

## The RED Extinction Model. I. An Upgraded Formalism

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### Abstract

Some modifications are introduced into the extinction correction formulae based on the RED (random elastic deformation) model developed earlier by the author [Kulda (1987). *Acta Cryst.* A43, 167–173]. The scattering cross section, which includes a correction for primary extinction, has been extended to allow for a more general angular variation of the effective deformation gradient. The originally proposed  $\cos \theta$  dependence is included as one of the limiting cases corresponding to a pure lattice-plane misorientation. A modified expression has been derived for the angular reflection curve profile which describes properly the broadening due to the finite dimensions of the diffracting region. This version of the RED model containing three free parameters has been employed in experimental tests reported in paper II [Kulda (1988). *Acta Cryst.* A44, 286–290].

### 1. Introduction

In a recent paper (Kulda, 1987), hereafter referred to as paper A, we have proposed the random elastic deformation (RED) model for extinction treatment in real crystals. Unlike the traditional approaches, reviewed, for example, by Becker (1977), which use the concept of mosaic structure, RED is based on a stochastic sequence of elastically deformed domains. It is just this feature which in the end makes it possible to cover primary extinction effects more adequately by a direct use of the dynamical diffraction theory (Kulda, 1984). Secondary extinction is treated in a conventional way by solving the Hamilton–Zachariasen intensity coupling equations.

Paper A was confined to development of the RED concept and to comparison of its basic characteristics with other existing extinction models. The aim of the present paper is to provide working formulae that could be built into a least-squares refinement program and used in practical performance tests of the RED model (Kulda, 1988). As the most important step in this direction we shall derive a modified expression for the angular distribution function  $w_{\text{RED}}(\varepsilon)$ , taking into account broadening caused by finite dimensions of the reflecting regions and allowing for a more general deformation type.

### 2. Generalized deformation gradient

In paper A, for the sake of simplicity, we set  $|\partial\Delta\theta/\partial s_0| = \cos \theta/R$ , thus considering the component of elastic bending that brings about pure lattice-plane misorientation as the only source of deformation. In the course of practical tests this assumption – though realistic for a particular crystal – proved too limiting for general use. As pointed out already in the discussion of paper A any real deformation consists of both misorientation components and components exhibiting changes of the lattice parameter. In the latter case with the diffraction vector parallel to the atomic displacement  $\mathbf{U}$  we would have  $|\partial\Delta\theta/\partial s_0| = \sin \theta/R$ . Therefore it appears reasonable to introduce a more flexible model  $|\partial\Delta\theta/\partial s_0| = C(c, \theta)/R$ , which could with the help of a free parameter  $c$  allow for both situations. Furthermore, the mosaic width parameter  $\alpha$  [cf. equations (13) and (14) of paper A, here referred to as (A13) and (A14)] is angle independent within the Becker & Coppens (1974, 1975) treatment which is known to be exact in the limit of pure secondary extinction (Kato, 1976). Thus also the possibility  $C(c, \theta) = \text{constant}$  should be covered by our improved formula. The simplest choice satisfying all three requirements is

$$C(c, \theta) = [c + (1 - 2c) \cos^2 \theta]^{1/2} \quad (1)$$

where  $c \in (0, 1)$  is an additional free parameter of the RED model.

The generalized angular distribution function  $w(\varepsilon)$  is now written in analogy with (A11) as

$$w_{\text{RED}}(\varepsilon) = \{R/[\bar{t}C(c, \theta)]\} \times \exp(-\pi\{R\varepsilon/[\bar{t}C(c, \theta)]\}^2). \quad (2)$$

This expression, with  $C(c, \theta)$  given by (1), can be interpreted as a joint distribution function of two superimposed random walk sequences of the same type (A7) differing just in the deformation gradients  $|\partial\Delta\theta/\partial s_0|_1 = \cos \theta/R$  and  $|\partial\Delta\theta/\partial s_0|_2 = \sin \theta/R$  and in the numbers of permitted states  $N_1, N_2$ . Putting  $c = N_2/(N_1 + N_2)$  we see that (2) is just a convolution of the distribution functions

$$w_i(\varepsilon) = (\bar{t}_i|\partial\Delta\theta/\partial s_0|_i)^{-1} \times \exp[-\pi\varepsilon^2/(\bar{t}_i|\partial\Delta\theta/\partial s_0|_i)^2].$$

Following this line we would, however, have to average in the next step the exponential terms of the reflection probability (A5) which would lead to a rather complex expression. Therefore we prefer to treat  $C(c, \theta)/R$  as an effective deformation gradient and substitute it for  $|\partial\Delta\theta/\partial s_0|$  directly into  $\sigma_{\text{RED}}$ .

