EXTINCTION EFFECTS IN CRYSTALS*

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ABSTRACT

The current state of the art regarding treatment of extinction effects in crystals is reviewed. The physical resonableness of the extinction parameters resulting from least squares refinement of crystal structures is examined.

INTRODUCTION

EXTINCTION effects in measured diffraction intensities and their corrections have been one of the important problems in structural crystallography. Nevertheless, until recently, the problem of extinction correction was not taken seriously by most crystallographers and strong extinction-affected reflections were rejected outright from the observed data sets. However, this approach is undesirable in high precision diffraction studies of current interest.

Historically, the treatments of extinction have been based on two distinct concepts originally proposed by Darwin[1], namely, those of primary and secondary extinctions. Darwin postulated that a real crystal could be considered to consist of a great many small perfect blocks or domains which are tilted very slightly relative to one another. The power loss suffered by the incident x-ray beam due to diffraction within one ideal crystal block is termed as primary extinction, while the cumulative power loss in the blocks traversed by the beam before it reaches a particular block under consideration is referred to as secondary extinction. A mosaic crystal is said to be ideally imperfect if the primary and the secondary extinctions are negligibly small for *all* reflections. A comprehensive account of the theoretical aspects of the early treatments of extinction has been given by Zachariasen[2]. He has shown that for the primary extinction to be negligible, the path length t in a single domain must be very small compared with the extinction length, $\Lambda(= V/F\lambda)$ where V is the volume of the unit cell and F is the structure factor. For secondary extinction to be negligible, the mosaic spread must be large compared with $(Q/\sqrt{2\pi}\,\mu)$ and $(\lambda/t\sin 2\theta)$ where Q is the kinematical integrated reflectivity per unit length and μ is the linear absorption coefficient.

Zachariasen[2] has derived the expressions for the integrated reflecting power in different diffraction geometries for absorbing and non-absorbing crystals based on Darwin's theory[3] which deals with crystals of infinite thickness. Before Zachariasen, Ramachandran[4] had already derived the fundamental equations for the amplitudes of the reflected and transmitted waves from crystals of finite thickness by combining Darwin's[3] recurrence relation approach and Lord Rayleigh's[5] theory for the reflection of light from a regularly stratified medium. This new Rayleigh-Darwin formalism due to Ramachandran was elegantly able to resolve[6] some of the apparent differences[2] in the results of the Ewald and the Darwin theories. Ramachandran further extended his work to obtain expressions for the integrated intensities of mosaic and perfect absorbing crystals under various conditions (for the Bragg case) and obtained many results of practical utility[7]. He also proved[8] that for weakly reflecting thin crystals, the integrated reflecting powers as calculated by the dynamical theory and the kinematical theory are identical. This implies that one cannot easily distinguish between the weak primary and secondary extinction effects.

Since the polarisation dependence of integrated intensity is different for the perfect and the ideally mosaic crystals, it is possible to examine the degree of perfection in crystals using polarised x-rays. Ramaseshan and Ramachandran[9] were the first to demonstrate experimentally that the polarisation factor of a reflection depends critically on the state of perfection of the crystal. Subsequently, this aspect was pursued theoretically by Chandrasekhar[10,11] who also demonstrated experimentally that polarised x-rays can be used to obtain the true value of the structure factor in the presence of extinction in a crystal of any shape and without having to make any special assumptions regarding the nature of extinction.

In view of the extensive work done by Prof G. N. Ramachandran and his colleagues on perfection of crystals, particularly in relation to the dynamical

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* This article was prepared on the occasion of Prof. G. N. Ramachandran's Sixtieth birthday which was celebrated recently.

theory of x-ray diffraction[12], we felt appropriate to write this article on the occasion of Prof. Ramachandran's sixtieth birthday.

