We may infer from our calculations that the hypothetical dimer crystal structures $A$ and $B$ and the experimental chain structure of acetic acid are equivalent with respect to their lattice energies. In view of the accuracy of the method, the differences calculated for the lattice energies are insignificant. We compared these results with the SCF perturbation method of Crowe & Santry (1973) which yielded $-49\cdot3$, $-48\cdot8$ and $-48\cdot4$ kJ mol$^{-1}$ for the dimer structures $A$ and $B$ and the chain structure respectively, thereby also attributing practically equal lattice energies to the three crystal structures. We may conclude that as long as the entropy is not taken into account, nothing can be said of the actual appearance of an acetic acid dimer crystal structure, but we have shown that structures with a packing energy as large as that of the experimental structure can indeed be constructed theoretically.

Clearly it would be interesting to determine the crystal structure of the high-pressure modification of acetic acid, which was shown to exist by Bridgman (1916).

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# International Union of Crystallography

## Commission on Crystallographic Apparatus and Commission on Charge, Spin and Momentum Densities

## A Critique of Zachariasen's Theory of Extinction*

BY J. L. LAWRENCE, *School of Physical Sciences, University of St. Andrews, St. Andrews, Scotland*

A description and assessment of the theory and application of Zachariasen's theory of extinction [Zachariasen (1973). *Acta Cryst.* **23**, 558–564] is given.

### Introduction

Extinction was first described by Darwin (1914) and can be described in terms of his mosaic block model. If the blocks are large and if a significant amount of energy is removed from the main beam by the planes close to the surface of each block, the remaining volume will receive less incident intensity, giving a diffracted intensity less than the kinematic value. This is primary extinction and is concerned with coherent scattering.

If the main beam intersects a significant number of blocks sufficiently well aligned to diffract a parallel beam of X-rays simultaneously, each block will take some energy out of the main beam, reducing the incident beam and, therefore, the scattered intensity. This is secondary extinction and is concerned with incoherent scattering.

The kinematic theory depends on there being the same incident intensity at all points in the crystal and, therefore, when extinction is present, the relationship between integrated intensities and the structure factor is unknown and the data cannot be processed. In a paper entitled *A General Theory of X-ray Diffraction in Crystals*, Zachariasen (1967) attempted to relate measured intensities to the true kinematic structure factor when extinction was present. This theory greatly renewed interest in extinction and, for a theory which has had such widespread use, an assessment of the approximations used in its development and of its applications is obviously important.

### Description and assessment of the theory

The theory is based on two differential equations pertaining to diffraction within a small, perfect crystal.

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These equations are

$$\frac{\partial I_0}{\partial t_1} = -\sigma I_0 + \sigma I \qquad \text{Z(4a)}$$

$$\frac{\partial I}{\partial t_2} = -\sigma I + \sigma I_0 . \qquad \text{Z(4b)}$$

$\sigma$ is the diffraction cross section. Equation Z(4a) [equation numbers from Zachariasen (1967) are prefaced by Z] gives the variation of the incident intensity, $I_0$, as a function of distance through the crystal in the direction of the main beam.

If a significant amount of energy is scattered from the main beam into the diffracted beam, some of this scattered energy will be rescattered into the main beam and this radiation will be coherent with the incident radiation. The equations, however, take no account of coherence since they involve only the intensities of the beams. They must be considered as basically kinematic in nature and will perhaps not be suitable for correction of severe primary extinction.

Werner (1974) and Becker & Coppens (1974) have pointed out that the coordinate system used by Zachariasen lacks a unique origin. However, Brown & Fatemi (1974) have concluded that this has very little effect on the final results.

