Short Communications

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Primary and secondary extinction.

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The assumption commonly made in the application of Zachariasen's extinction correction, *i.e.* that primary extinction is negligible, is shown to be invalid in many cases.

The recent increase in interest in extinction effects in single crystals is undoubtedly due to the work of Zachariasen in formulating an analytical approach to the problem in his paper on a *General Theory of X-ray Diffraction in Crystals* (Zachariasen, 1967). This theory has been applied to data from many substances (Zachariasen, 1968*a*, *b*; Cooper & Rouse, 1970) and in general has been found to increase significantly the agreement between the calculated and corrected structure factors. The usual method of analysis in these tests is to assume primary extinction negligible and refine an extinction parameter with the thermal and positional parameters and the scale factor. When data from two wavelengths are available, the values of the extinction parameters obtained from the two refinements can be compared and the crystal categorized into either Type I or Type II. A type I crystal has been defined by Zachariasen as a crystal in which the mosaic spread is greater than the diffraction pattern from a single mosaic block and a type II crystal has been defined as a crystal in which the pattern from a single mosaic block is greater than the mosaic spread.

In his theory, Zachariasen states that primary extinction will (in general) be negligible for the largest structure factors when the block size is less than 10^{-4} cm and this figure is in agreement with the one that can be deduced from Weiss (1966). For mosaic block sizes of this order of magnitude and less, any extinction must be predominantly secondary extinction.

Consider the conditions necessary for secondary extinction to occur. Assume there exists a crystal in which

T = geometrical path length of the incident beam through the crystal
M = mosaic spread (radians)
$\bar{t}$ = geometrical path length of the incident beam through a mosaic block.

The number of blocks encountered will be $T/\bar{t}$ and, since the width of the diffraction peak from each is approximately $\lambda/\bar{t}$ where λ is the wavelength of the radiation, an estimate of the number of blocks, N, which can diffract a parallel beam of X-rays is given by

$$N = T\lambda/M\bar{t}^2.$$

For secondary extinction to occur, N must be much greater than unity. For example, for a crystal which has $T = 0{\cdot}02$ cm and $M = 0{\cdot}005$ radians, the block size must be an order of magnitude less than 2×10^{-4} cm for secondary extinction to occur and, if extinction is present in a sample of this size, then it can only be of the secondary type if the block size or the mosaic spread are very small.

Since a real crystal is an arrangement of imperfections and dislocations, rather than a distribution of equal mosaic blocks, it is of interest to convert the mosaic block size into the more meaningful physical concept of dislocation density to examine the order of magnitude of the postulated dislocation density. A block size of 10^{-4} cm is equivalent to a dislocation density of 10^8 cm^{-2} and the values of dislocation densities quoted for most substances mainly lie in the range 10^5 to 10^8 cm^{-2}. Secondary extinction cannot occur in a crystal of the size quoted ($T = 0{\cdot}02$ cm) unless the dislocation density is greater than that measured for most substances. Some of these measurements have been made on large crystals and the act of making these crystals smaller, to the size normally used by crystallographers by cutting and grinding, will tend to increase the dislocation density. Nevertheless it does appear that extinction in many cases must be of the primary and not the secondary type.

The mathematical form of the primary and secondary extinction corrections of Zachariasen for spherical crystals are very similar. Assuming the secondary extinction to be type II, to which type Zachariasen suggests most crystals belong, the corrections can be written [using the notation of Zachariasen (1967)],

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

where, for primary extinction $x = \frac{3}{2}Ar_p^2$
and for secondary extinction $x = A\bar{T}r_s$.

A is a constant for a particular reflexion, r_p and r_s are the radii of the mosaic blocks which would be calculated assuming primary and secondary extinction respectively and $\bar{T}$ is the effective path length through the crystal which, for spherical crystals of low absorption, varies very little since most extinguished reflexions tend to occur at low $\sin\theta$ values. If, for each extinguished reflexion, a value of the block size is obtained, then for primary extinction

