tative criterion – as the final and most accurate criterion.

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X-ray Structural Damage of Triglycine Sulphate (TGS)

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The complete spectrum emitted by a conventional X-ray diffraction Cu target produces damage in a small TGS crystal which is evident from the variation of integrated intensities of X-ray reflexions with irradiation time. An interpretation of the data is proposed which assumes that the trapping of irradiation products causes an exponential decrease of mosaic-block diameters. An empirical correction of the Zachariasen extinction factor for crystals belonging to type II is suggested, since the TGS crystal is of this type.

Introduction

Structure analysis requires the accurate determination of both integrated intensities and structure factors. It is well known that X-rays used to collect data have undesirable effects on the crystals. These effects are ascribed to material instability, or to defects produced by X-ray damage. Young (1969) and Milledge (1969) have made detailed reviews of the different problems concerning the precise determination of integrated X-ray reflexion intensities, emphasizing how to avoid the effects of damage rather than explaining the production mechanism.

There is a copious bibliography covering the topic of irradiation damage with special reference to X-ray diffraction effects. Examples are Lonsdale, Nave & Stephens (1966), Kolontsova & Telegina (1969), Krueger, Cook, Sartain & Yockey (1963), Telegina & Kolontsova (1970), Larson & Young (1972) and Baldwin & Dunn (1972). Work on X-irradiated TGS crystals has been carried out by Petroff (1971), who detected planar defects, and Mendiola & Alemany (1970), who pointed out large variations in the intensities of X-ray reflexions with cumulative doses.

In this paper we study the variation of integrated intensities of X-ray reflexions with time when a single crystal is irradiated by the complete spectrum emitted from a conventional X-ray diffraction Cu target. For reflexions with $F \geq 16$, a continuous increase in intensity is observed until a maximum is reached, followed by a decrease; but for reflexions with $F < 16$ the intensities diminish from the beginning. This behaviour is fairly well explained by an empirical correction to the Zachariasen extinction factor for crystals belonging to type II, as we suggest for TGS crystals, and assuming an exponential decrease of mosaic-block radius as well.

The TGS lattice parameters and the observed and calculated structure factors of the reflexions used in this paper are the early ones reported by Hoshino, Okaya & Pepinsky (1959). The results obtained there are substantially the same as those deduced from the fractional atomic coordinates x,y,z and temperature factors B_{ij} given by Itoh & Mitsui (1971). However we do not follow the latter paper because no extinction correction is made. In this paper we show that the inclusion of an extinction correction is necessary.

Theory

The concepts that are used in discussing the results have been exhaustively developed by Zachariasen (1967*a*,*b*; 1968*a*,*b*,*c*,*d*; 1969). According to his theory, the integrated intensity of a reflexion from a symmetrically shaped crystal of volume v, assumed to consist of nearly spherical domains of radius r, is given by

$$I = I_k \, . \, y \qquad (1)$$

for unpolarized X-rays, where

$$I_k \text{ (the kinematical value)} = I_0 v A Q_0 \left(\frac{1+\cos^2 2\theta}{2}\right) \quad (2)$$

$$y \text{ (the extinction factor)} = (1+2x)^{-1/2} \quad (3)$$

$$x = \frac{1+\cos^4 2\theta}{1+\cos^2 2\theta} Q_0 \lambda^{-1} T r^* = Z \,.\, r^* \quad (4)$$

$$Q_0 \lambda^{-1} = \left[\frac{e^2 \lambda F}{mc^2 V}\right]^2 \cdot \frac{1}{\sin 2\theta} \quad (5)$$

$$T = -\frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}\mu} \quad (6)$$

$$r^* = r\left[1+\left(\frac{r}{\lambda g}\right)^2\right]^{-1/2} . \quad (7)$$

I_0 is the incident intensity, v the volume of the specimen, A the transmission factor and g the factor determining the misorientation of the perfect domains in the crystal. The other symbols have their usual meanings. Zachariasen (1967*b*) shows that very large extinction effects cannot occur in crystals of type I (for which $r/\lambda g \gg 1$) whilst they are possible for crystals of type II (*i.e.* $x \gg 1$ and $r/\lambda g \ll 1$, whence $r^* = r$).