The next important relation used by Zachariasen was

$$P(\varepsilon_1) = \int \frac{\partial I}{\partial t_2} \, dv . \qquad \text{Z(6)}$$

$P(\varepsilon_1)$ is the power in the diffracted beam at some angle $\varepsilon_1$, close to the diffracting angle $\theta$, and it can be determined provided $I$ is known from the differential equations. A very important function $\varphi(\sigma)$ is then introduced in the equation

$$P(\varepsilon_1) = I_0 v \sigma \varphi(\sigma) . \qquad \text{Z(7)}$$

This function can be determined for crystals of known, regular shape and is usually expressed as an infinite series in $\sigma t$. It also depends on the scattering angle and the coefficients are therefore functions of this angle and the shape of the crystal. The form of the equation used by Zachariasen was

$$\varphi(\sigma) = \frac{1}{1 + \sigma t} , \qquad \text{Z(19)}$$

which is the exact solution for a parallel plate crystal in the Bragg case and was assumed to be a good approximation for a sphere. This treatment severely underestimates the angular dependence. One reason for this was the omission of a $\sin 2\theta$ term in the expression used for the diffraction cross section. The approximate form of the diffraction cross section used was

$$\sigma(\varepsilon_1) = \frac{\frac{4}{3} Q \alpha}{1 + (\frac{4}{3} \pi \alpha \varepsilon_1)^2} \qquad \text{Z(26)}$$

where $\alpha$ should be given by

$$\alpha = \frac{l \sin 2\theta}{\lambda}$$

where $l$ is the thickness of the crystal.

The total integrated intensity, $P$, is given by

$$P = \int P(\varepsilon_1) \, d\varepsilon_1 \qquad \text{Z(8)}$$

and Zachariasen obtained an expression for the extinction factor for a small, perfect crystal, i.e. the correction for primary extinction. Using equations and assumptions similar to those already described, he then obtained an extinction factor for a real mosaic crystal, assuming a Gaussian distribution of mosaic blocks. Finally, three expressions for the extinction parameter in terms of the block size, the distribution of mosaic blocks, the reflectivity of the planes, the wavelength of the radiation and the size of the mosaic crystal, are given, but the expression inevitably used is

$$y = (1 + 2x)^{-1/2} . \qquad \text{Z(47b)}$$

$x$ includes the correction for both primary and secondary extinction.

The important approximations used in the development of the theory are, therefore:

(1) The variation of the intensities of the main and diffracted beams are given by the transport equations Z(4a) and Z(4b).

(2) The form of the function $\varphi(\sigma)$ applicable for a parallel plate in the symmetrical Bragg case is a sufficiently good approximation for a small, spherical crystal.

(3) The scattering power may be described by a Lorentzian distribution.

(4) The misalignment of the mosaic blocks obeys a Gaussian distribution law.

Of these approximations, the first is probably the most fundamental and must limit the usefulness of the equations. Since for the mosaic crystals the shapes and sizes of the blocks are unknown, it is impossible to determine the intensities from the blocks with coherence taken into account, which limits the applicability of the corrections to secondary extinction and small primary extinction. There is also an obvious need for experimental investigation of the other assumptions.

## Applications of the theory

In the majority of the applications of this theory one assumption is always made – there is no primary extinction. Some of the block sizes obtained in such studies are rather large, greater than $10^{-4}$ cm although Zachariasen states that the block size must be less than $10^{-4}$ cm for primary extinction to be neglected. The mathematical forms of the corrections for the two types of extinction are similar but the constants have different meanings, and it is obviously important to know what type of extinction is present.

If the crystal is of thickness $T$, mosaic spread $M$ and block size $t$, there will be $T/t$ blocks intercepting the main beam and, since the peak width for each block will be approximately $t/\lambda$, the number of blocks diffracting simultaneously, $N$, will be

$$N = \frac{T\lambda}{Mt^2} .$$

A criterion for the presence of secondary extinction can be that $N > 1$, hardly exacting considering that Zachariasen imposes a distribution of mosaic blocks which can only be correct if a large number of blocks, much greater than one, are diffracting at once. For this condition, $t < 2 \times 10^{-4}$ cm for $M = 0.1°$, $T = 0.01$ cm, and such a small block size would produce considerable strain inside the crystal. A much smaller block size would be required to increase $N$ to a significant value, this block size for many crystals being

physically unreasonable. Since the blocks must be diffracting singly, any extinction must be of the primary type.