### 3. Broadening of the reflection curve

Until now the angular profile of any reflection was determined solely by the properties of the stochastic sequence of the deformed domains. It is clear that with increasing deformation, as the conditions for diffraction on individual domains approach the kinematical case, an additional broadening of the angular profile has to be expected, which requires further generalization of (2). Within the mosaic model an analogous step, allowing for type II extinction, is performed by convoluting the mosaic distribution function with the kinematic rocking curve  $r_k(\varepsilon)$ . For symmetrical diffraction geometry on a plane-parallel crystal plate we may write

$$r_k(\varepsilon) = \alpha_k (\sin \pi \alpha_k \varepsilon / \pi \alpha_k \varepsilon)^2, \quad (3)$$

where  $\alpha_k = l \sin 2\theta / \lambda$  and  $l$  represents the averaged reflected beam path.

Let us for a while rewrite (3) in terms of the dynamical diffraction theory (Sears, 1978) as

$$r'_k(Y) = \sin^2(A_G Y) / Y^2 \quad (4)$$

where  $A_G = l\lambda F_G / \Omega$  and  $Y = \varepsilon \pi \Omega \sin 2\theta / (F_G \lambda^2)$  represent the reduced beam path and angular deviation, respectively. Equation (4) can easily be related to the expression for the dynamical rocking curve for the symmetrical transmission geometry,

$$r'_d(Y) = \sin^2[A_G(Y^2 + 1)^{1/2}] / (Y^2 + 1). \quad (5)$$

We see that only for sufficiently small  $A_G$  (say  $A_G < 1$ ) may unity be neglected in comparison with  $Y^2$  over a major part of the rocking curve and (5) may be replaced by (4), where the structure factor  $F_G$  cancels out. In practice  $F_G$  often varies by orders of magnitude within a single data set so that it may not be safe to assume that for all reflections the kinematical expression (4) is valid. Instead, the value of  $A_G$  should be checked for each individual reflection.

Unfortunately such simple but rigorous considerations based on the dynamical theory cannot be easily extended to the case of deformed crystals. The description starting from the Takagi-Taupin equations deals with two directions defined once and for all (those of the transmitted and reflected beams) and does not explicitly account for any broadening effects. In order to include them in our treatment we recall firstly the well established fact (e.g. Gronkowski & Malgrange, 1984) that the reflection takes place in that part of a deformed domain where the Bragg-angle

deviation does not much exceed the dynamical rocking-curve width (Fig. 1). Later on we shall assume that the reflecting region is confined just to the range  $-1 \leq \Delta Y \leq +1$  (hatched area in Fig. 1). This assumption is supported by the independently derived equation (A4) which relates the probability of interbranch transitions just to this range. For large deformations the thickness of such a layer becomes much smaller than the extinction distance and we shall assume that in this limit we may apply the kinematical formula (3) directly. The reflected beam path  $\Delta s_G$  is equal to the distance  $BC$  in Fig. 1, i.e.

$$\begin{aligned} \Delta s_G &= \Delta Y (d\theta/dY) (ds_G/d\theta) \\ &= [F_G \lambda^2 / (\pi \Omega \sin 2\theta)] [R/C(c, \theta)]. \end{aligned} \quad (6)$$

From this value we shall derive the angular width of the rocking curve (3)

$$\begin{aligned} \alpha_k &= \lambda / (\Delta s_G \sin 2\theta) \\ &= [\pi \Omega / (F_G \lambda)] C(c, \theta) / R \\ &= \Delta_G C(c, \theta) / R, \end{aligned} \quad (7)$$

where  $\Delta_G$  is the extinction length measured along the diffracted-beam direction. The use of the kinematical formula is justified whenever the thickness of the hatched region in Fig. 1 is appreciably less than the extinction distance or, in other words, whenever  $\alpha_k$  several times exceeds the width of the Darwin curve. This requirement does not mean any serious limitation for our purpose because the broadening term is important in  $\sigma_{\text{RED}}$  only when  $\alpha_k$  is comparable to the width of  $w_{\text{RED}}$ .

Finally let us [in analogy to Becker & Coppens (1974, 1975)] approximate the expression (3) by a Gaussian  $r_k(\varepsilon) = \alpha_k \exp(-\pi \alpha_k^2 \varepsilon^2)$  and write down the complete formula for  $w_{\text{RED}} * r_k$ :

$$\begin{aligned} \bar{w}_{\text{RED}} &= \frac{R}{(\bar{t}^2 + \Delta_G^2)^{1/2} C(c, \theta)} \\ &\times \exp \left[ -\frac{\pi}{\bar{t}^2 + \Delta_G^2} \left( \frac{R\varepsilon}{C(c, \theta)} \right)^2 \right]. \end{aligned} \quad (8)$$

Equation (8) differs in an important way from analogous expressions of the Becker & Coppens and other traditional treatments: broadening of the reflec-

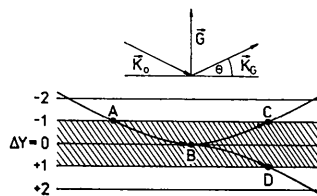


Fig. 1. Beam trajectories in a reflecting region of a deformed domain:  $AB$  incident,  $BC$  reflected and  $BD$  transmitted (via interbranch transition) beams.

tion curves depends not only on the Bragg angle and wavelength, but also on the structure-factor magnitude. The reason for this is the definition of  $\Delta_{SG}$  in (6) based on the fact that the beam interacts only with a part of any individual domain. The final effect of this modification is similar to that called for when comparing the kinematical and dynamical rocking curves in the beginning of this section: broadening will appear starting from weak reflections, often characterized by high  $hkl$  and large  $\theta$ .