The equation $y=(1+2x)^{-1/2}$ prevails over the two other theoretical expressions of the extinction factor (Zachariasen, 1967*b*) as shown in Table I from Zachariasen (1968*a*) where the calculated values of y are equal to or less than 0·5. Nevertheless, there is no experimental evidence of $y=(1+2x)^{-1/2}$ for y values close to unity (*i.e.* $x \ll 1$) since weak reflexions of small structure factor have never been corrected for extinction.

Let us restrict our discussion to crystals of type II ($r^*=r$). Now if r tends to zero through an external agent such as irradiation damage, x moves toward zero and y towards unity; therefore it is not necessary to make any extinction correction according to Zachariasen. However, as r diminishes, the blocks contain progressively fewer unit cells and in the limit $r=0$ (*i.e.* $x=0$), the crystal periodicity is completely lost and consequently so is the diffracted beam. Thus we propose a correction to Zachariasen's extinction factor for $x \ll 1$ in order to obtain a function that matches qualitatively the full-line curve in Fig. 1. Now, we may write for such a function

$$y=(1+2x)^{-1/2} \,.\, F(x) \quad (8)$$

where

$$F(x)=0 \quad \text{for} \quad x=0$$
$$F(x)\simeq 1 \quad \text{for} \quad x \geq 1 \,. \quad (9)$$

The last boundary condition comes from the experimental verification of Zachariasen's extinction factor for $x \geq 1$. Our present extinction function y shows a maximum with coordinates x_{max}, y_{max}.

Experimental

The crystals were grown by evaporation from a water solution of triglycine sulphate obtained through chemical reaction of pure products. In the first stages, needle-like crystals along [001] were obtained, from which a small specimen 0·2 × 0·3 × 0·5 mm was chosen. In order to make a correction for absorption, according to equation (6), the sample has been regarded as a sphere of diameter $T = 2·3 \times 10^{-2}$ cm.

The crystal was centred along [001] on a goniometer head in a G.E. XRD-6 diffractometer at a distance of 5·73 in from the target. An unfiltered circular beam from a conventional Cu X-ray tube GE/CA-8S operating at 40 kV and 17 mA and equivalent to a radiation rate of 400 R/min was used to irradiate the sample, producing continuous damage. Meanwhile the sample was successively set at the Bragg angles of several reflexions for λ(Cu $K\alpha$), and the diffracted beams recorded by means of a proportional counter after being β-filtered, using a 2θ scanning speed of 0·4° min^{-1}, a range of ± 0·6° about each Bragg angle, and a receiving slit of 0·2°. With this procedure the dead time between successive irradiations was eliminated, avoiding the possible recovery of the crystal (Mendiola & Alemany, 1970). Correction for thermal diffuse scattering has been disregarded.

The integrated intensities before irradiation, I_0, were obtained with nickel-filtered radiation, which it was assumed does not cause any defects. The experimental attenuation factor was 2·165, the sample being maintained at room temperature.