Experimental differentiation between primary and secondary extinction can only be made by examining the variation of the extinction with path length – primary extinction being independent of path length, secondary extinction being dependent on it. There has been some experimental evidence to show that primary extinction is the main type of extinction in some very simple materials, e.g. LiF, MgO (Lawrence, 1972, 1973), but very little either way in larger molecules. When extinction corrections using Zachariasen's equations have been applied good agreement has often been obtained between the calculated and corrected structure factors, but it cannot be automatically assumed that such agreement justifies either the mathematical form of the extinction or the assumption that only secondary extinction is present.

Consider Zachariasen's equations for both primary and secondary extinction:

$$y = (1 + 2x)^{-1/2}$$

where $x = \frac{2}{3}Ar_p^2$ ($A$ = constant for each reflexion) for primary extinction and

$$x = A\bar{T}r_s$$

for secondary extinction.

If the corrections are applied, firstly assuming only primary and then assuming only secondary extinction, the two block sizes obtained would be related by

$$r_p^2 = \frac{2}{3}\bar{T}r_s .$$

If during the calculation for secondary extinction, a block size of about $10^{-4}$ cm was found (justifying the assumption that no primary extinction was present), a block size of about $10^{-3}$ cm would have been obtained in the primary extinction calculation, and for this block size, no secondary extinction would have been present. The size of the block cannot therefore be used as a justification of the type of extinction assumed.

It should be possible to justify the extinction corrections by determining whether the parameters which are obtained make sense physically. The model may lack physical reality but the parameters should have some physical meaning; the block size should be a measure of the average size of perfect crystal regions in the crystal and the mosaic spread should be a measure of the width of the diffraction pattern from the crystal. Both these quantities can be determined experimentally and this has been done for an organic crystal, $\alpha$-oxalic acid dihydrate. This structure has been refined in a neutron diffraction study by Coppens & Sabine (1969) who used a crystal of thickness approximately 0·14 cm. During the refinement an extinction parameter was refined and a block size of about $10^{-4}$ cm obtained.

Michell, Smith & Sabine (1969) then determined the block size as about $10^{-2}$ cm by determining the dislocation density from X-ray topography and they concluded that

'Zachariasen's theory gives physically unrealistic results'. However, if the extinction corrections had been carried out assuming primary extinction, a block size of $3 \times 10^{-3}$ cm would have been obtained, which is of the same order as that from topographs.

Other evidence of primary extinction comes from a recent intensity project carried out by Denne (1972) in which he measured the integrated intensities from six crystals of $\alpha$-glycine whose volumes varied by a factor of up to fifty. Large amounts of extinction were found in the data, this extinction being the same for all crystals, independent of the crystal dimensions, indicating primary extinction.

Since the appearance of Zachariasen's paper, the theory has been adapted and improved, particularly by Becker & Coppens (1974) but the approach is, however, still based on the differential equation in intensity. We will never obtain a fully general solution to this problem because of the difficulty of describing the perfect region of a crystal and defining the correct boundary conditions. In the mean time, many data sets are measured which suffer from extinction. If the standard least-squares routines are used to refine an extinction parameter, it must be remembered that such a parameter may contain only a secondary extinction correction term, which may be inadequate, and it will inevitably use Zachariasen's original equation, Z(47b), which has been found to produce good agreement between the observed and calculated structure factors only when both the extinction and the absorption are small. If a very accurate structure is necessary or if physical effects are to be ascribed to the differences between observed and calculated structure factors, a least-squares technique using Zachariasen's equation is not appropriate. In these situations some experimental approach is best. Perhaps the most straightforward technique would be to measure the data at a range of wavelengths and find the kinematic structure factor by extrapolating to zero wavelength. Using this method, no parameters of doubtful physical significance are used and it is irrelevant whether the extinction is of a primary or secondary type.

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