EXTINCTION CORRECTIONS IN STRUCTURAL CRYSTALLOGRAPHY

Although there were many treatments of the type described in the last section for correcting the extinction effects, none of them was convenient for use in routine crystal structure determinations. The first breakthrough in this direction came when Zachariasen[13] proposed an approximate closed form solution to the Darwin energy transfer equations:

$$\frac{\partial I_0}{\partial S_0} = -(\bar{\sigma}+\mu)I_0 + \bar{\sigma} I_h$$

$$\frac{\partial I_h}{\partial S_h} = -(\bar{\sigma}+\mu)I_h + \bar{\sigma} I_0 \tag{1}$$

where the incident and diffracted intensities, I_0 and I_h, are functions of positions within the crystal specified by coordinates S_0 and S_h along the incident and diffracted directions and depend on the divergence angle ε of the incident beam from ideal Bragg condition, and $\bar{\sigma}(\varepsilon)$ is the average effective diffracting power. The correction for secondary extinction Y_s, defined as the ratio of the integrated power P of the diffracted beam to its kinematical limit P_k, is evaluated as

$$Y_s = \frac{(1+2X_0)^{-1/2} + K^2(1+2K^2 X_0)^{-1/2}}{(1+K^2)} \tag{2}$$

where, $K = \cos 2\theta$ for x-rays and $= 1$ for neutrons

$$X_0 = (2/3)Q_0 \alpha^* \bar{T}_\mu,$$
$$\bar{T}_\mu = (1/A(\mu)) \int (T_1 + T_2) \exp$$
$$[-\mu(T_1+T_2)] \, dv,$$
$$\alpha^* = \alpha/[1+(2\alpha/3g)^2]^{1/2},$$
$$\alpha = t_\perp / \lambda.$$

The quantity $t_\perp$ is the mean domain thickness perpendicular to the incident beam ($= 3r/2$ for spherical domains), and g is related to the width of the mosaic spread distribution. Crystals for which $r \gg \lambda g$ are classified as type I, while those for which $r \ll \lambda g$ as type II. To obtain the above solution for Y_s, Zachariasen had assumed. (i) The effects of absorption and extinction could be separated. It must be mentioned that Werner et al[14] had already worked out a more exact solution without having to separate the two effects, in the form of an infinite series of Bessel functions. (ii)

The power diffracted in the direction can be expressed as

$$P(\varepsilon) = I_0 \nu \bar{\sigma}(\varepsilon) \phi(\bar{\sigma}),$$
$$\phi(\bar{\sigma}) = (1+\bar{\sigma}\bar{T})^{-1},$$
$$\bar{\sigma}(\varepsilon) = \int \sigma(\varepsilon+\Delta) W(\Delta) d\Delta,$$

where $W(\Delta)$ describes the misorientation (Δ) distribution of the mosaic blocks.

LIMITATIONS AND MODIFICATIONS OF ZACHARIASEN'S THEORY

Chandrasekhar et al[15] were the first to verify the polarisation dependence of Y and to suggest an experimental method for determining the extinction factor. Many workers have examined the validity of Zachariasen's theory and pointed out its limitations. Its main limitations are (i) It underestimates severe extinction[16,17]. (ii) It does not satisfactorily account for the angle and wavelength dependence[16]. (iii) It does not take account of the dynamical interactions responsible for primary extinction[18].

A number of workers have also attempted to modify or revise Zachariasen's theory. Cooper and Rouse[16] tried to improve its angle dependence by introducing an analytical function of X and $\sin \theta$. Coppens and Hamilton[19] extended it to include anisotropic extinction effects. Sequeira et al[17] suggested an empirical but easily programmable modification of the type

$$Y = [1+2x+ax^2]^{-\frac{1}{2}}, \tag{3}$$

which was found to give quite satisfactory corrections upto values of Y as low as 0.06 observed in L-glutamic acid HCL (see figure 1).

A notable revision has been due to Becker and Coppens[20,21] who suggested that (a) The domain radius r should be replaced by ($r \sin 2\theta$). This implies different angle dependence for type I and type II crystals and hence possible distinction between the two even when extinction is isotropic. (b) In order to correct for primary extinction effect, the value of $\bar{\sigma}$ in the Darwin transfer equations is damped by Y_p, which is calculated for diffraction by an average block. The combined extinction correction can then be evaluated as

$$Y = Y_p (X_p) Y_s (Y_p X_s) \tag{4}$$

with

$$X_p = (2/3)Q_0 (\bar{r})^2 \lambda^{-1} \sin 2\theta$$

Our results discussed in the last section (tables 1, 2) seem to favour the introduction of Y_p but do not favour the replacement of r by $r \sin 2\theta$.

