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## COMMENT

## Comment on ‘The lattice contraction of nanometre-sized Sn and Bi particles produced by an electrohydrodynamic technique’

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**Abstract.** The contraction in lattice parameter observed in nm-sized grains of Sn and Bi appears to be dominated by the effects of surface stress, not the presence of vacancies.

In a recent paper, Yu *et al* (1999) find a striking change in lattice parameter as the grain sizes of Sn and Bi are reduced. They attribute this to differences in vacancy concentrations associated with the differences in formation conditions. However, there is another, long-known effect which would seem to be the major factor in their case. Just as the surface tension of a liquid drop generates a pressure which changes the density of that liquid, so does the surface stress change the lattice parameter. The analogy for solids is well known (Nicholson 1955; fuller references are given by Mortimer 1976), and results are very similar to those for liquids. For solids, there are subtleties: the surface energy and the surface stress are not equal in general; the surface stress will differ from one crystallographic face to another and there can be negative surface stresses as well as positive ones (for discussion and references, see Stoneham 1977, 1981).

The simplest result is that for a spherical particle of radius  $R$ , compressibility  $\beta$  and surface stress  $\sigma$ . In this case, the fractional change in volume  $V$  is given by:

$$\Delta V/V = -2\beta\sigma/R.$$

Generalizations to faceted shapes are given by Stoneham (1977); it is straightforward to generalize to anisotropic solids. How big an effect is predicted? Let us ignore anisotropy for the moment. For Sn, the bulk modulus is  $5.29 \times 10^{10} \text{ N m}^{-2}$ ; the surface tension for liquid Sn is about  $0.48 \text{ N m}^{-1}$  (Eustathopoulos and Drevet 1998). Thus  $2\beta\sigma$  is about  $1.83 \times 10^{-2} \text{ nm}$ . For a sphere of the same size as the smallest grains considered by Yu *et al* (with diameter 9.6 nm and so radius 4.8 nm), one expects a reduction in the lattice parameter of the order of 0.4%. The value quoted by Yu *et al* is a reduction of 0.36%, virtually identical. Similarly, for Bi,  $\beta$  is  $3.19 \times 10^{10} \text{ N m}^{-2}$ , and  $\sigma$  is  $0.43 \text{ N m}^{-1}$  (Eustathopoulos 1983; I am indebted to Professor Eustathopoulos for pointing out that the surface stress of the solid is about 15% larger than the liquid). The smallest grains considered by Yu *et al* have diameter 8.9 nm. These numbers imply a fractional reduction in volume of 0.61%; the observed value is 0.66%. Thus, *at least for the smallest grains, the lattice parameter change can be attributed entirely to surface stress.*

Further comments are in order. First, the calculation above ignores anisotropy and faceting. Given data for the elastic constants and surface stresses for different grain boundaries, then

there are expressions suitable for predicting  $\Delta a/a$  and  $\Delta c/c$ . In principle, the  $\Delta a/a$  and  $\Delta c/c$  data of Yu *et al* offer a measure of the anisotropy of the surface stress for Sn. Secondly, the predicted  $1/R$  dependence of  $\Delta V/V$  does not seem to be obeyed in the results of Yu *et al*; their data indicate a stronger dependence on  $R$ . Yet it is known from other systems, even with constraints, such as Pt or Au on a C film (Solliard and Flueli 1985) or Pd in an amorphous matrix (Lamber *et al* 1995), that the expected  $R$  dependence is often seen. Why should a different  $R$  dependence be seen by Yu *et al*? One possibility is that the faceting of small grains is not the same as the faceting of large grains. Thus an initial nucleus may have mainly one type of face exposed, with other surfaces becoming more important as growth occurs. This behaviour is known to occur in CVD diamond because of the different growth rates of different faces. Microscopic examination of the samples of Yu *et al* might show such changes in faceting. Thirdly, Yu *et al* suggest that the change in lattice parameter is determined by different vacancy concentrations. This may be a small part of the explanation, but it raises problems. Not least, it is hard to see why any simple trend with radius should result. Moreover, vacancies make a more natural contribution to the density (through the extra sites created) than to the lattice parameter change from lattice relaxation and from the Fermi level change.

In summary, a more natural explanation of the interesting data of Yu *et al* follows simply from the strain due to surface stress. Simple estimates suggest this is the dominant mechanism.

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