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The diffraction spectrum of twinned domains: determination of domain wall width

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Abstract. The lineshapes for x-ray or neutron diffraction are derived for ideally twinned structural domains in an approximate but realistic model. Expressions are given for the distortion of the main peaks and for the scattering intensity between them; the latter shows a shallow minimum at the mid-point. Some experimental and fitting procedures for the determination of domain wall widths in diffraction experiments are discussed.

1. Introduction

The properties of interfaces between twinned structural domains depend on both the elastic properties of the lattice and microscopic interactions, and have attracted interest from both fundamental and applications viewpoints. The twinned orthorhombic domains that appear below the tetragonal–orthorhombic transition in ferroelectrics such as KH_2PO_4 (KDP) and in the copper oxide superconductors are widely studied examples. Such domain walls can be characterized by their twinning angle, separation, shape, and width. The twinning angle depends simply on the orthorhombic strain and can be measured easily in diffraction experiments, and domain wall spacings can usually be obtained from optical or electron microscopic studies. The shape of the domain walls is not readily determined but a hyperbolic tangent dependence of the strain through the wall is predicted from analysis and widely accepted. Reliable results for wall widths, however, are difficult to obtain. The widths, typically a few unit cells, are too small for optical measurements, and while electron microscopy techniques can provide some information, they are not suitable for all crystals and the data may not be representative of the bulk material.

Several groups have carried out x-ray and neutron diffraction experiments on twinned crystals with the objective of determining the domain wall width [1–5]. Since unit cells within the domain wall will have different parameters from those in the bulk domain regions, they will scatter differently. If this anomalous but weak scattering can be measured, the domain wall width can be deduced. The results obtained have generally had reasonable magnitudes and temperature dependence but their accuracy has not yet been established. The present investigation began as an attempt to improve upon earlier measurements of domain wall widths in KDP. The experiments were not successful because of the small domain wall width/separation ratio for this system, but our efforts to analyse our spectra have led to some insights which should be valuable for the interpretation of this type of experiment for more favourable systems. This paper therefore is primarily a derivation of

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the expected diffraction spectrum from twinned domains and a discussion of the extraction of domain parameters from it. For definiteness we will consider a twinned orthorhombic crystal, but the results should apply to related structures.

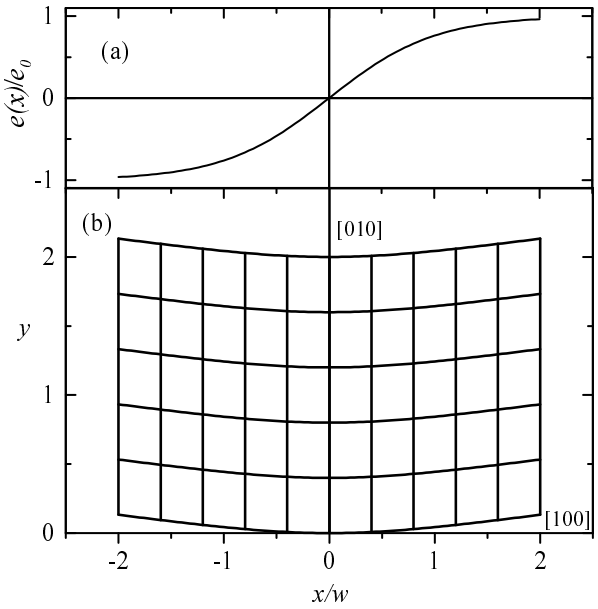

Figure 1. The predicted strain distribution (a) and lattice deformation (b) for a twin wall at $x = 0$.