#### 4. Summary and discussion

The scattering cross section  $\sigma_{RED}$  with the modifications introduced in the preceding sections can be written in the form

$$\sigma_{RED}(\varepsilon) = \{1 - \exp[-QR/C(c, \theta)]\}(\bar{l}^2 + \Delta_G^2)^{-1/2} \times \exp\left\{-\frac{\pi}{\bar{l}^2 + \Delta_G^2} \left[\frac{R\varepsilon}{C(c, \theta)}\right]^2\right\}, \quad (9)$$

with  $C(c, \theta)$  given by (1) and  $\Delta_G = \pi\Omega/F_G\lambda$ . In order to have a measure of primary extinction we may rearrange the right-hand side of (9) as  $y_p Q\bar{w}_{RED}(\varepsilon)$  with

$$y_p = \{1 - \exp[-QR/C(c, \theta)]\}C(c, \theta)/(QR). \quad (10)$$

Here  $y_p$  is the primary extinction factor, the magnitude of which depends on the effective deformation gradient  $C(c, \theta)/R$ . For a given  $c$  and  $R$  the mutual proportion between primary and secondary extinction is determined by the mean free path  $\bar{l}$  and its relation to the mean beam path  $T$  in the sample, as discussed in paper A (§ 4).

The expression (9) for  $\sigma_{RED}$  can be used within the energy transfer equations (ETE) whenever they are believed to be applicable. For some special crystal shapes, such as plane-parallel plates, where an analytical solution of the ETE exists (e.g. Dietrich & Als-Nielsen, 1965), the new expression for the extinction factor can be obtained if  $\sigma_{RED}$  given by (9) is substituted (with some care) for the kinematical cross section  $\sigma$ . For crystals of isotropic or slightly anisotropic shape the numerical solution of the ETE presented by Becker & Coppens (1974, 1975) may be used. In such a case the extinction factor is usually calculated with the help of the approximative expressions (A16); within RED the parameter  $x$  is

given by

$$x_{RED} = \frac{2}{3}\{1 - \exp[-QR/C(c, \theta)]\}T/(\bar{l}^2 + \Delta_G^2)^{1/2}. \quad (11)$$

Since we have introduced the quantity  $\Delta_G$  it is no longer possible to rearrange (11) in a form analogous to (A15) as the parameter  $A$  would depend on the structure factor  $F_G$  through  $\Delta_G$ .

Irrespective of the particular way in which the ETE are solved,  $\sigma_{RED}$  contains up to three free parameters,  $\bar{l}$ ,  $R$ ,  $c$ , to be adjusted by a least-squares fit to experimental data. This is one more than in the case of mosaic models (parameters  $g$  and  $r$ ), which, however, possess an additional freedom in the choice of the functional form of  $w(\varepsilon)$  not present in RED. To examine whether or not an additional degree of freedom is justified within RED we may use significance tests on the agreement factors (Hamilton, 1965). They become particularly important in the case of  $R$  being sufficiently small for primary extinction to vanish ( $y_p = 1$ ), where (11) can be written as

$$x_{RED} = \frac{2}{3}[QR/C(c, \theta)][T/(\bar{l}^2 + \Delta_G^2)^{1/2}]. \quad (12)$$

In such situations the angular dependence of the deformation gradient is often unimportant [ $C(c, \theta) = \text{constant}$ , i.e.  $c = 0.5$ ] and the RED model yields results analogous to the Becker & Coppens mixed type except for the different description of the broadening effects. The transition to type I or type II is now a matter of the relation between the magnitudes of  $\bar{l}$  and the largest  $\Delta_G$ ; in either of these limiting cases only a single free parameter,  $R/\bar{l}$  (type I) or  $R$  (type II), is required in (12). As soon as primary extinction begins to play a role, both  $\bar{l}$  and  $R$  become essential for usual data sets including weak and strong reflections simultaneously so that only the significance of the parameter  $c$  needs to be questioned.

