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Extinction Corrections for a Highly Perfect Crystal ($SrTiO_3$)*

BY J. HUTTON AND R. J. NELMES†

Department of Physics, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, Scotland

AND HANS J. SCHEEL

IBM Research Laboratory, CH-8803 Rüschlikon, Switzerland

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Abstract

Accurate neutron-diffraction data from a highly perfect crystal of $SrTiO_3$ have been used to assess the extinction model of Becker & Coppens [*Acta Cryst.* (1974), A**30**, 129–147, 148–153; *Acta Cryst.* (1975), A**31**, 417–425] in refining reliable thermal parameters from data very strongly affected by extinction. The model incorporates approximations not evidently reasonable in this case – namely, the (usual) kinematical approximation and the mosaic-block description of crystal microstructure. However, it is shown that a careful choice of parameterization within the overall model (*e.g.* between a Gaussian and a Lorentzian function for the distribution of mosaic-block orientations) can yield a uniformly good description of the extinction *per se* – except for reflections extinguished by more than about 90% on intensity. The refined thermal parameters are in remarkably good agreement with values obtained independently from lattice-dynamical calculations.

1. Introduction

In the last decade or so various models have been developed to calculate correction factors for the extinction of measured intensities in elastic-diffraction experiments. Of these models, the most useful are those which provide general solutions parameterized in a way suitable for ready incorporation into standard crystallographic least-squares refinement programs [see, for example, Zachariasen (1967); Cooper & Rouse (1970); Becker & Coppens (1974, 1975)]. A common feature of these models is that they are based on kinematical approximations for intensity transfer and a highly idealized description of crystal microstructure in terms of mosaic blocks. Although the theoretical shortcomings of any kinematical approach are recognized (Takagi, 1961), it has so far proved extremely difficult to formulate similarly general solutions from more rigorous concepts – especially for physically realistic descriptions of crystal microstructure. The lack of such a rigorous foundation has not, however, prevented the widespread use and acceptance of corrections based on the kinematical and mosaic-block approximations, because the primary purpose of making extinction corrections is (usually) not to obtain information about the crystal microstructure itself: rather corrections are made so as to obtain more accurate estimates of the parameters describing crystal structure. In such cases the physical approximations used in obtaining the extinction corrections matter relatively little, and primary importance attaches to the accuracy of the calculated corrections – however derived (Nelmes, 1980).

Nevertheless, it must be remembered that the extinction corrections made routinely in current crystallographic refinements are *not* physically rigorous [except in the limit of very thin crystals – see Becker (1977)]; their range of validity should, therefore, not be taken for granted. For this reason, it is important – especially when extinction is severe – to ensure (i) that the most suitable corrections have been made and (ii) that any inadequacy in the corrections has not significantly biased the crystal-structure parameters.

The work presented here developed from a series of high-resolution structural studies of some cubic perovskites by neutron diffraction (Hutton & Nelmes, 1981). In the course of the data collection from a $SrTiO_3$ sample, it became clear that the extinction was very severe and, further, that it was markedly anisotropic. In cubic $SrTiO_3$ the only variable crystal-structure parameters are the thermal parameters – all the positional parameters are fixed by symmetry. The refined thermal parameters could thus be expected to be even more than usually sensitive to the accuracy of extinction corrections. $SrTiO_3$ also happens to be one of those (few) materials for which accurate values of the thermal parameters are independently available

* Diffraction data were collected with the facilities of the Institut Laue–Langevin, Grenoble.

† To whom correspondence should be addressed.

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from lattice-dynamical calculations (Stirling, 1972). We were thus able to bring together

(i) accurate, high-resolution data,

(ii) severe extinction,

(iii) refinements in which the accuracy of extinction corrections affects thermal parameters alone, and

(iv) good independent estimates of those thermal parameters

to assess the effectiveness and the range of validity of the extinction models currently used in crystallographic refinements. Only the model of Becker & Coppens (1974, 1975) – now the most commonly used – has been tested explicitly here; from the work of Cooper & Rouse (1976), it appears that qualitatively similar results might be expected with the approach of Cooper & Rouse (1970).