2. Theory

For analysis we consider a single static twin wall between two domains differing only in unit-cell orientation. It is convenient to choose unit cells as shown in figure 1 so that the cell basal section goes from square to diamond-shaped below the tetragonal–orthorhombic transition. Thus in figure 1 the twin wall contains the [010] axis which is the y-axis. An alternative choice of unit cell where the basal plane axes are rotated by 45° in orientation and where the section changes from square to rectangular at the phase transition is also widely used. From continuum elasticity theory [6, 7] the equilibrium strain for a twin wall is found to be

$$e(x) = e_0 \tanh(x/w). \tag{1}$$

Thus the strain goes smoothly from e_0 for large positive x through zero at the centre of the wall to $-e_0$ for large negative x as shown in figure 1. w is a width parameter for the strain distribution: we take the width of the wall as $2w$. The displacements $u(x, y)$ corresponding to this strain are

$$u_x = 0 \tag{2a}$$

$$u_y = e_0 w \ln[\cosh(x/w)]. \tag{2b}$$

These results are valid for small strain although Jacobs [8] has given expressions for displacements to $O(e_0^4)$. We assume small strains throughout, consistent with typical experimental values of $e_0 \sim 0.01$. e_0 will depend on temperature, but our interest is essentially

in the limiting low-temperature value. Note that a line which is horizontal when $e_0 = 0$ acquires a slope of $e_0 \tanh(x/w)$ below the transition. Thus the unit-cell axis makes an angle $\psi(x)$ with the x-axis which is just equal to the strain $e(x)$, and they both have the same tanh dependence.

If the x-axis in figure 1 runs from $-d/2$ to $+d/2$ where d is the spacing between twin walls, we can use this section of material to calculate the scattering function $S(Q)$, and hence the lineshape, for neutron or x-ray diffraction. It is clear that if $e_0 = \psi_0$ is given, the diffraction lineshape will depend only on the ratio w/d. If this ratio is vanishingly small, unit cells in either domain will be uniformly tilted by $\pm\psi_0$, so a single diffraction peak may be expected to split into two peaks of equal intensity and shape below the transition. If w/d is not small there will be a measurable intensity between the peaks due to scattering from unit cells for $x \approx 0$.

From the displacements given by equation (2) it is straightforward in principle to compute the structure factor and hence $S(Q)$ numerically for appropriate choices of d and w. This approach has some computational difficulties, and is furthermore inconvenient for extended analysis and fitting of experimental lineshapes. Instead we will pursue an analytical treatment of lineshapes with simplifications and approximations where possible.

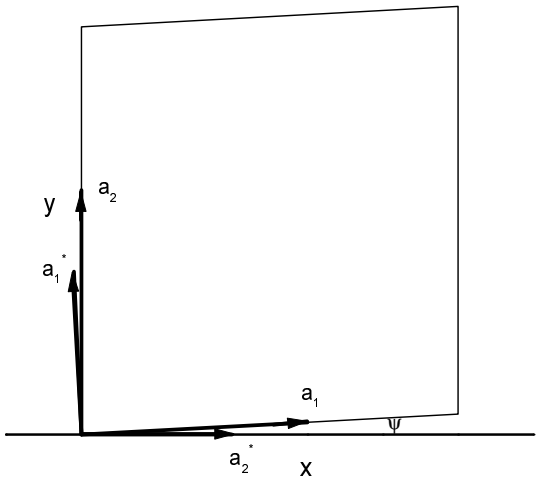

Figure 2. The strained unit cell with the x-axis tilted by the angle ψ. Direct and reciprocal-lattice vectors are shown.

The essential assumption is that if strains are small and vary slowly on the scale of a unit cell, the only significant change in the unit cell is the tilt of its x-axis. The strained unit cell with a tilt angle of ψ is shown in figure 2 along with the direct and reciprocal-lattice vectors. For scattering vector $(hk0)$ it is readily shown that the separation between scattering planes for the tilted cell is

$$d(hk0) = \frac{a}{(h^2 + k^2 - 2hk\sin\psi)^{1/2}} \tag{3}$$

where a is the unit-cell parameter in the basal plane for the undistorted phase. In experiments, our primary interest will be in Bragg peaks that behave simply in the twinned phase, such as $(h00)$, $(0k0)$, and $(hh0)$. Equation (3) shows that the plane spacings for the peaks $(h00)$ and $(0k0)$ are unchanged by the strain, while peaks $(hh0)$ are split linearly in

ψ. A powder experiment would therefore show no change in the (h00) and (0k0) peaks while (hh0) peaks would be split symmetrically since strains $\pm\psi$ are equally probable.