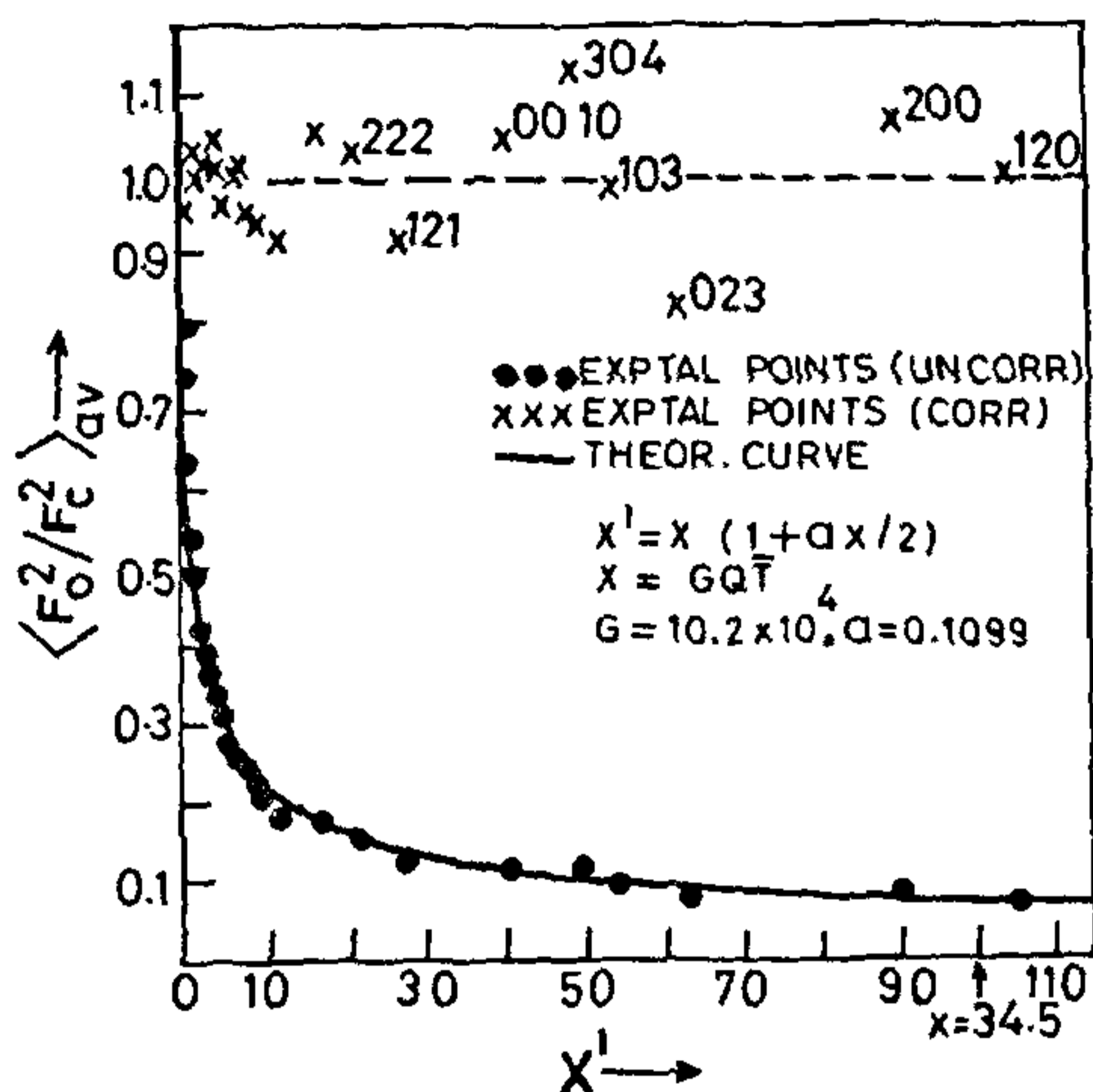EXTINCTION CURVE FOR L-GLUTAMIC ACID. HCL

$$Y = [1 + 2x + ax^2]^{-1/2}$$

Figure. 1. Average observed F_0^2/F_c^2 values and the extinction curve calculated using the expression $Y = [1 + 2x + ax^2]^{-\frac{1}{2}}$ for L-glutamic acid. HCl.