2. The $SrTiO_3$ crystal

The growth of $SrTiO_3$ crystals is described by Scheel (1976), Scheel, Bednorz & Dill (1976) and Bednorz & Scheel (1977). The following observations are extracted from these papers and from recent crystal growth results:

(i) Crystals grown from high-temperature solutions show lower dislocation densities, by a factor $>10^3$, than crystals grown from melts; and they have a mosaic line-width less, probably much less, than 1′ of arc. Accordingly, crystals with natural faces are (optically) completely isotropic in polarized light. This high structural perfection is explained by the lower growth rates (by a factor $>10^2$), the smaller temperature gradients (by a factor $>10^2$) at the growing crystal interface, and the lower growth temperature in crystal growth from solution rather than melt.

(ii) A systematic evaluation of many solvents has shown that the Li–Sr–borate system gives the best solution-growth results and yields crystals of high purity (≤ 10 in 10^6 Li). The crystals have a yellow tinge caused by iron traces (~ 10 in 10^6).

The sample used in this study was cut along its $\langle 100 \rangle$ faces to a cuboid with sides $3{\cdot}2 \times 3{\cdot}0 \times 2{\cdot}8$ mm. When examined under crossed polars, it was found to show very clear signs of strain birefringence although only one inclusion, contributing no more than a few percent of the total birefringence, was identified. The remaining strain was thought to originate from damage to the crystal surfaces during cutting. The characteristics of such damage in $SrTiO_3$ have been comprehensively studied by Aso (1976) who finds, for specimens cut as here, that (i) residual strain may be quite noticeable up to 100 μm below the surface, and (ii) the induced extinction directions are (preferentially) those of the specimen axes.

In an attempt to eliminate as much of the strain as possible, about 100 μm was etched off the sample with concentrated phosphoric acid at about 550 K. The sample was then found to be uniformly black under crossed polars, with only a little stray light emanating from some residual surface pitting.

3. Experimental details and data processing

Full details of the experiment and data processing are given elsewhere (Hutton & Nelmes, 1981); only a brief summary is presented here. High-resolution, elastic-diffraction data were collected on the D9 four-circle diffractometer at the Institut Laue–Langevin (ILL), Grenoble, with an incident neutron wavelength $\lambda = 0{\cdot}397$ Å. During the measurements the sample was enclosed in a cryostat maintained at $T = 112 \pm 1$ K, in the cubic phase a few degrees above the cubic → tetragonal phase transition temperature, T_c. (The sample was *not* taken through the transition.) Usually two, and sometimes three, symmetry-equivalent reflections were measured for each of about 50% (randomly selected)* of the total number of reflections independent by symmetry out to Bragg angle $\theta_B = 60°$. Altogether this gave 452 measurements, with a resolution $(\sin\theta_B/\lambda)_{max} = 2{\cdot}1$ Å^{-1}. Thermal diffuse scattering corrections were calculated by the anisotropic, one-phonon procedure of Merisalo & Kurittu (1978), with elastic constants taken from the work of Bell & Rupprecht (1963).

4. Refinements

Standard crystallographic least-squares refinements were carried out, minimizing the quantity

$$\sum_{hkl} \{|F_{obs} - F_{calc}|/\sigma(F_{obs})\}^2, \qquad (1)$$

where F_{obs} and $\sigma(F_{obs})$ are the observed structure amplitudes and their estimated standard deviations respectively, and the summation is over all 452 measured reflections. [Expression (1) is hereafter abbreviated to $\sum w\Delta^2$, where $w = 1/\sigma^2(F_{obs})$ and $\Delta = |F_{obs} - F_{calc}|$.] The $\sigma(F_{obs})$ were based on the counting statistics, but subject to an empirically estimated lower limit of $\sigma(F_{obs})/F_{obs} \geq 0{\cdot}01$. Averaging of symmetry-equivalent reflections was not carried out because of the apparent anisotropy of the extinction. F_{calc} are the structure amplitudes calculated from

$$F_{calc}(\mathbf{Q}) = \mathrm{Sc}\, E(\mathbf{Q}) \left|\sum_i b_i (\cos \mathbf{Q}.\mathbf{r}_i) W_i(\mathbf{Q})\right|, \qquad (2)$$

where Sc is the overall scaling factor, $E(\mathbf{Q})$ is the

* The practice of measuring only a subset of the independent reflections has been shown by us (unpublished) to lead to no significant bias in the refined parameters – provided the selection is statistically random.

extinction-correction factor, b_i are the coherent neutron scattering lengths, $\mathbf{Q}$ is the reciprocal-lattice vector, $\mathbf{r}_i$ are the atomic position vectors, $W_i(\mathbf{Q})$ are the temperature factors, and i labels the ions in the cubic unit cell. The values of b_i were taken from the recent compilation of Koester (1977). From the results of Hutton & Nelmes (1981), it is clear that the thermal motion of each ion is adequately described by the conventional harmonic $W_i(\mathbf{Q})$: thermal anharmonicity is therefore not considered further in this paper.

