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Experimental Differentiation between Primary and Secondary Extinction with Application to Radiation Disorder in Sodium Chlorate

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It is shown that X-ray intensities measured under conditions of both single and triple diffraction permit the separation of primary from secondary extinction effects. The method is applied to a sodium chlorate crystal which suffered radiation damage under exposure to X-rays. It is shown that the irradiation had little effect on secondary extinction, but eliminated primary extinction.

Primary and secondary extinction are distinct physical phenomena in a mosaic crystal. Nevertheless it has proved difficult to distinguish experimentally between these two types of absorption due to Laue–Bragg scattering.

It is the purpose of this article to show that the combined use of intensity data obtained under conditions of single and of triple diffraction permits the separation of extinction effects into primary and secondary type.

Single diffraction

The integrated intensity of X-ray diffraction for an ideally imperfect crystal of volume v and intensity I_0 of the unpolarized incident beam is

$$P_c = I_0 Q v A \tag{1}$$

where $vA = \int e^{-\mu(T_1+T_2)} dv$ and $Q = |e^2 F/mc^2 V|^2 \lambda^3 \mathrm{L} p_1$. L is the Lorentz factor and $p_n = (1+\cos^{2n} 2\theta)/2$.

Because of extinction the actually observed integrated intensity is reduced from this ideal value P_c to a smaller value P. In the first place the scattering absorption within a given mosaic block (primary extinction) may not be negligible, causing a reduction in the diffraction power per unit volume from Q to Q'. Secondly the alignment of the mosaic blocks may be so good that also secondary extinction has to be considered. If the latter effect is so small that only a first order correction need be made one has

$$P/P_c \simeq y[1-xy] \tag{2}$$

$$y = Q'/Q,\ x = gQ\bar{T}p_2/p_1^2 \,.$$

$y = Q'/Q$ is the correction factor for primary and $1-x$ for secondary extinction. In the expression for x the effective path length $\bar{T} \equiv A dA^{-1}/d\mu$ and $g = \int W^2 d\Delta$, $W(\Delta)$ being the distribution function for the misalignment Δ of the mosaic blocks.

The form of the correction factor y depends upon the size and shape of the mosaic block. It is precisely known only for a mosaic block in the shape of a layer of thickness t_0 and indefinitely large lateral extension. Quite generally y may be expanded in a power series: $y = 1 - h_1 Q p_2/p_1^2 + h_2 Q^2 p_3/p_1^3 + \cdots\cdots$. An approximate expression for h_1 if the block is a cube of edge t_0 is

$$h_1 \simeq 4t_0^2 (\sin 2\theta + \cos 2\theta)/3\lambda\, (1+\cos 2\theta) \,. \tag{3}$$

Experimentally one observes the quantity P/P_c (if the structure of the crystal is known). If y and $1-x$ vary with the scattering angle in markedly different ways, it is possible in principle to separate the primary from the secondary extinction. However, in practice this procedure is difficult and has met with little success.

Triple diffraction

Triple diffraction due to symmetry can be produced for any wave length for a non-triclinic crystal (Zachariasen, 1965). Under such conditions equation (2) is no longer valid.

Let P_1^*, P_2^*, P_3^* be the observed intensities under triple diffraction, and let, for the sake of convenience, the three reflections be so chosen that $P_1 = P_2 \gg P_3$. For single diffraction one has

$$P_3 = P_{3c} = I_0 Q_3 v A_3$$

since the reflection by presumption is so small that extinction is negligible.

Using the results given in the reference above one finds

$$P_3^* - P_3 \simeq I_0 v A_3 \frac{p_{11}(3)}{p_1^2} \left(\frac{L_1^*}{\mathrm{L}_1}\right)^2 \bar{T}_3 g Q_1'^2. \tag{4}$$

In this equation Q_3^2 and $Q_1'Q_3$ are neglected in comparison with $Q_1'^2$ because of the stipulation $P_1 \gg P_3$. L_1^* is the Lorentz factor and $p_{11}(3) = [2\cos^2 2\theta_1 + (\cos 2\theta_3 - \cos^2 2\theta_1)^2]/2$ the polarization factor for the triple diffraction situation.