$$r_p^2 = \frac{1}{3A}\left(\frac{1}{y^2} - 1\right)$$

and for secondary extinction

$$r_s = \frac{1}{2A\bar{T}}\left(\frac{1}{y^2} + 1\right)$$

$$\therefore\ r_p^2 = \tfrac{2}{3}\bar{T}r_s\,.$$

If, assuming secondary extinction, a block size of 10^{-4} cm is obtained (small enough to assume no primary extinction) then a block size of 2×10^{-3} cm would be obtained assuming primary extinction, large enough to discount the existence of secondary extinction. Obviously, in this case the values of the mosaic block size deduced can in no way be used as a justification of the type of extinction assumed. The similarity of the mathematical corrections for the two kinds of extinction ensures that the agreement between the corrected and calculated structure factors would be the same for both. The mosaic block size obtained from the correction assuming primary extinction would be an order of magnitude larger than from that assuming secondary and would perhaps have a value more in keeping with the dislocation density values.

Identification of the type of extinction can only be done by testing the variation of extinction with path length, primary extinction being independent of the path length through the crystal. This can be examined either by using large crystals in which symmetry-related reflexions have different path lengths or by using many crystals of different sizes and the same mosaic character. It has been shown, Lawrence (1972, 1973), that both lithium fluoride and magnesium oxide suffer from primary extinction and Denne (1972), using α-glycine crystals of different sizes, showed that the amount of extinction in these crystals was independent of their shape and size, again suggesting primary extinction.

Doubts about the kind of extinction present must render the increasingly common use of the secondary extinction parameter refinement in a least-squares analysis physically meaningless. It must be again emphasized that little significance can be placed on extinction-corrected structure factors unless the correction is made experimentally.

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$Ni(NO_3)_2.6NH_3$, another example of KCN-type anomalous thermoelastic behavior.

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The temperature dependence of all elastic constants of cubic $Ni(NO_3)_2.6NH_3$, measured from the transition point at $-34{\cdot}2$ to 150°C by ultrasonic methods, exhibits KCN-type anomalous behaviour. Within a wide temperature range all elastic wave velocities increase with higher temperature. The shear resistance $c''=(c_{11}-c_{12})/2$ corresponds to the constant c_{44} in KCN. The change of c'' with absolute temperature obeys a logarithmic law like c_{44} in KCN, namely $c''=a \log T/T_0$ with $a=0{\cdot}05975 \,.\, 10^{11}$ dyn cm^{-2} and $T_0=156{\cdot}22$°K. The anomalous elastic behaviour should be assigned mainly to the thermally activated motions of the NO_3 ions. The phase transition is directly related to the low c'' value.

Recently anomalous thermoelastic behaviour of cubic potassium cyanide was reported which is characterized by the following features (Haussühl, 1973):

(*a*) All elastic wave velocities increase with higher temperature over a wide temperature range.

(b) One elastic shear resistance (in KCN the elastic constant c_{44}) tends towards zero when approaching the transition point coming from higher temperatures according to $T_{44}=d(\log c_{44})/dT=1/(T \log T/T_0)$, where T is temperature in °K and T_0 a specific constant.

(c) Bulk compressibility and also thermal expansion do not exhibit comparable anomalies in their temperature dependence.

With the older elastic and thermoelastic values of cubic $Ni(NO_3)_2.6NH_3$(NNA), which had been determined by ultrasonic pulse echo measurements in the vicinity of 0°C (Haussühl, 1963), a similar anomalous behaviour could only be suggested (Haussühl, 1973). Those measurements have now been expanded over a wider temperature range with higher precision in order to decide whether or not NNA behaves like KCN.

Measurements

The blue crystals of NNA, which had been grown from aqueous solutions by evaporation at a constant temperature of about 35°C to dimensions of several cm, undergo a phase transition at about $-34{\cdot}2$°C in agreement with earlier results of Jensen & Beevers (1938) and also of Long & Toettcher (1940) who found an anomaly in specific heat between -27 and -34°C with a maximum at $-29{\cdot}9$°C. Thomas, Staveley & Cullis (1952) observed a certain hysteresis which seems to depend on surface decomposition processes. The transition occurs spontaneously and is reversible. It is assigned to the order–disorder type of transition in which the orientation of the NO_3 ions is changing from an ordered arrangement to a statistically distributed multi-site arrangement similar to the motions of CN ions in KCN. The optical transparency of the crystals is lost during the transition by microcracks parallel to the cleavage faces {111}. In contrast to KCN the crystals did not regain their original transparency after retransition to higher temperatures. Up to about 170°C the crystals