As already noted in § 1, the $\mathbf{r}_i$ are all fixed by symmetry, and so the (harmonic) $W_i(\mathbf{Q})$ are the only crystal-structure parameters to be refined.

Preliminary refinements were carried out to assess the need to make full, anisotropic corrections for extinction [with the Becker & Coppens (1974, 1975) model]. Irrespective of the description of the extinction chosen (see below), it was found that the anisotropic form, with five additional parameters, always gave a *significantly* better fit than the corresponding isotropic form. [Taking Model 1 (below) as a specific example, it was found that the statistical significance of the five additional parameters – as quantified by the R-factor ratio test of Hamilton (1965) – was very much greater than 99·9%.] Consequently, only the anisotropic forms of the following descriptions are investigated here:

Model 1: type I extinction with a Lorentzian mosaic-spread distribution;
Model 2: type I extinction with a Gaussian mosaic-spread distribution;
Model 3: type II extinction; and
Model 4: mixed type extinction with a Lorentzian mosaic-spread distribution and with the 'perfect' mosaic blocks parameterized by a single dimension (spherical blocks).

In Models 1, 2 and 4 the (anisotropic) mosaic angular distribution was represented by the formalism of Thornley & Nelmes (1974). The earlier Coppens & Hamilton (1970) formalism – still sometimes used – has been shown by Nelmes (1980) to be incorrect in all cases and was not considered. For each description (Models 1 to 4), four refinements were carried out: the first, (*a*), with the complete data set of 452 reflections (242 of them non-symmetry-equivalent); and three others, with data sets obtained by omission of those reflections for which (*b*) $\theta_B < 10°$, (*c*) $\theta_B < 20°$ and (*d*) $\theta_B < 30°$ (leaving 446, 403 and 315 reflections respectively). Refinements were carried out with the reduced data sets in order to assess the range of validity of each description in terms of both θ_B and $E(\mathbf{Q})$. The selected cut-off values of θ_B have no special significance. But truncation of the data set according to θ_B was made because truncation according to $E(\mathbf{Q})$ would have complicated the comparison of the different descriptions – the number of reflections in the reduced data sets would then have become description-dependent. [Correlation between $E(\mathbf{Q})$ and θ_B does, however, mean that omission of low-angle reflections selectively excludes those most severely extinguished.]

5. Results

Convergence of the refinements carried out with Model 4 was very poor – a consequence of the (expected) high correlation between the parameter describing the domain size and those describing the mosaic spread. Good convergence was, however, obtained with each of the other Models. The thermal parameters and goodness-of-fit indices derived from these refinements are shown in Fig. 1 and Table 1, respectively.

Examination of Table 1 shows the goodness-of-fit with the *full* data set to be critically dependent upon the extinction parameterization; and then the difference in the fits becomes very much smaller as the most