Combining equations (2) and (4) gives

$$\begin{aligned} & P_1/P_{1c} = y(l-xy) \\ & (P_3^* - P_3)/P_1 = axy/(1-xy) \\ & y = Q_1'/Q_1 \qquad\qquad x = gQ_l\bar{T}_l p_2/p_1^2 \\ & a = \frac{A_3\bar{T}_3}{A_1\bar{T}_1} \left(\frac{\mathrm{L}_1^*}{\mathrm{L}_1}\right)^2 \frac{p_{11}(3)}{p_2} \,. \end{aligned} \tag{5}$$

These equations can be solved for x and y with the following result:

$$x = \frac{a^{-1}(P_3^* - P_3)P_{1c}}{[P_1 + a^{-1}(P_3^* - P_3)]^2}$$

$$y = P_1/P_{1c} + a^{-1}(P_3^* - P_3)\ . \qquad (6)$$

Thus the two correction factors $1-x$ and y have been determined separately.

In the course of the derivation it is tacitly assumed that the triple diffraction effects within a given mosaic block are negligible. This assumption is not valid for large primary extinction. If such an effect is present, the quantity $a^{-1}(P_3^* - P_3)$ in the above equations would be reduced.

If there is no primary extinction ($y=1$) equations (5) give

$$P_1/P_{1c} \simeq 1-x \qquad (7a)$$

$$(P_3^* - P_3)/P_1 = ax/(1-x) \qquad (7b)$$

so that x can be determined experimentally either from equation (7*a*) or from equation (7*b*). If the two values of x so obtained do not agree, it must be concluded that primary extinction is present.

Application to sodium chlorate

A crystal of sodium chlorate was ground into a nearly perfect sphere of radius 0·181 mm and examined with Cu $K\alpha$ radiation. The sphere was mounted with the [1$\bar{1}$0] direction vertical and the reflection 220 was measured in the equatorial plane. This arrangement corresponds to the triple diffraction case B' (Zachariasen, 1965), the three reflections being 200, 020 and 220. The 200 and 220 reflections were also measured under single diffraction.

X-rays produce appreciable radiation damage in sodium chlorate. Table 1 gives the actual intensity of some of the reflections as measured with a counter over a period of 28 working days (6 hours X-ray exposure per day).

During the 26–28th day 99 distinct reflections were measured and these data were used for a least-squares refinement of the structure. Corrections were made for anomalous dispersion, none for extinction and all observed structure factors were assigned equal weight. The refinement gave $R=0{\cdot}040$ and the parameter values shown in Table 2. The thermal parameters include the effect of the radiation damage. The interatomic distances (using $a=6{\cdot}577$ Å) are Cl–3O = 1·493 Å, Na–3O = 2·410 Å, Na–3O = 2·500 Å.

Table 2. *Structural parameters* (× 10⁴)

	Na Value	σ	Cl Value	σ	O Value	σ
x	685	5	4186	3	3033	7
y	(685)		(4186)		5938	8
z	(685)		(4186)		5065	9
β_{11}	153	6	126	3	186	14
β_{22}	(153)		(126)		110	11
β_{33}	(153)		(126)		215	15
β_{12}	−5	7	3	4	28	12
β_{13}	(−5)		(3)		30	11
β_{23}	(−5)		(3)		−23	12

Let the subscript A refer to measurements taken at the beginning and subscript B at the end of the 28 day period. The observed intensity changes for single diffraction correspond to the formula

$$\frac{P_B}{P_A} = \varphi C e^{-2b \sin^2\theta/\lambda^2}$$

$$\varphi = \frac{y_B(1-x_B y_B)}{y_A(1-x_A y_A)}$$

with $C=0{\cdot}87$ and $b=0{\cdot}76$ Å². $1-C$ measures the fraction of the sodium chlorate phase destroyed by the radiation and b the displacement disorder. The observed value for b corresponds to a root mean square displacement of 0·10 Å. The quantity φ takes account of the change in extinction in the course of the irradiation.

The method described in the preceding section will next be used to determine the four quantities x_A, y_A, x_B, y_B.

Table 1. *Intensity changes under irradiation**

Day	110	200	220		400	600	550	800
			P^*	P				
1	81							
2		489	31·2	16·3	21·4			
3						90		
4	77	544						
5							4·0	53
7	78	640	40·4		20·3			
9						82	3·5	44·5
11		660			18·6			
12						76		39·8
14					18·0	72		36·6
17		678			17·6	71		
18								32·5
24		676			16·7	65		27·5
26–28	69	680	39·8	13·1	16·2	63	2·3	26·8

* For the reflection 220, P^* refers to measurements under triple diffraction, P to single diffraction.

