Lattice distortions in cubic crystals

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TETRAGONAL DISTORTION

For a cubic crystal, we know that for instance the {100} family of planes all give the same reflections - (100), (010), and (001) all give a diffraction peak at the same angle. Now consider a small distortion along the c axis. That makes (001) not equivalent to (100) and (010), and the single diffraction peak now becomes a doublet: a peak of relative intensity 2 for the (100) and (010) overlapping reflections, and a peak of relative intensity 1 for the (001) reflection. Below we derive an expression for the ratio of the lattice constants a/c presuming that it is close to unity, i.e., small distortions.

For a tetragonal system, we have

$$\sin^2\theta = \frac{\lambda^2}{4a^2}\left(h^2+k^2\right) + \frac{\lambda^2}{4c^2}l^2 \tag{1}$$

$$\Longrightarrow \qquad \frac{4\sin^2\theta}{\lambda^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \tag{2}$$

For the sake of concreteness, consider a reflection (hhl) occurring at angle θ_1 and reflections (lhh) and (hlh) occuring at angle θ_2. The difference in $\sin^2$ values is then

$$\sin^2\theta_1 - \sin^2\theta_2 = \frac{\lambda^2}{4}\left(\frac{h^2+h^2}{a^2} + \frac{l^2}{c^2} - \frac{l^2+h^2}{a^2} - \frac{h^2}{c^2}\right) = \frac{\lambda^2(h^2-l^2)}{4}\left(\frac{1}{a^2} - \frac{1}{c^2}\right) = \frac{\lambda^2(h^2-l^2)}{4a^2}\left(1 - \frac{a^2}{c^2}\right) \tag{3}$$

We can simplify the left-hand side. Let $\theta_o = (\theta_1+\theta_2)/2$ and $\delta = \theta_1 - \theta_2$, so $\theta_1 = \theta_o + \delta/2$ and $\theta_2 = \theta_o - \delta/2$. This make θ_o the original peak position before distortion, and δ is the peak splitting after the distortion. Then:

$$\sin^2\theta_1 - \sin^2\theta_2 = \sin^2\left(\theta_o + \frac{\delta}{2}\right) - \sin^2\left(\theta_o - \frac{\delta}{2}\right) \tag{4}$$

$$= \left(\sin\theta_o\cos\frac{\delta}{2} + \cos\theta_o\sin\frac{\delta}{2}\right)^2 - \left(\sin\theta_o\cos\frac{\delta}{2} - \cos\theta_o\sin\frac{\delta}{2}\right)^2 \tag{5}$$

$$= \sin^2\theta_o\cos^2\frac{\delta}{2} + 2\sin\theta_o\cos\theta_o\sin\frac{\delta}{2}\cos\frac{\delta}{2} + \cos^2\theta_o\sin^2\frac{\delta}{2} \tag{6}$$

$$- \sin^2\theta_o\cos^2\frac{\delta}{2} + 2\sin\theta_o\cos\theta_o\sin\frac{\delta}{2}\cos\frac{\delta}{2} - \cos^2\theta_o\sin^2\frac{\delta}{2} \tag{7}$$

$$= 4\sin\theta_o\cos\theta_o\sin\frac{\delta}{2}\cos\frac{\delta}{2} = 2\sin 2\theta_o\sin\frac{\delta}{2}\cos\frac{\delta}{2} \tag{8}$$

Since δ is small, $\cos\frac{\delta}{2} \approx 1$ and $\sin\frac{\delta}{2} \approx \frac{\delta}{2}$, and

$$\sin^2\theta_1 - \sin^2\theta_2 \approx \delta\sin 2\theta_o \tag{9}$$

Using Eq. 2,

$$\delta\sin 2\theta_o \approx \frac{\lambda^2(h^2-l^2)}{4a^2}\left(1 - \frac{a^2}{c^2}\right) \tag{10}$$

$$\frac{a}{c} \approx \sqrt{1 - \frac{4a^2\delta\sin 2\theta_o}{\lambda^2\left(h^2-l^2\right)}} \tag{11}$$

Thus, once the peaks are indexed, from the peak splitting δ and the average angle $2\theta_o$ we can find the a/c ratio.