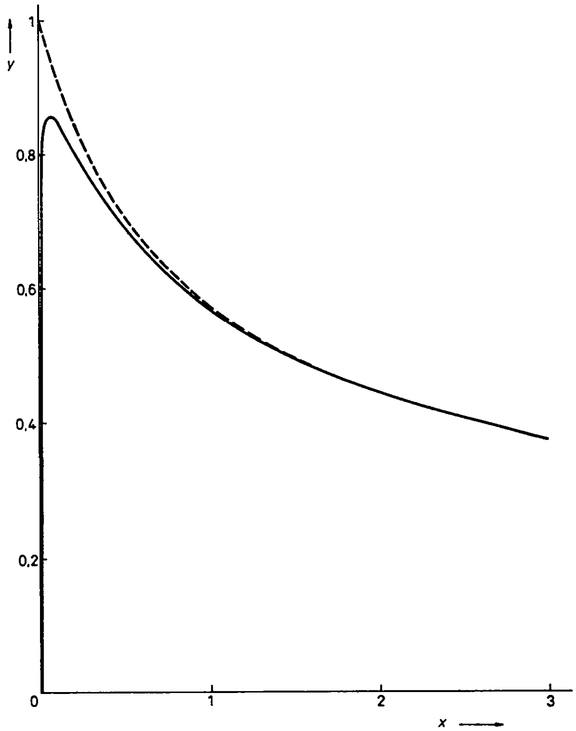

Fig. 1. Zachariasen's extinction factor (broken curve) and the proposed factor (solid curve).

Results and discussion

The data summarized in Fig. 2 show that intensity increases to a maximum and then decreases, except for the 051 reflexion. In Table 1 the reflexions considered are shown together with the observed and calculated structure factors, the Z-function values [as defined in equation (4)], the irradiation times, and the intensity ratios at the maximum.

A separate irradiation experiment was conducted with a new sample in the paraelectric phase at 68 °C where the behaviour of the integrated intensity of the 040 reflexion was studied. This intensity is compared in

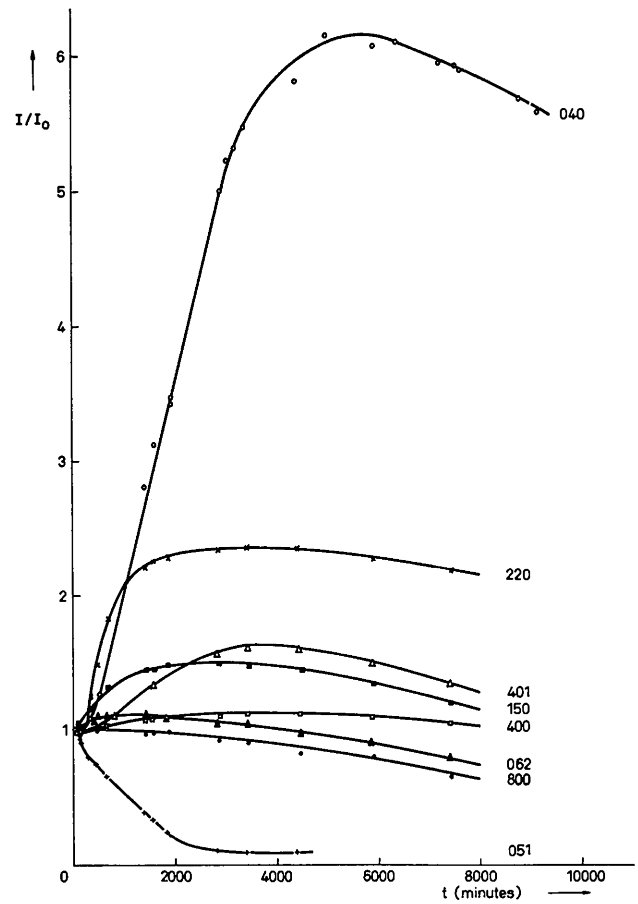

Fig. 2. Experimental X-ray integrated intensities *versus* irradiation time.

Fig. 3 with that obtained at room temperature. From this Figure it follows that the large intensity change upon irradiation is independent of whether the crystals are below or above their Curie temperature. On the other hand, there is a small intensity decrease during the first few minutes of irradiation which does not appear when the crystal is in the paraelectric phase. A sharp decrease of electrical capacitance has been found to occur during this short initial period (Alemany, Mendiola, Jimenez & Maurer, 1973) which suggests a probable relationship between the initial minimum in the intensities and the ferroelectricity, and hence an improvement of the crystal structure connected to the trap of domain walls; since there are no domain walls in the paraelectric phase, the initial minimum in the integrated intensities does not appear. Krueger, Cook, Sartain & Yockey (1963) have also observed an increase in perfection of γ-irradiated Rochelle salt resulting from low levels of radiation.