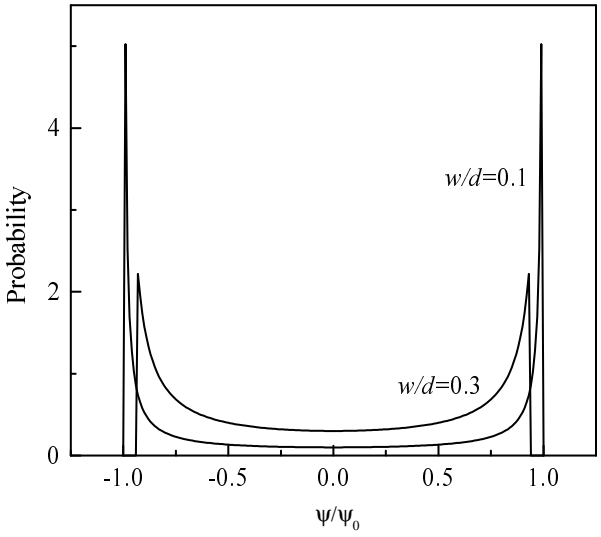

Figure 3. The lineshape for ideally twinned domains as predicted by equation (4) for two (large) values of w/d.

Most experiments to date have been on single crystals, and in this case (h00) peaks will show a splitting for fixed scattering angle when the crystal is rotated. The separation of the peaks corresponding to strain angles $\pm\psi$ will just be 2ψ, so this experiment is particularly simple and direct. We are then interested in the general case when unit cells with all angles between $\pm\psi_0$ are contributing to the scattering, and wish to find the resulting lineshape when the sample is rotated. The scattering intensity at a particular scattering angle ψ, measured from the peak position $\psi = 0$ in the undistorted phase, will be proportional to the probability that a particle is scattered in a unit cell with strain angle ψ. Since we know that the probability of a scattering event at x is just $P(x) = 1/d$ independently of x, and there is a one-to-one correspondence between x and $\psi = e$ through equation (2), the probability $g(\psi)$ of a scattering event at ψ is found by equating $P(x)\,\mathrm{d}x = g(\psi)\,\mathrm{d}\psi$. Noting that the maximum permitted value for ψ is $\psi_m = \psi_0 \tanh(d/2w)$ we obtain

$$g(\psi) = \begin{cases} \dfrac{\psi_0 w/d}{\psi_0^2 - \psi^2} & \text{if } |\psi| \leqslant \psi_m \\ 0 & \text{if } |\psi| > \psi_m. \end{cases} \tag{4}$$

This expression for $g(\psi)$ is not divergent and is correctly normalized to unity. In our model, therefore, equation (4) represents the expected scattering intensity lineshape for an ideally twinned sample. It is shown in figure 3 for values of w/d chosen unreasonably large for illustrative purposes.

To make comparisons with experiments it is necessary to convolute $g(\psi)$ with the spectrometer resolution function $f(\psi)$, which may typically have a Gaussian form. In practice the evaluation of $I(\psi) = \int f(\psi - y)g(y)\,\mathrm{d}y$ through the Fourier convolution theorem is difficult because the Fourier transform of $g(\psi)$ contains a very wide range of frequencies. However, in the usual case where $f(\psi)$ is much narrower than the splitting

$\sim 2\psi_0$ we expect $I(\psi)$ to resemble $g(\psi)$ in figure 3 except that the sharp peaks will be spread out. For $w/d \to 0$, $g(\psi)$ resembles a pair of δ-functions at $\pm\psi_0$ and the convolution integral will then give each peak the spectrometer lineshape $f(\psi)$. For w/d not small there will be substantial scattering intensity between the peaks associated with unit cells within the domain wall, but this intensity falls smoothly to a shallow minimum at $\psi = 0$. This contrasts with the claim made in a number of papers that a broad *peak* is found at $\psi = 0$ due to domain wall scattering. We believe that apparent observations of a peak are either related to more complex domain structures, which indeed occur in many crystals, or are not justified by the experimental statistics.