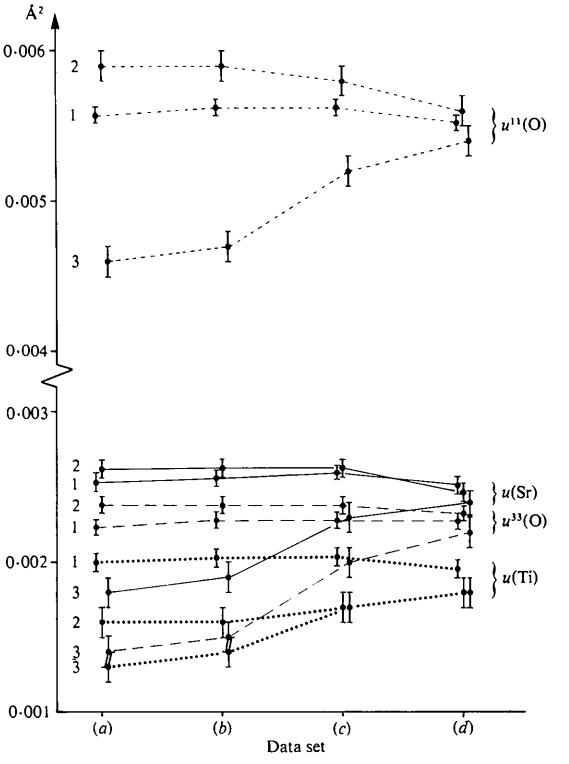

Fig. 1. The refined values for the mean-square thermal amplitudes, in Å². The (harmonic) thermal motion of Sr, at (0,0,0), and Ti, at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, is isotropic and hence is described by a single parameter – u(Sr) and u(Ti): the anisotropic thermal motion of O, at $(\frac{1}{2},\frac{1}{2},0)$, $(0,\frac{1}{2},\frac{1}{2})$ and $(\frac{1}{2},0,\frac{1}{2})$, has an amplitude u^{33}(O) along the O–Ti direction, and $u^{11}(\mathrm{O}) = u^{22}(\mathrm{O})$ perpendicular to that direction. The lines which join together the values obtained with each of the data sets (*a*), (*b*), (*c*) and (*d*) are intended only as guides to the eye. Each line is labelled at the left of the figure according to the extinction Model (1, 2 or 3) used. Full, dotted, short-dashed and long-dashed lines connect, respectively, values of u(Sr), u(Ti), u^{11}(O) and u^{33}(O).

Table 1. *The goodness-of-fit index, R_w, for Models 1, 2 and 3 – as indicated in brackets – for each of the four data sets (a)–(d)*

R_w, the weighted R index, is defined as $[\sum w\Delta^2/\sum wF_{obs}^2]^{1/2}$.

Data set	(a)	(b)	(c)	(d)
Number of reflections	452	446	403	315
$R_w(1)$	0·030	0·029	0·028	0·028
$R_w(2)$	0·058	0·053	0·044	0·035
$R_w(3)$	0·065	0·057	0·036	0·030

extinguished reflections are progressively removed. It is clear that the best fits are obtained with Model 1. First, corresponding residuals, R_w, are significantly lower than those obtained with the other Models. Secondly (and equally importantly), only for Model 1 are both of the following criteria satisfied when the data set is reduced: (i) the value of R_w remains essentially constant, and (ii) the refined values of the parameters (including extinction parameters) do not change significantly (see Fig. 1).

Fig. 1 illustrates how the wide discrepancy in refined parameters with the full data set progressively diminishes as the most extinguished reflections are omitted. It would appear that for data set (*d*) – for which $E^2(\mathbf{Q}) \geq 0{\cdot}2$ – all three Models yield very similar parameter values and, thus, that the need to choose carefully between the available parameterizations may be important only if very highly extinguished data are used. However, Table 1 shows that quite large differences in the R_w values remain even for data set (*d*) – in particular it is noteworthy that the largest difference is between the fits afforded by the superficially very similar parameterizations of Models 1 and 2.

In contrast to the results reported for severely extinguished $LiOH.H_2O$ data by Becker & Coppens (1975), good convergence was obtained here by assuming the extinction to be type II (Model 3). It was found, however, that the extinction parameters refined with data sets (*a*) and (*b*) were unphysical (negative mosaic-block dimensions). The inadequacy of the type II description of strong extinction is further demonstrated by the poor fits obtained with these data sets (Table 1). This accords with the observation of Becker & Coppens (1975) that the present theory does *not* provide an adequate description of primary extinction in very large mosaic blocks. [The extinction parameters refined with data set (*d*) correspond to mosaic-block dimensions that are comparable with estimated extinction lengths for the most severely affected reflections.]

It has been established beyond reasonable doubt that – of the options available with the model of Becker & Coppens (1974, 1975) – the type I (Lorentzian) extinction parameterization (Model 1) yields by far the best corrections in this case. Having said that, it still remains to be shown whether or not even these corrections are satisfactory over the entire range of the present analysis. The partial residuals obtained from refinements of Model 1 with data sets (*a*) and (*d*) are shown as a function of $E^2(\mathbf{Q})$ in Fig. 2, and for data set (*a*) the disproportionate contribution from the nine reflections that are more than 90% extinguished [$E^2(\mathbf{Q}) < 0{\cdot}1$] is very clear. A less expected, but important, conclusion to be drawn from Fig. 2 is that the failure of the extinction model appears to be *confined* to $E^2(\mathbf{Q}) < 0{\cdot}1$: the fit for $0{\cdot}1 < E^2(\mathbf{Q}) < 0{\cdot}2$ is as good as for much smaller extinction.* The dashed line in Fig. 2 shows that the dependence of the partial residuals upon $E^2(\mathbf{Q})$ becomes entirely negligible when those reflections for which $\theta_B < 30°$ are omitted from the refinement – even though some of the remaining reflections are still severely extinguished [$E^2(\mathbf{Q}) < 0{\cdot}3$]. The consistency of the refined parameter values between the different data sets is not, therefore, a validation of extinction Model 1 over the entire range of $E^2(\mathbf{Q})$. What *is* established is that the number of reflections which are inadequately corrected by Model 1 is sufficiently small that the good fit to the remaining reflections is not biased.