From Table 1 and equation (1), it follows that:
for the 220 reflexion,

$$\frac{I_{\max}}{I_0} = \frac{y_{\max}}{y_0} = 2{\cdot}34 ;$$

for the 040 reflexion,

$$\frac{I_{\max}}{I_0} = \frac{y_{\max}}{y_0} = 6{\cdot}15 .$$

That is to say, these reflexions have very large extinction effects and therefore TGS crystals may be assigned to type II which according to Zachariasen (1967*b*) fulfil $r^* = r$.

Gilleta, Taurel & Lauginie (1969) observed dislocations in TGS crystals produced by irradiation. Assuming these dislocations intermingle with the Frank network which forms the mosaicity of real crystals (Hedges & Mitchell, 1953), a continous decrease of the mean radius of mosaic blocks with time should be obtained. Let us suppose the decrease of radius is

$$r = r_0 \exp\left(-\frac{t}{\tau}\right) \tag{10}$$

where r_0 is the mean radius of mosaic blocks in the undamaged crystal.

From (4) we can put

$$x = Zr_0 \exp\left(-\frac{t}{\tau}\right) . \tag{11}$$

Table 1. *Reflexions considered, together with observed and calculated structure factors, Z-function values, irradiation times and intensity ratios at the maxima*

Reflexion	F_o	F_c	Z_o(cm^{-1})	Z_c(cm^{-1})	$t_{\max}$(min)	$I_{\max}/I_0$
051	5·53	9·62	43·36	131·20	—	—
800	16·58	16·26	290·75	279·64	20	1·02
062	24·45	26·24	641·39	738·75	1000	1·11
400	31·72	27·39	1369·80	1021·35	3000	1·13
150	47·07	51·27	3351·17	3975·89	3200	1·48
401	57·30	62·94	3770·14	4548·85	3500	1·61
220	73·47	74·21	12709·01	12966·31	4500	2·34
040	102·22	117·94	21065·78	28043·23	5500	6·15

As x diminishes, the representative points of the reflexions move along the full curve of Fig. 1 according to the previous time dependence. If $x > x_{max}$, this latter value will be reached at t_{max}, when the maximum intensity is obtained. This value can then be written

$$x_{max} = Zr_0 \exp\left(-\frac{t_{max}}{\tau}\right)$$

$$\frac{t_{max}}{\tau} = \ln Z - \ln\frac{x_{max}}{r_0}\,. \qquad (12)$$

In Fig. 4, the experimental t_{max} values *versus* ln Z are shown to lie on a straight line, thus confirming the hypothesis of exponential decrease of the radius of mosaic blocks. From the ordinate intercept and slope of the graph we obtain

$$\frac{x_{max}}{r_0} = 266 \text{ cm}^{-1}$$

$$\tau = 1180 \text{ min}\,. \qquad (13)$$

Finally, by determining x_{max}, we can calculate the mean radius of the blocks in the undamaged crystal.

As (8) shows, x_{max} will depend on the function $F(x)$, but the exact form of this function is not known at this stage. We have approached the problem empirically, trying several forms of $F(x)$ to fit the curves of I_t/I_0 *versus* radiation time for the eight reflexions studied. The following forms were used:

$$F(x) = \exp\left(-\frac{a}{x^n}\right) \quad \text{for} \quad n = \tfrac{1}{2}, \tfrac{1}{3}, \tfrac{1}{4}, 1 \text{ and } 2$$

and

$$F(x) = 1 - \exp\left[-a(2x)^n\right] \quad \text{for} \quad n = 1, \tfrac{1}{2}, \tfrac{1}{3}, \text{and } \tfrac{1}{4} \qquad (14)$$

as well as

$$y = (1+2x)^{-1/2} - (1+2x)^{-a}\,.$$

The best fit was obtained by putting

$$F(x) = 1 - \exp\left[-a(2x)^{1/4}\right] \qquad (15)$$

to give

$$y = (1+2x)^{-1/2}\{1 - \exp\left[-a(2x)^{1/4}\right]\}\,. \qquad (16)$$

The (x_{max}, y_{max}) coordinates are given as a function of the a parameter. By using equations (1) and (16), Fig. 5 shows the experimental and theoretical I_{max}/I_0 values *versus* Z. An a-curve family is then obtained, those for $a=4$ fitting best the experimental points. Only the 040 reflexion does not lie on the empirical curve, probably because the structure-factor error has been exaggerated by X-ray damage.

