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Measurement of surface tension by lattice parameter changes: theory for facetted microcrystals

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Abstract. A number of workers have estimated surface tensions of solids from measurements of the differences in the lattice parameters of bulk crystals and microcrystals. The data are then analysed by an expression valid only for spherical, isotropic microcrystals. Real microcrystals are usually facetted, resulting in a number of possible problems which are discussed here.

The main results given are:

(i) A general expression for the change in volume of a microcrystal for an arbitrarily anisotropic surface tension and arbitrary crystal habit; common special cases are also given; and

(ii) a discussion of the relation between the volume change and the change in x-ray lattice parameter. This includes the effects of the dispersions in crystalline sizes and shapes, and the possible non-uniformity in internal strain produced.

The main conclusion is that errors are likely to be modest, almost certainly less than a few tens of percent.

1. Introduction

Surface effects become particularly important in small microcrystals. One of the simplest effects is the reduction in lattice parameter produced by surface tension. Consider, for example, an elastically-isotropic sphere of compressibility β and radius r. Its surface tension γ produces an effective pressure $2\gamma/r$, leading to a fractional volume change $-2\beta\gamma/r$. The change in radius which results is $-\frac{2}{3}\beta\gamma$, independent of r, so that small spheres will show the largest effects on lattice parameter. If the lattice contracts uniformly, the lattice spacing a seen is altered by

$$\Delta a = -\tfrac{2}{3}(a/r)\beta\gamma. \tag{1}$$

This expression has been used to estimate γ, the surface tension (e.g. Nicholson 1955; a fuller list of references is given by Mortimer 1976).

The problem with (1) is that it ignores the faceting of many microcrystals, the anisotropy of surface tension and elasticity, and makes further assumptions about the relationship between volume and lattice parameter changes. Generalization of (1) proves to be simple in most respects, and is the main point of this note. It is worth stressing that γ refers to the actual, probably dirty, surface, and not to any imagined ideal surface.

2. Volume changes from surface forces

A convenient general formula, valid for any harmonic system, follows from the Betti Reciprocity Theorem (Temkin 1970; see also Stoneham 1975 p 185). Suppose the surface forces $\boldsymbol{F}_s$ (however caused, but including all terms which result from the microcrystal not being embedded in an infinite crystal) cause atomic displacements $\boldsymbol{\delta}_s$. Likewise, suppose a hydrostatic pressure by itself leads to forces $\boldsymbol{F}_p$ and displacements $\boldsymbol{\delta}_p$. Then the theorem asserts that

$$\sum \boldsymbol{F}_s . \boldsymbol{\delta} = \sum \boldsymbol{F}_p . \boldsymbol{\delta}_s. \tag{2}$$

Temkin has shown that this expression simplifies to give a volume change:

$$\Delta V = \sum_{ij} \sum_{k} G_{ij} s_{ijkk} \tag{3}$$

where **s** is the compliance tensor. The virial **G** has components:

$$G_{ij} = \sum_{l} R_{li} F_{sj}(\boldsymbol{R}_l) \tag{4}$$

where the vectors to the sites $\boldsymbol{R}_l$ at which the forces are applied are measured from the point in the microcrystal which remains fixed when a hydrostatic pressure is applied to the body, i.e. the geometric centre in all simple cases.

These expressions hold for systems of arbitrary symmetry. However, most systems of interest have much higher symmetry. We shall concentrate on systems with at least tetrahedral symmetry. Thus the elastic properties and surface tension parameters are appropriate to cubic crystals, and the crystal habit is assumed to have the same symmetry. Cubic habits are seen, for instance, for MgO (which forms cubes); diamond often forms octahedra, and many systems (e.g. NiO) form more complex shapes like tetrakaidecahedra. In these systems G_{ij} reduces to $G\delta_{ij}$, and the volume change becomes:

$$\Delta V = \beta G. \tag{5}$$

If the crystal volume is V_0, and if the strain is homogeneous, then the lattice parameter change is

$$\Delta a = \tfrac{1}{3} a \beta G / V_0. \tag{6}$$

These expressions can now be discussed in certain simple cases. Most of the analysis concerns equation (5), where the volume change appears. But the step from this to the measured $\Delta a/a$ is not trivial, and this will also be discussed.

3. Calculation of the virial

The volume change follows very simple once (4) has been calculated. In essence, the virial is like a moment of the surface forces. Some special cases are now considered where the surface forces can be found; given these, it is straightforward to find **G**.