RHOMBOHEDRAL DISTORTION

For a rhombohedral crystal with an angle α between axes, we have

$$\frac{1}{d^2} = \frac{(h^2+k^2+l^2)\sin^2\alpha + 2(hk+kl+hl)(\cos^2\alpha - \cos\alpha)}{a^2(1-3\cos^2\alpha+2\cos^3\alpha)} \tag{12}$$

Here we assume we have a nearly cubic crystal with a small rhombohedral distortion, such that the lattice angle is $\alpha = \frac{\pi}{2} + \delta$, where δ is the distortion. This corresponds to a stretch (or compression) along the body-diagonal of the cubic unit cell. This leaves the 100 cubic peak unsplit, but splits the 111 cubic reflection into two peaks (111 and $11\overline{1}$) since there are two different body-diagonal distances in the rhombohedral unit cell.

In this case, for small δ,

$$\sin\alpha = \sin\left(\frac{\pi}{2}+\delta\right) = \cos\delta \approx 1 - \frac{\delta^2}{2} \tag{13}$$

$$\cos\alpha = \cos\left(\frac{\pi}{2}+\delta\right) = -\sin\delta \approx -\delta \tag{14}$$

This gives

$$\frac{1}{d^2} = \frac{(h^2+k^2+l^2)(1-\frac{\delta^2}{2})^2 + 2(hk+kl+hl)(\delta^2+\delta)}{a^2(1-3\delta^2-2\delta^3)} \tag{15}$$

Expanding, and neglecting terms of order δ^4 and higher (so $(1-\delta^2/2)^2 \approx 1-\delta^2$),

$$\frac{1}{d^2} = \frac{(h^2+k^2+l^2)(1-\delta^2) + 2\delta(hk+kl+hl)(1+\delta)}{a^2(1-3\delta^2-2\delta^3)} \tag{16}$$

$$= \frac{(h^2+k^2+l^2)(1-\delta)(1+\delta) + 2\delta(hk+kl+hl)(1+\delta)}{a^2(1+\delta)(1-\delta-2\delta^2)} \tag{17}$$

$$= \frac{(h^2+k^2+l^2)(1-\delta) + 2\delta(hk+kl+hl)}{a^2(1-\delta-2\delta^2)} \tag{18}$$

$$\tag{19}$$

In terms of the measured reflection angle θ,

$$\sin^2\theta = \frac{\lambda^2}{4d^2} = \frac{\lambda^2}{4a^2}\frac{(h^2+k^2+l^2)(1-\delta) + 2\delta(hk+kl+hl)}{(1-\delta-2\delta^2)} \tag{20}$$

In order to obtain δ, we make use of the splitting of fundamental lines. For a doublet with peaks at angles θ_1 and θ_2, the first term in the numerator will be the same for both peaks, and the difference in $\sin^2\theta$ values simplifies. Assuming the lines are (hkl) and $(\overline{h}kl)$,

$$\frac{4a^2}{\lambda^2}(\sin^2\theta_1 - \sin^2\theta_2) = \frac{2\delta}{1-\delta-2\delta^2}(hk+kl+hl-\overline{h}k-kl-\overline{h}l) = \frac{2\delta}{1-\delta-2\delta^2}(2hk+2hl) = \frac{4\delta}{1-\delta-2\delta^2}(hk+hl) \tag{21}$$

Since the lattice distortion is expected to be small (verified by the small degree of doublet splitting), $\delta \ll 1$ (in radians) we may simplify the previous expression to:

$$\frac{\delta}{1-\delta-2\delta^2} \approx \delta \approx \frac{a^2(\sin^2\theta_1 - \sin^2\theta_2)}{\lambda^2(hk+hl)} \tag{22}$$

Using the lattice constant a, λ, and miller indices for each of the double peaks, one may use the difference between the squared sines of the doublet angles to find the degree of rhombohedral distortion δ. This procedure gives little error for the small distortion angles considered, and has the advantage of simplifying analysis a great deal.