The formalisms discussed so far are essentially based on Darwin's primary and secondary extinction concepts which imply the presence of *completely coherent* or incoherent waves. The partly coherent and partly incoherent nature of waves in real crystals is presumed to be taken care of by the mosaic crystal model which is inadequate for a wide range of degree of imperfections existing in real crystals. Kato[22-25] has recently developed a new theory which incorporates *both* coherent and incoherent processes associated with diffraction of waves in crystals without any *a priori* assumptions. The theory offers new possibilities for developing extinction corrections based on a more realistic description of the distorted crystal.

KATO'S STATISTICAL DYNAMIC THEORY OF EXTINCTION

Kato's formalism is based on the postulation that the observed intensity is an ensemble average of the dynamical intensities evaluated using Takagi-Taupin[26] equations of the type

$$\frac{\partial D_0}{\partial S_0} = i K_{-h} \phi D_h - \tfrac{1}{2} \mu D_0,$$

$$\frac{\partial D_h}{\partial S_h} = i K_h \phi^* D_0 - \tfrac{1}{2} \mu D_h, \tag{5}$$

where D_0 and D_h are the wave fields of the direct and reflected waves, $K_{\pm h}$ is the dynamic reflection coefficient per unit length, and $\phi = 2\pi i h u$ is the lattice phase factor which depends on the displacement vector $u(r)$ for the distorted lattice relative to a perfect lattice. These phase factors are constant for a perfect crystal but have to be evaluated by statistical averaging for a real crystal. In order to evaluate the measured intensity, a second order correlation function, $f(z)$ and a correlation length τ are introduced;

$$f(z) = \langle \phi(0) \phi^*(z) \rangle = \langle \phi^*(0) \phi(z) \rangle,$$

$$= E^2 + (1 - E^2) g(z) \tag{6}$$

where z is the distance between two scattering points in the crystal and $E = \langle \phi \rangle = \langle \phi^* \rangle$, is zero for an ideally imperfect crystal and $= 1$ for a perfect crystal.

$$\tau = \int_0^\alpha g(z)\,dz. \tag{7}$$

Kato has obtained the solutions for (5) assuming

$$\tau \ll \Lambda = |k_h k_{-h}|^{-\frac{1}{2}}$$

and shown that the coherent component, I_h^c ($= \langle D_h \rangle^2$) of measured intensity is governed by the following equations

$$\frac{\partial \langle D_0 \rangle}{\partial S_0} = i E k_{-h} \langle D_h \rangle - \tfrac{1}{2} \mu_e \langle D_0 \rangle,$$

$$\frac{\partial \langle D_h \rangle}{\partial S_h} = i E k_h \langle D_0 \rangle - \tfrac{1}{2} \mu_e \langle D_h \rangle, \tag{8}$$

while the incoherent components obey the equations

$$\frac{\partial I_0^i}{\partial S_0} = -\bar{\mu}_e I_0^i + \bar{\sigma}_h I_h^i + \sigma_{-h}(1 - E^2) I_h^c,$$

$$\frac{\partial I_h^i}{\partial S_h} = -\bar{\mu}_e I_h^i + \bar{\sigma}_h I_0^i + \sigma_h(1 - E^2) I_0^c, \tag{9}$$

where

$$\mu_e = \mu + 2(1 - E^2) \tau \operatorname{Re}(k^2)$$

$$\sigma_{\pm h} = 2|k_{\pm h}|^2 \tau,$$

$$\bar{\sigma}_{\pm h} = 2|k_{\pm h}|^2 [(1 - E^2)\tau + E\Lambda]$$

$$\bar{\mu}_e = \mu + 2[(1 - E^2)\tau + E\Lambda] \operatorname{Re}(k^2),$$

$$k^2 = k_h k_{-h}.$$

It is possible to evaluate the parameters E and τ if some statistical model of the crystal is given and hence to predict the measured integrated intensity and the extinction factor. It also seems possible to extend the method of solution to cases where $\tau > \Lambda$, the extinction length.