The pertinent intensity observations all reduced to an arbitrary scale on which $P_{1c}=814$ are listed in Table 3. For the 200 and 220 reflections one has $A_3/A_1=1{\cdot}09$, $\bar{T}_3/\bar{T}_1=0{\cdot}90$, $\mathrm{L}_1^*/\mathrm{L}_1=1{\cdot}46$, $p_{11}(3)/p_2=0{\cdot}97$ giving $a=2{\cdot}04$. On absolute scale one calculates $Q_1=29{\cdot}1\times10^{-3}$, $Q_3=0{\cdot}54\times10^{-3}$, and $\bar{T}_1=1{\cdot}81\times10^{-2}$ cm.

Table 3. *Initial* (*A*) *and final* (*B*) *intensities*

Reflection	*A*	*B*	Calculated
200	489	807	814
220	16·3	16·2	16·4
220*	31·2	49·1	—

Insertion of the data from Table 3 in equations (6) gives

$$x_A=2{\cdot}5\times10^{-2} \qquad y_A=0{\cdot}61$$
$$x_B=1{\cdot}9\times10^{-2} \qquad y_B=1{\cdot}00\ (1{\cdot}01)\,.$$

The corresponding values of the secondary extinction coefficient g are $g_A=46$ and $g_B=36$. Equation (3) suggests that $t_0\simeq6\times10^{-4}$ cm for the "virgin" crystal.

In other words the data show that the secondary extinction in the specimen is small, *i.e.* that there is poor alignment of the mosaic blocks. The initial large primary extinction in the specimen is practically eliminated in the course of the irradiation, *i.e.* the dimensions of the coherently scattering regions in the crystal are greatly reduced as a consequence of the radiation disorder.

Clearly, the practical usefulness of the proposed method for distinguishing between primary and secondary extinction ought to be given further tests.

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Multiple Diffraction in Imperfect Crystals

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It is shown that many experimental diffraction intensities used for structure determination have been obtained under conditions of multiple diffraction, and it is pointed out that some of the intensities measured under such circumstances may be appreciably in error.

The intensity effect has been studied theoretically for frequently encountered cases of double, triple and quintuple diffraction in imperfect (mosaic) crystals. Exact solutions have been obtained for a plane parallel plate and approximate formulas are given for crystals of arbitrary shape.

The results of the theoretical study show that multiple diffraction may double or triple the extinction correction for strong reflections and, in some cases, increase the intensity of weak reflections manifold.

The first objective of this article is to demonstrate that multiple diffraction due to symmetry is a much more common phenomenon in crystal structure studies by X-rays, electrons or neutrons than is generally realized.

The second purpose is to give the results of a theoretical study of the intensity effects due to multiple diffraction in an imperfect crystal.

Multiple diffraction due to symmetry

Most intensity measurements reported in the literature, and used for structure determination, have been made under conditions of multiple diffraction. The classical example of symmetry-caused simultaneous diffraction is a Laue photograph taken with the incident beam parallel to a symmetry axis or plane. Every Laue spot of an equivalent set is produced at the same time by the same wave length component of the incident radiation, and as many as twelve reflections may occur simultaneously.

A more important example of double diffraction (case *A*) is illustrated in Fig. 1. The Laue–Bragg equation $\mathbf{k}_i-\mathbf{k}_0=\mathbf{H}_i$, where $\mathbf{k}_i=\lambda^{-1}\mathbf{u}_i$, is simultaneously satisfied for two reciprocal lattice vectors $\mathbf{H}_1$ and $\mathbf{H}_2$ for which, by symmetry, $|\mathbf{H}_1|=|\mathbf{H}_2|$. In Fig. 1, O is the origin of the reciprocal lattice, $\mathbf{H}_1$ and $\mathbf{H}_2$ lie in the plane of the paper, and the circle is the intersection of this plane with the sphere of reflection. The situation shown in Fig. 1 is bound to occur for any wave-length when the normal beam Weissenberg technique is used with a non-triclinic crystal rotating about [010] (and for any crystal of orthorhombic or higher symmetry rotating about [100] or [001]). Reflections *HKL*