3.1. Isotropic continuum

Consider a solid with a surface tension independent of orientation, and a smooth, unfaceted surface. Then the surface force at any point is proportional to the curvature at that point and directed towards the centre of curvature. If the radius of curvature is

$\rho(\boldsymbol{R})$ and the normal to the surface is $\boldsymbol{n}(\boldsymbol{R})$, then

$$\boldsymbol{F}_s(\boldsymbol{R}) = [2\gamma/\rho(\boldsymbol{R})]\boldsymbol{n}(\boldsymbol{R}) \tag{7}$$

is the force per unit area. This result obviously reduces to give (1) in an appropriate limit, but it is not suited to the faceted systems used in experiments.

3.2. Faceted systems

In these systems the surface tension can be represented by a force $\gamma \boldsymbol{n} dl$ on each element of dl of the edge of each facet. Here $\boldsymbol{n}$ is a vector in the plane of the facet, normal to the edge in all simple cases. The surface tension γ depends on which facet is considered; it will be different for the hexagonal and square faces of a tetrakaidecahedron, for example.

It is easy to write down general expressions for the virial. They are complicated, so we show later that it is easier to make more direct calculations for especially simple structures. First, consider a straight edge of a facet. Then the force is constant along the length, and terms like $\Sigma_l R_{li} F_{sj}(\boldsymbol{R}_l)$ summed along the edge reduce to the contribution of the total force acting at the centre of the edge. Secondly, if the force is indeed normal to the edge, its direction cosines $(\lambda_1, \lambda_2, \lambda_3)$ can be expressed in terms of those of the edge itself, (l, m, n) and those of the normal to the facet, (L, M, N):

$$(\lambda_1, \lambda_2, \lambda_3) \equiv (mN-nM, nL-lN, lM-mL). \tag{8}$$

Thus, if $\boldsymbol{R}^I_{cJ}$ corresponds to the centre of edge J of face I, the edge having length Λ^I_J and the face a surface tension γ_I, the contribution to the virial is G^{IJ}_{ij}

$$G^{IJ}_{ij} = R^I_{cJi}\gamma_I \Lambda^I_J \lambda^{IJ}_j, \tag{9}$$

and the total from all faces is

$$G_{ij} = \sum_{\text{faces } I} \sum_{\text{edges } J} G^{IJ}_{ij}. \tag{10}$$

Note that a given edge contributes to the two faces it bounds. These expressions are purely for surface tension and ignore the 'edge' tension itself, although this can be built in, as above, in any case it is believed important.

3.3. Results for simple systems

The simple isotropic sphere discussed in §1 had a fractional change in volume

$$\text{Sphere:} \qquad \frac{\Delta V}{V_0} = -\frac{2\beta\gamma}{R}. \tag{11}$$

where β is the compressibility and R the radius. Similar results are now given for a cube of side $2a$ and for an octahedron with distance $2b$ between opposite vertices. Only $G \equiv G_{xx}$ is needed in these cases.

For the cube, only the eight edges normal to the x axis contribute to G_{xx}, and each contributes $2a^2\gamma$. Thus G_{xx} is $16\ a^2\gamma$, and

$$\text{Cube:} \qquad \frac{\Delta V}{V_0} = -\frac{2\beta\gamma}{a}. \tag{12}$$

This is exactly equivalent to (11): if γ is the same in both cases, $\Delta V/V_0$ is the same for both a cube and its inscribed sphere.

The octahedron is more complex, but the six faces each have two edges which contribute to G. After simplification, G is $6\gamma b^2/\sqrt{3}$:

$$\text{Octahedron}: \frac{\Delta V}{V_0} = -\frac{3\sqrt{3}}{2}\frac{\beta\gamma}{b} \simeq -\frac{2{\cdot}59\beta\gamma}{b}. \tag{13}$$

Again, the expression is very similar to those for cube or sphere.