PHYSICAL REASONABLENESS OF THE EXTINCTION PARAMETERS

Although it is now possible to correct extinction effects in diffraction data rather precisely and routinely using the Zachariasen's theory or some of its modifications, the physical reasonableness of the derived extinction parameters has often been in doubt. We will now examine this aspect for the refinement of accurate neutron diffraction data on two different crystals, by comparing them with the direct estimates of the domain sizes from x-ray topography and mosaic spreads from multicrystal diffractometry.

KCl Crystal: The neutron data set consisting of 54 reflections in an octant of reciprocal space was recorded in 0–2θ mode from a crystal of size $2.2 \times 2.6 \times 4.2$ mm^3 using a computer-controlled diffractometer at Trombay[27]. The data were moderately affected by extinction ($Y_{min} = 0.7$). The results of refinement based on various extinction models are given in table 1.

It is clear from these results that it is not possible to choose between the primary and secondary extinction models. When the parent crystal was examined by multicrystal diffractometry (MCD) and x-ray topography[28], a mosaic spread of 14 min of arc (FNHM) and an average particle radius of 8 microns were indicated, supporting the parameters resulting from the primary extinction model.

L-glutamic acid. HCl: The data set[29] consisting of 639 independent reflections $(\lambda = 1.406$ Å$)$ was severely affected by extinction $(Y_{min} = 0.06)$. The positional and anisotropic thermal parameters were refined along with a scale factor and isotropic extinction parameters. The R-values and extinction parameters resulting from various models are summarised in table 2.

Models (1c), (1d), (2b) and (3) all yielded consistent structural parameters while models (1a) and (1b) were yielding non-positive definite thermal parameters for some of the atoms. The equivalent mosaic spread ($\simeq$ 1 sec of arc) resulting from models (1c), (2) and (3) was much too small when compared with the value of 45 sec obtained from multicrystal diffractometry[28]. However, a constrained refinement (model 1d) using a g-value of 0.29 (corresponding to 45 sec mosaic width) yielded a particle radius of 133 microns which was consistent with the x-ray topographs.

CONCLUSION

The studies on perfection of crystals using x-ray

Table 1 *Results of KCl refinement from various extinction models*

Model	R-Factor(F)	$B(K)$Å^2	$B(Cl)$Å^2	Avg. particle radius (rms) (microns)
1. Isotropic primary (Zachariasen)	0.0152	1.82	1.99	13.5
2. Isotropic primary (Becker and Coppens*)	0.0168	1.57	1.76	21.3
3. Isotropic secondary	0.0154	1.83	1.87	0.12
4. Anisotropic primary (Zachariasen)	0.0067	1.82(3)	1.89(3)	10.5
5. Anisotropic primary (Becker and Coppens*)	0.0097	1.83	1.94	—
6. Anisotropic secondary (Zach. Type I)	0.0098	1.83	1.87	—
7. Anisotropic secondary (Zach. Type II)	0.0066	1.80	1.86	0.10
8. Anisotropic secondary (Becker and Coppens*)	0.0118	1.70	1.81	—

* Replaces particle radius r by $(r \sin 2\theta)$.