Since figure 3 shows that the effect of twinning is to redistribute the scattering through the whole range between $\pm\psi_0$ it would be desirable to analyse the entire observed distribution to verify the characteristic scattering function $g(\psi)$ and hence determine w/d. We have not been able to calculate the convoluted lineshape $I(\psi)$ for a particular resolution function $f(\psi)$, but we have obtained approximate results for the case of narrow $f(\psi)$ and small w/d that should be useful at least in preliminary analysis. We consider only $\psi > 0$, and derive an expansion for $I(\psi) = \int f(\psi - y)g(y)\,\mathrm{d}y$ for ψ close to ψ_0. In this case $f(\psi - y)$ will only be non-zero for $y \approx \psi_0$, and it can be expanded in a Taylor series about ψ_0:

$$f(\psi - y) \approx f(\psi - \psi_0) + f'(\psi - \psi_0)(\psi_0 - y) + \frac{1}{2}f''(\psi - \psi_0)(\psi_0 - y)^2 + \cdots. \tag{5}$$

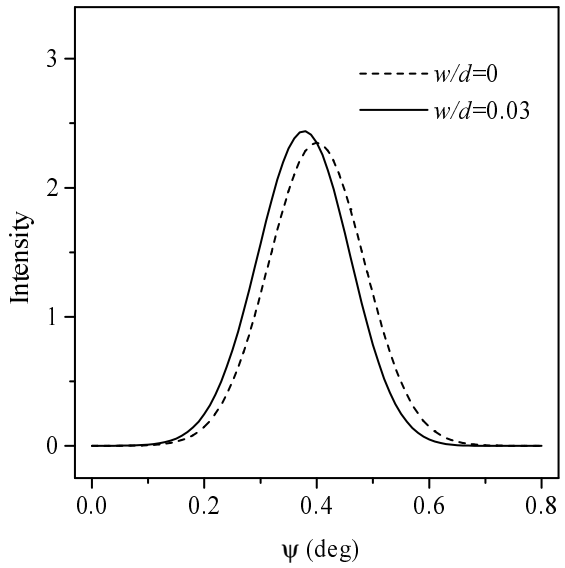

Figure 4. The diffraction peak lineshape showing the effect of twinning according to equation (6).

With this substitution in $I(\psi)$ and with $g(\psi) \approx (w/2d)/(\psi_0 - \psi)$ near $+\psi_0$, evaluation of the integrals gives, to first order in w/d,

$$g(\psi) \approx \frac{1}{2}f(\psi - \psi_0) + (w/d)\psi_0 f'(\psi - \psi_0) + \cdots. \tag{6}$$

The first term in equation (6) is recognizable as the contribution that would arise if $g(\psi)$ were a δ-function. The second term adds a fraction of the first derivative of the resolution

function, in effect shifting some intensity from the outside of the line to the inside, and broadening it slightly. This is illustrated in figure 4, for a Gaussian $g(\psi)$ with a FWHM of 0.1°, a strain angle ψ_0 of 0.4°, and w/d = 0.03. At first sight figure 4 implies that the perturbation of the lineshape due to twinning should be experimentally detectable for quite small values of w/d, but in reality the dominant effect of the term in w/d is to shift the location of the peak from its position for vanishing w/d, and that of course is not measurable. The perturbed line does become asymmetric with respect to the new peak position, but the skewness appears only in higher orders in w/d.