4. Relation to lattice parameter changes

The expressions (11)–(13) show that the formal values for $(\Delta V/V_0)$ depend rather little on crystallite shape. For any given material, the dependence of γ on facet will probably give a larger effect. Likewise, the effect of impurities and defects can have a profound effect. Experimentally, it is normal to measure the change in the position of an x-ray diffraction peak, which gives a change in lattice parameter, $\Delta a/a$, rather than a volume change. There need be no simple relationship between $\Delta a/a$ and $\Delta V/V_0$. It is well known, for example, that defects like vacancies have entirely different effects on the two values in bulk crystals (Simmons and Balluffi 1960). Suppose the effect of the surface is to produce displacements $\boldsymbol{u}_i$ from sites $\boldsymbol{r}_{i0}$ appropriate to the perfect bulk crystal. Then the diffraction peak at scattering vector $\boldsymbol{k}_0$ is shifted to $\boldsymbol{k}_0 + \Delta\boldsymbol{k}$ where (see e.g. Willis *et al* 1977 for a fuller discussion)

$$\sum_\alpha \Delta k_\alpha A_{\alpha\beta} = -\sum_\alpha k_{0\alpha} B_{\alpha\beta} \tag{14}$$

with the tensors **A**, **B** defined by:

$$A_{\alpha\beta} = \sum_i r_{i0\alpha} r_{i0\beta} \tag{15}$$

$$B_{\alpha\beta} = \sum_i u_{i\alpha} r_{i0\beta}. \tag{16}$$

Equations (14)–(16) are fundamental in determining the apparent change in lattice parameter. Then the following comments can be made:

(i) Suppose the microcrystals all have the same shape, but a distribution of sizes. Then, even if the strain in the microcrystals in non-uniform, the apparent change in lattice parameter is proportional to $\langle a^{-1}\rangle$, i.e. the average over the reciprocal of the mean dimension a. This follows from (6), bearing in mind that $V_0 \sim a^3$ and $G \sim a^2$. Now estimates of a from x-ray line broadening also measure $\langle a^{-1}\rangle$. Thus the distribution of sizes has no important effects provided the mean size is estimated from line-broadening and provided the shape and size are uncorrelated.

(ii) Suppose the microcrystals have some very complex shape, but are free from vacancy aggregates. Then, provided they are randomly oriented and provided the strain field is uniform within each microcrystal, $\Delta a/a$ and $\frac{1}{3}\Delta V/V_0$ are identical. Even if the strain is non-uniform, we may still show:

$$\frac{\Delta k}{k} = -\tfrac{1}{3}\left\{\sum_\alpha \frac{B_{\alpha\alpha}}{A_{\alpha\alpha}}\right\} \equiv -\tfrac{1}{3}\sum_\alpha \left\{\frac{\Sigma_j u_{\alpha j} r_{\alpha j}}{\Sigma_j r_{\alpha j} r_{\alpha j}}\right\} \tag{17}$$

where the axes i are the principal axes of the **A** tensor.

(iii) The source of most difficulty is the possible non-uniformity of the strain: one expects the strain to be altered close to edges, for example. There seem to be no calculations of the strain distribution inside faceted crystallites, although some special cases deserve comment. First, in an elastically-isotropic ellipsoid, the strain may be expected to be uniform (Eshelby 1957). Secondly, some authors have assumed that most of the distortion takes place in a region close to the surface. This is true of the model calculations of Anderson and Scholz (1968), for example. In such cases $\Delta a/a$ will be much less than $\frac{1}{3}\Delta V/V_0$: the position of the diffraction peak is dominated by the relatively undistorted bulk of the microcrystal. However, effects are likely to be small in reality. For uniform strain, the displacements increase linearly from the origin: $u \sim r^N$ with $N = 1$. For a more general N we find for a spherical particle:

$$\frac{\Delta a}{a} = \tfrac{1}{3}\left(\frac{\Delta V}{V}\right)\left(\frac{5}{N+4}\right), \tag{18}$$

so that modest changes in N produce only slight errors from non-uniformity.

5. Conclusion

Attempts to measure surface tensions by observing the crystal size dependence of the lattice parameter have been based on (1), valid for spherical microcrystals. The effects of facetting and other aspects of real microcrystal shapes have been discussed, and shown to require only small corrections in most cases. But the distinction between measurements of volume change and lattice parameter change is important in principle, and it may be necessary to make experimental tests of its importance, for example by measuring the apparent change in lattice parameter using a range of different x-ray scattering vectors.

Changes in lattice parameter can also be inferred from other measurements. A recent example is given by the recent resonance work of Rappaz *et al* (1976) on small crystallites of $SrCl_2:Gd^{3+}$. The advantage of these methods is that the lineshape contains information about the distribution of strain inside the crystallite, at least when there is no surface segregation of the impurity ions.

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