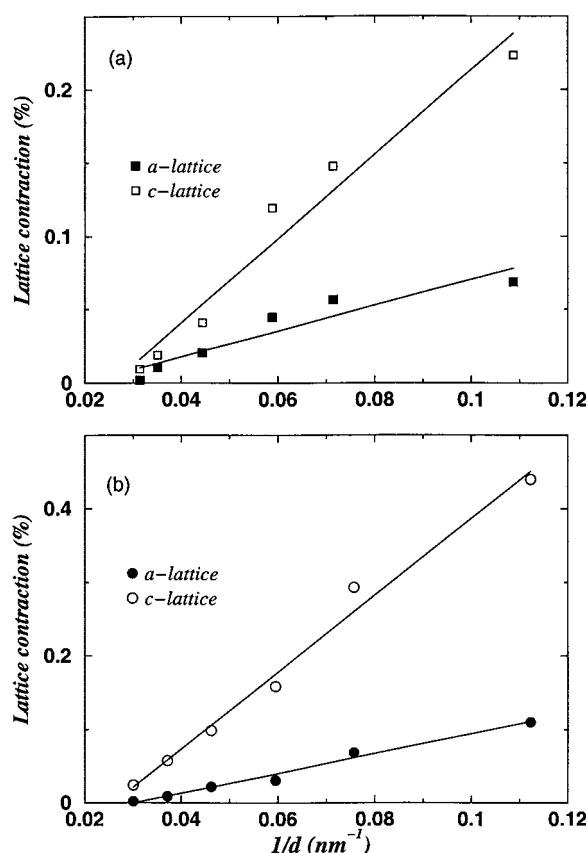


Figure 1. Size dependence of lattice contraction for (a) Sn and (b) Bi nanoparticles. The data are taken from [1]. The solid lines represent the least-squares fits to the experimental data.

There are also reports of lattice expansion as the particle size is reduced [8, 9] which cannot be explained by the liquid drop model. It is important to note that Palkar *et al* [9] have reported a lattice expansion as the particle size of CuO decreases, whereas Borgohain *et al* [10] have reported a lattice contraction as the particle size of CuO decreases. The only difference is the synthesis procedures. Recently, Qin *et al* [11] have developed a model based on the fact that the grain boundaries of nanocrystalline materials contain a large number of vacancies, that explain the lattice expansion as the particle size is reduced. Interestingly, the high resolution electron

microscopic (HREM) studies indicate the crystal lattice expansion mainly exists near the grain boundaries [12]. Moreover, surface-tension-like forces would lead to a lattice contraction in small particles and the presence of grain boundaries would lead to a lattice expansion. Overall, it is postulated that the liquid drop model applies to nanoparticles for which the contribution of grain boundaries is less.

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References

- [1] Yu X F, Liu X, Zhang K and Hu Z Q 1999 *J. Phys.: Condens. Matter* **11** 937
- [2] Sun C Q 1999 *J. Phys.: Condens. Matter* **11** 4801
- [3] Solliard C and Flueli M 1985 *Surf. Sci.* **156** 487
- [4] Qadri S B, Yang J, Ratna B R, Skelton E F and Hu J H 1996 *Appl. Phys. Lett.* **69** 2205
- [5] White G K 1969 *J. Phys. C: Solid State Phys.* **2** 575
- [6] White G K 1964 *Phys. Lett.* **8** 294
- [7] Plus B *et al* 1990 *Surf. Sci.* **239** 282
- [8] Liu X D, Zhang H Y, Lu K and Hu Z Q 1994 *J. Phys.: Condens. Matter* **6** L497
- [9] Palkar V R, Ayyub P, Chattopadhyay S and Multani M 1996 *Phys. Rev. B* **53** 2167
- [10] Borgohain K *et al* 2000 *Phys. Rev. B* **61** 11 093
- [11] Qin W, Chen Z H, Huang P Y and Zhuang Y H 1999 *J. Alloys Compounds* **292** 230
- [12] Ping D H, Li D X and Ye H Q 1995 *J. Mater. Sci. Lett.* **14** 1536