#### References

- BECKER, P. (1977). *Acta Cryst.* **A33**, 243–249.  
 BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* **A30**, 129–147.  
 BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst.* **A31**, 417–425.  
 DIETRICH, O. W. & ALS-NIELSEN, J. (1965). *Acta Cryst.* **18**, 184–187.  
 GRONKOWSKI, J. & MALGRANGE, C. (1984). *Acta Cryst.* **A40**, 515–521.  
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.  
 KATO, N. (1976). *Acta Cryst.* **A32**, 458–466.  
 KULDA, J. (1984). *Acta Cryst.* **A40**, 120–126.  
 KULDA, J. (1987). *Acta Cryst.* **A43**, 167–173.  
 KULDA, J. (1988). *Acta Cryst.* **A44**, 286–290.  
 SEARS, V. F. (1978). *Can. J. Phys.* **56**, 1261–1288.

## The RED Extinction Model. II. Refinement of Extinction and Thermal Vibration Parameters for SrF<sub>2</sub> Crystals

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### Abstract

The RED extinction model reported previously [Kulda (1987). *Acta Cryst.* A43, 167–173] was applied to several neutron diffraction data sets, some of them already used in the design of the Cooper & Rouse [*Acta Cryst.* (1971), A27, 622–628] empirical extinction formula and in the tests of the Becker & Coppens [*Acta Cryst.* (1974), A30, 129–147] formalism. The results of least-squares refinements fully confirm the expected gain in agreement due to an improved description of the coherent part of the wave interaction by the RED model, whose adequacy is further supported by the realistic values of the refined effective deformation gradient and mean free path between subsequent reflections. The RED-based harmonic thermal vibration parameters are systematically somewhat larger than those obtained within the Becker & Coppens formalism and follow more closely the expected quasi-harmonic temperature dependence. Significant differences are also found between the two models in terms of the derived room-temperature Debye–Waller parameters. The RED values  $B_{\text{Sr}} = 0.557(10) \times 10^{-2}$  and  $B_{\text{F}} = 0.830(10) \times 10^{-2} \text{ nm}^2$  agree better with the results of shell model calculations based on experimental phonon dispersion curves.

### 1. Introduction

In two recent articles (Kulda, 1987, 1988), hereafter papers *A* and *B*, respectively, we reported a new extinction formalism based on the RED (random elastic deformation) model of a real imperfect crystal. It was concluded that its main advantage should arise from direct application of the dynamical diffraction theory to the description of the coherent part of the wave interaction responsible for primary extinction and broadening of the reflection curve due to particle-size effects. Secondary extinction is treated by solving the energy transport equations for crystals of isotropic shape given by Becker & Coppens (1974*a*, 1975) – hereafter B&C.

The present paper deals with a demonstration of the practical use of the RED formalism in the least-squares refinement of extinction and thermal vibration parameters. For comparison of the performance

of several extinction models we chose the neutron diffraction data on SrF<sub>2</sub> collected by Cooper & Rouse (1970, 1971). To these data the Cooper & Rouse (1970) extinction formula was tailored and, later on, they were employed by Becker & Coppens (1974*b*) and Cooper & Rouse (1976) for tests of the B&C formalism. For the following discussion of the influence of the extinction model on the refined thermal vibration parameter values we have added further data on SrF<sub>2</sub> published by Mair, Barnea, Cooper & Rouse (1974) which include results of measurement at elevated temperatures. For all these data the traditional mosaic models can be claimed to work satisfactorily. Best agreement is usually attained within the B&C formalism which will therefore be used in what follows for comparison with RED.

### 2. Method of data analysis

The refinement on all of the data sets was performed with the help of a purpose-written computer code, *THERM*, based on a Levenberg–Marquardt-type nonlinear least-squares algorithm [*e.g.* procedure *CURFIT* in the book by Bevington (1976)] using numerical calculation of derivatives. The quantity minimized was  $\sum w_i (F_{oi}^2 - F_{ci}^2)^2$ ,  $F_o$  and  $F_c$  representing the observed and calculated structure factors, respectively. Individual data points were weighted by squared reciprocals of the estimated standard deviations published together with the data. Values of the thermal diffuse scattering correction were taken from the same source. The effects of thermal motion on the structure factors were represented by the Willis (1969) formalism employed in the paper of Mair *et al.* (1974) and both harmonic vibration parameters  $\alpha_{\text{Sr}}$ ,  $\alpha_{\text{F}}$  and the anharmonic parameter  $\beta_{\text{F}}$  were refined. For evaluation of the extinction correction  $y = y_s(x_{\text{RED}})$  within the RED approach we employed the analytical approximation (A16) [equation (16) of paper *A*] to the B&C solution for secondary extinction with a Gaussian angular distribution. Equation (B11) was used to calculate  $x_{\text{RED}}$  depending on the free parameters  $\bar{l}$ ,  $R$  and  $c$ . In order to eliminate the influence of possible differences in the efficiency of various least-squares minimization algorithms in all cases we also used a refinement based on the B&C