Table 2 *Results of L-glutamic acid. HCl refinement*

Isotropic Extinction Model	R-Factor(F) (No-639)	Extinction Parameters	
		$g \times 10^{-4}$	r (microns)
1. *Zachariasen*			
a) Secondary	0.0530	17.1(1.3)	—
b) Primary	0.0542	—	178(8)
c) Secondary + Primary	0.0478	9.5(1.0)	24(1)
d) -do- (Constrained)	0.0489	0.29	133(4)
2. *Becker & Coppens* (Type I Lorentzian)			
a) Secondary	0.0493	10.1(0.6)	—
b) Secondary + Primary	0.0475	8.5(0.6)	29(2)
3. *Modified Zachariasen* $Y = [1 + 2x + ax^2]^{-1/2}$	0.0475	9.9(0.8)	a = 0.12(0.01)

topography, γ-ray diffractometry and other techniques are assuming added importance in recent years due to both its technological importance and to its providing a realistic picture of the defect structure in crystals. There have also been many important attempts to theoretically predict the effects of perfection—or the lack of it—on x-ray and neutron diffraction from crystals. In these studies, Prof. G. N. Ramachandran and his colleagues have played a notable part. In the current state of the art, one can say that the extinction parameters obtained from least squares refinement of crystal structures give a realistic description of the mosaic structure of crystals if the extinction effects are not too severe and if the choice of the extinction model is supported by topography or rocking curve measurements.

ACKNOWLEDGEMENTS

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MICROTOPOGRAPHY ON THE ZIRCON MEGA CRYSTALS FROM PUTTETTI, SOUTH INDIA

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ABSTRACT

Zircon mega crystals of unusually large size and morphological perfection are associated with a diopside-syenite at Puttetti. They have wormy noodle-like microtopographic furrows on all faces. Though lacking in geometric definition, they seem to have a preferred orientation on the prism and pyramidal faces. A preliminary study of the crystal surfaces suggest that the microtopography is the result of dissolution by fluids at the solid-liquid interface, at the prevailing magmatic temperature and pressure. Scanning electron microscope studies revealed numerous sub-microscopic fractures within the furrows, filled by a greyish-white cryptocrystalline matter. Step-like terraces on the apparently flat interspaces between the furrows indicate crystal growth by layers.

INTRODUCTION

MICROTOPOGRAPHIC features relate to the conditions of growth almost at the end of the growth process. Crystals of minerals often show such features and they are the result of dissolution by natural fluids. Very often they show geometric form and the apparent symmetry is consistent with the orientation of the symmetry elements of the whole crystal[1]. A crystal face is never ideally planar over thousands of identity periods, but contains a multitude of imperfections. There are also other variations from ideality such as foreign inclusions and dislocations[2]. The growth mechanism of the crystal can be worked out by correlation of the detailed microtopographic studies of different habit faces of a number of crystals. The existence of internal impurities and/or dislocations will, to a great extent, affect the surface patterns developed by growth process. While impurities and/or dislocations on the surface of a growing crystal retard its growth, during dissolution they will be centres of the more unstable points on the surface of the crystal. Hence at these points the solvent can prize open the less yielding lattice front and cause development of microtopography[3]. The first direct proof that dislocations can be revealed by means of etching was given[4].

Geologic Set-Up

Zircon phenocrysts occur in a zircon-bearing diop-

side syenite at Puttetti, in the Kanyakumari district of Tamil Nadu (8° 14′ & 77° 12′—Survey of India topo sheet 58 H/4). The syenite body is in the form of a ridge (0.4 × 0.25 km), trending N-NW S-SW which is the regional strike of the crystalline rocks of the area, the charnockite-khondalite suite. Distributed unevenly in the massive syenite ridge, zircon crystals crop out on the southwestern flank. A close examination of the rock would reveal that far from any uniformity in their distribution, they occur haphazardly either as clusters or separated far apart with barren areas where apparently no crystals are seen. Such a cluster would contain zircons of all sizes from a millimeter to over 100 mm. The charnockites comprised of the intermediate and acid types, surround the syenite body. No distinct contact is seen between the two rock types. Instead, there is a gradual merging of the one with the other. A traverse across the syenite to the nearest charnockite outcrop would reveal traces of quartz gradually appearing in the peripheral parts of the syenite body. Based on field and laboratory studies, a common consanquinity is suggested[5].

The diopside syenite is greenish-grey, coarse-grained and essentially composed of feldspar (80%) and diopside (12%). The accessories (8%) include hornblende, sulphides, iron ores, sphene, mica and apatite in the order of abundance. It is significant that the charnockite-khondalite suite of rocks and their associates constitute the provenance for the renowned