Putting $a=4$ in equation (16) we obtain the curve shown in Fig. 1 with $x_{max} = 0{\cdot}067$ and $y_{max} = 0{\cdot}855$. Using this value of x_{max} in equation (13) a value for $r_0 = 2{\cdot}52 \times 10^{-4}$ cm is obtained. This is the mean radius of the blocks for the undamaged crystal and agrees satisfactorily with the expected order of magnitude for a real crystal. At the same time we note that r_0 is slightly dependent on $F(x)$ provided that the parameter a has

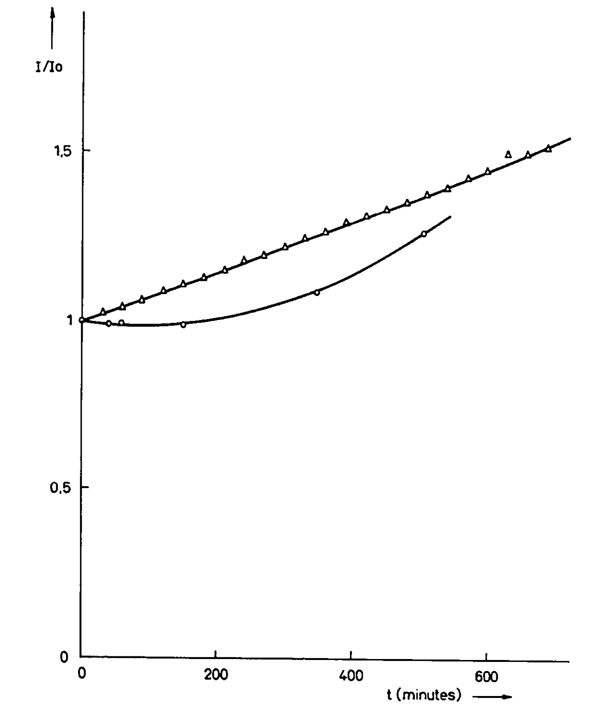

Fig. 3. Irradiation-time dependence of the 040 X-ray integrated intensity (○: crystal at 22 °C; △: crystal at 68 °C).

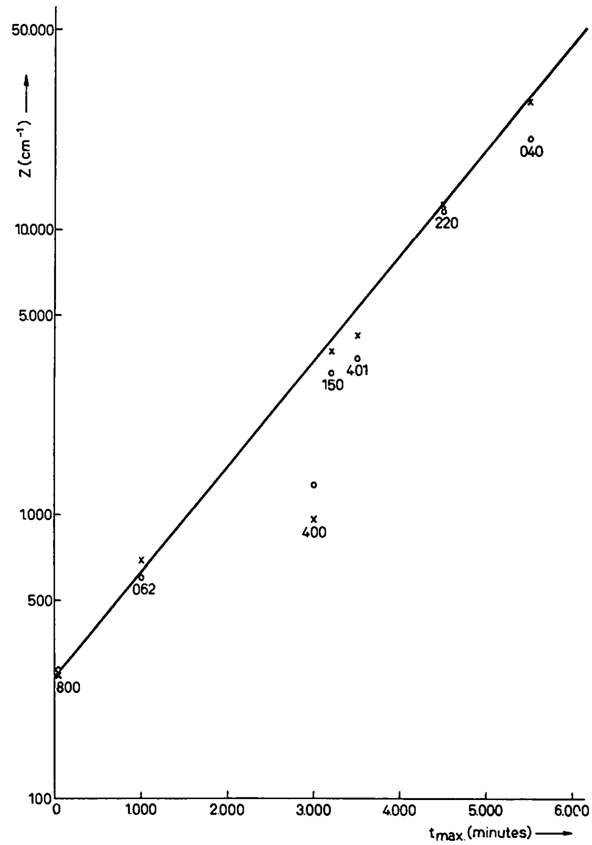

Fig. 4. Z values *versus* experimental t_{max} (○: from F observed; ×: from F calculated).

been chosen according to the limitations set by equation (9). Thus we can represent each reflexion by the function $I_t/I_0 = y_t/y_0$ since we know all the parameters, as shown in Fig. 6. In order to obtain the best agreement, a new value of the structure factor for 040 is also proposed in Fig. 6.