Equation (6) will not be a good approximation away from the line peaks, and therefore gives no information about the intensity midway between the two peaks where unit cells near the centre of the domain wall contribute most strongly. In that region, however, $g(\psi)$ is almost flat and can be taken as $g(\psi) \approx w/(d\psi_0)$ for small ψ. For the case where again $f(\psi)$ is much narrower than ψ_0, and hence there is negligible intensity at $\psi \sim 0$ from the peaks at $\pm\psi_0$,

$$I(0) \approx \int f(-y)\frac{w}{d\psi_0}\,\mathrm{d}y = \frac{w}{d\psi_0} \tag{7}$$

if $f(\psi)$ has unit area. The linear dependence of $I(0)$ on w/d was previously found [4] in numerical calculations for this strain distribution. A comparison of $I(0)$ with the intensity of one of the peaks gives the ratio

$$\frac{I(0)}{I(\psi_0)} = \frac{2w}{d\psi_0 f(0)} = 2.13\frac{wu}{d\psi_0} \tag{8}$$

for the Gaussian $f(\psi)$ with width (FWHM) $= u$. Under suitable conditions this may be a useful method of determining w/d.

3. Discussion

In this section we discuss at greater length the implications for experimental investigations of the above analysis. Since the effects of twinning on diffraction lineshapes depend strongly on the w/d ratio, crystals with closely spaced domains have a much better chance of giving successful results. If the domain wall widths are expected to be just a few unit cells wide, crystals with wall separations d rather less than 1 μm are desirable. Some of the cuprate superconductors have wall separations d of order 0.2 μm [4] and should be very favourable systems.

For this type of diffraction experiment there are some fairly obvious points about experimental design. It is important to aim for high spectrometer resolution so that the strong peaks at $\pm\psi_0$ do not obliterate the scattering at angles between the peaks. Long counting times will be required to provide the statistics necessary to detect contributions that are perhaps of order $(w/d)^2$. In general it will be important to know the spectrometer resolution function $f(\psi)$ accurately. For many purposes a Gaussian function can be assumed but in practice more intensity is often observed in the wings of the line than a Gaussian provides. Frequently a Voigt function is found to give a very good fit out into the wings but since this is itself a convolution integral its use for $f(\psi)$ would exacerbate an already difficult computational problem. It would be desirable to determine $f(\psi)$ experimentally by fitting a normal Bragg peak carefully, ideally by observing the same peak, unsplit, above the transition temperature. Another complication is that for many crystals the shape of the Bragg peak depends both on the spectrometer resolution and the crystal quality. The crystal can contribute to the Bragg lineshape through mosaic and texture imperfections, but this

can be minimized in some cases by careful choice of samples or by limiting the region probed by the beam. These sample contributions can be eliminated by the choice of doing a powder experiment rather than a single-crystal experiment, but this may have significant disadvantages in statistics and in resolution. Another possibility which may provide a useful compromise is to make use of a single-crystal sample, but rotate it about the tetragonal axis, which is perpendicular to the scattering plane, to average out the textural contributions.

Since the accuracy of the outcome is likely to be limited by counting statistics the preferred method of analysis would be to use all of the data by fitting the entire two-peak scattering intensity profile to the predicted distribution $I(\psi)$. Obviously this will not be straightforward since $I(\psi)$ is a convolution integral, but it should be within the capabilities of some commercial data-fitting software as well as custom-written software. As figure 3 shows, the parameter w/d controls the ratio of the mid-peak and peak intensities and would be directly determined in the fit.

A second approach is to look for an asymmetry or skewness of one of the peaks and to use equation (6) to extract an estimate of w/d. One problem with this is the possible presence of some asymmetry due to overlap with the other peak, but this can be allowed for if the lineshape is accurately known from measurements above the transition temperature. To take the best advantage of the available statistics, the recommended approach would be to first establish $f(\psi)$ and then use measured data over the whole peak to fit directly to equation (6).

The third approach is similar to that used by Salje and collaborators which is based on the intensity midway between the peaks where the domain wall region makes the strongest contribution. If allowance is made for the intensity contributed at that point by the main peaks, which again requires accurate knowledge of $f(\psi)$, equation (8) or an equivalent should give a direct estimate of w/d. This method makes use of only a limited portion of the available data, but avoids complicated numerical fitting.

In summary, we have derived a simple expression for the diffraction lineshape characteristic of twinned domains that should be a reasonable approximation in practical cases. Fitting procedures based on this expression have the potential to yield reliable estimates for domain wall widths in many materials.

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