The physical interpretation of the refined mosaic-spread tensor is simplified by solving the eigenvalue equations. From the extinction parameters refined for Model 1 with data set (*a*), it is found that the half-width misorientations of the 'perfect' crystallites are respectively 0·36″, 0·38″ and 0·16″ of arc around the directions [100], [0, 0·98, 0·20] and [0, −0·20, 0·98] with respect to the axes of the cubic unit cell. This near coincidence of the cut specimen axes (see § 2) and the extinction directions is in agreement with the conclusions of Aso (1976) quoted in § 2.

* The high partial residuals for reflections with $E^2(\mathbf{Q}) < 0{\cdot}1$ are not an artefact of the empirical limit $\sigma(F_{obs}) \geq 0{\cdot}01F_{obs}$ (see § 4): all reflections with $E^2(\mathbf{Q}) < 0{\cdot}2$ have $\sigma(F_{obs}) \simeq 0{\cdot}01F_{obs}$.

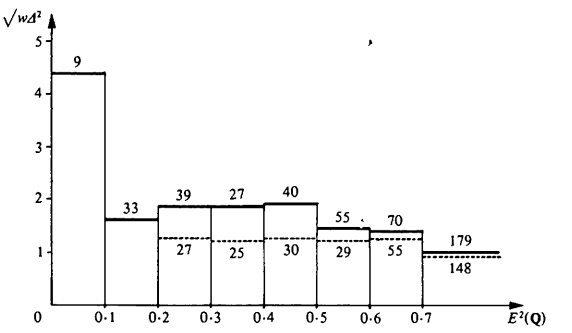

Fig. 2. The average value of $[w\Delta^2]^{1/2}$ within successive intervals of the extinction parameters for the refinements of Model 1 with data sets (*a*) and (*d*). The continuous line refers to the full data set, (*a*), and the dashed line to the reduced ($\theta_B \geq 30°$) data set, (*d*). Also shown is the number of observations within each interval.

The thermal parameters refined for Model 1 are in close agreement with those derived by Stirling (1972) from lattice-dynamical calculations. Stirling made the calculations for several different dynamical models which, for the present purposes, are most readily distinguished in terms of the values he obtained for u(Ti): the other thermal parameters, particularly u^{11}(O) and u^{33}(O), are relatively model-independent. The best agreement between the refined and calculated values of u(Ti) is obtained with Stirling's model 5, which – it is worth noting – was the model that gave the best overall fit to the dynamical data (Stirling, 1972). The calculated values for model 5, corrected to 112 K, are u(Sr) = 0·0029, u(Ti) = 0·0020, u^{11}(O) = 0·0052 and u^{33}(O) = 0·0024 Å^2 – expected to be accurate within 5–10%. In the same sequence, the refined parameters for Model 1 with data set (*d*) are 0·00252 (5), 0·00196 (6), 0·00552 (5) and 0·00228 (5) Å^2. The values agree within the estimated uncertainties. [The overall agreement is not critically dependent on the selection of Stirling's model 5 because of the relative insensitivity of u(Sr), u^{11}(O) and u^{33}(O) to the choice of model.]

6. Conclusions

The results presented here show the importance of giving adequate consideration to the choice of extinction parameterization – in this case among the options within the model of Becker & Coppens (1974, 1975). Adoption of an inappropriate parameterization can lead to the refinement of significantly inaccurate thermal parameters, and a poor fit. The identification of the most suitable choice was straightforward in the present case. Then remarkably good values for the thermal parameters were apparently obtained, despite the high extinction levels.

Even when the best choice of parameterization has been made, it appears probable that the useful range of validity of the Becker & Coppens model does not extend in this case to intensities extinguished by more than about 90%. [The initial impression that it *does* (from the consistency of the residuals in Table 1) is probably an artefact of the analysis, arising from the relatively small number of data with that very high level of extinction.] But, importantly, this study also appears to show that the Becker & Coppens model can give a *uniformly* good description of all extinction that is less than the estimated limit [*i.e.* for $E^2(\mathbf{Q}) \gtrsim 0{\cdot}1$ in this case].

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