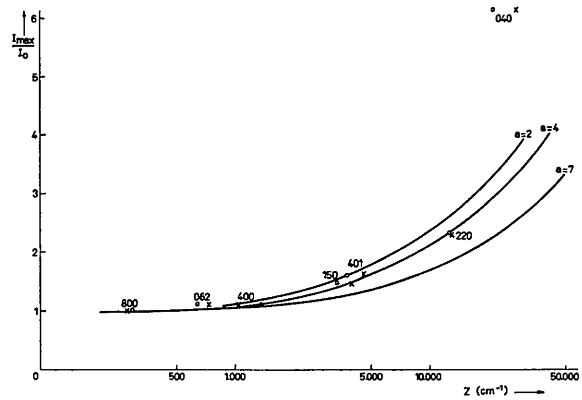

Fig. 5. I_{max}/I_0 *versus* Z. The curves are the theoretical values corresponding to different selected a parameters; ○ and × are the experimental points obtained when observed or calculated F are used to get Z.

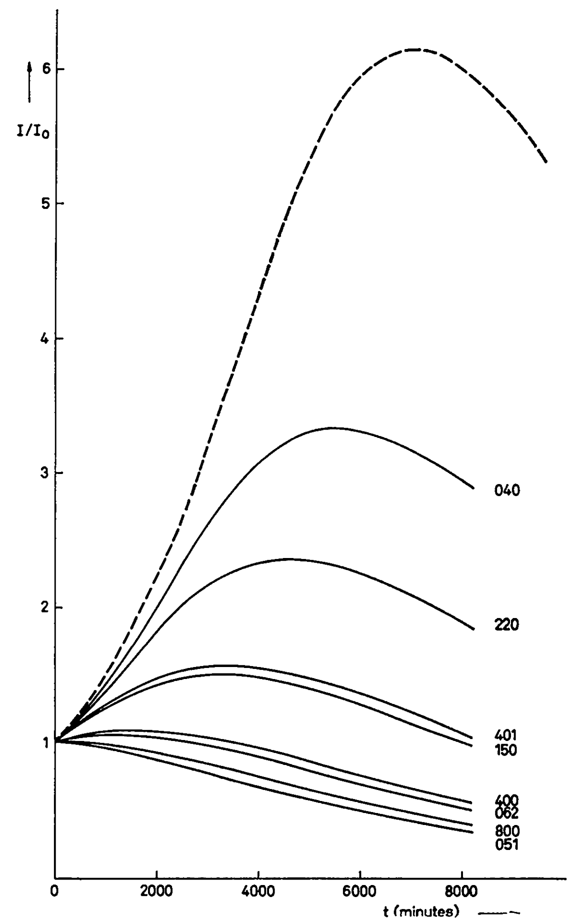

Fig. 6. Calculated X-ray integrated intensities obtained by using F_c *versus* irradiation time. The broken curve corresponds to 040 when the proposed $F = 223$ is used.

Disagreement between the experimental and calculated values could be due to large errors in Z resulting from inaccurate knowledge of the TGS crystal structure and also because of the simplicity of Zachariasen's mosaic-crystal model which only considers spherical blocks.

Conclusions

Defects created in TGS by large X-ray exposures perturb the crystal periodicity and therefore the X-ray difraction extinction factor.

The proposed model assumes an exponential decrease, due to a defect-trapping process of lattice dislocation, in the mean radius of spherical blocks as the irradiation time increases, and a correction for the Zachariasen extinction factor for $x \ll 1$ in his theory of real crystals.

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