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The Determination of Structure Factors by means of Intensity Measurements from Large Single Crystals*

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Errors are considered which arise when structure factors are measured on perfect crystals. These include long wavelength harmonics in the incident radiation, TDS, and absorption effects.

In the good old days of X-ray diffraction, the structure factor was obtained by forcing crystals to behave as imperfectly as possible so that one could apply the kinematical theory to the measured intensities. This required much skill and ingenuity on the part of the experimenter and in certain instances considerable imagination. Modern technology has allowed us to reverse this trend by using perfect crystals and applying dynamical theory to obtain structure factors from observed integrated intensities.

The Darwin reflection from perfect crystals has an integrated intensity which is nearly proportional to the structure factor. Absolute measurements can be made with a double crystal diffractometer whereby the primary and diffracted intensities are of the same order of magnitude so that the problem of measuring two highly disparate intensities is avoided. There are however pitfalls which can cause large errors. One source of error is long wavelength harmonics (Batterman, 1961). As an example, a measurement of the 555 reflection from silicon in the parallel mode will have long wavelength components diffracted from the white spectrum by both crystals. This would be composed of $5/4\lambda$, $5/3\lambda$, and 5λ components from the 444, 333, and 111 reflections respectively. Since the integrated intensities are generally larger the lower the order, appreciable errors can occur.

Another source of error is thermal diffuse scattering (TDS) (Chipman & Batterman, 1963). Since perfect crystal integrated intensities are smaller than those for kinematic (imperfect) crystals and thermal scattering is always kinematic, TDS corrections are larger for the perfect crystal. For double crystal diffractometer measurements however, the volume of reciprocal space contributing to thermal scattering is extremely small due to the very low divergences involved, and the correction is negligible. However, if the measurement is not made in the parallel mode, or with a highly divergent primary beam, the errors can be substantial. Using a singly bent LiF monochromator with a 2° divergence to measure a Si 555 reflection, TDS can produce an error as high as 70% (Chipman & Batterman, 1963).

A further problem in Darwin curve measurements concerns the nature of the tails of the perfect crystal curve. These fall to zero as $\frac{1}{4}\eta^2$ where η is an angular variable such that 2η is the width of the total reflection curve. To reduce the error from intensity in the tails outside the angular range of measurements to 1%, a scan of 18 peak widths must be made, and for a 0·1% error the width must be 180 peak widths.

Absolute measurements on perfect crystals can probably be made to accuracies of 1%. Some recent measurements of this nature are given in the following papers: Jennings, Chipman & De Marco (1964); De Marco & Weiss (1965); and Batterman & Patel (1968).

A problem indirectly related to Darwin type measurements has come up in our laboratory. We have been measuring the temperature dependence of the integrated intensities in CaF_2 to check on the possibility of anharmonicity in the vibration of the fluorine atom, as reported by Willis (1965). The integrated intensities of high order reflections from ground flat-faced crystals were somewhat inconsistent, which prompted us to make an absolute measurement of the integrated intensities. We found to our surprise that the as-grown crystals cut to orientation, with either polished and etched or ground surfaces, had integrated intensities lying roughly halfway between the perfect and imperfect values. These two extremes differed by as much as a factor of 4 for the 911 reflection.

Table 1. *Theoretical and experimental values of the absolute integrated intensities of the* 911 *and* 10,00 CaF_2 *reflections at room temperature*

M/P is the ratio of the mosaic to perfect values. The undeformed measurements were from as-grown specimens, purchased from the Harshaw Chemical Co. Cleveland, Ohio, whose surfaces were ground with 1200 mesh emery powder. These crystals were statically loaded at 650°C to produce the deformed crystals.

$h^2+k^2+l^2$	83	100
hkl	(911)	(10,00)
Perfect	$1{\cdot}02\times10^{-6}$	$0{\cdot}41\times10^{-6}$
Expt. undeformed	$2{\cdot}65\times10^{-6}$	$0{\cdot}74\times10^{-6}$
Mosaic	$4{\cdot}37\times10^{-6}$	$0{\cdot}99\times10^{-6}$
M/P	4·29	2·41
Expt. deformed	$3{\cdot}97\times10^{-6}$	$0{\cdot}84\times10^{-6}$

Some measurements and calculations are given in Table 1 and show how plastic deformation at elevated temperature brought the measurements more in line with the expected mosaic intensity. The relevance of these data to the present discussion involves the temperature dependence of the integrated intensity of a

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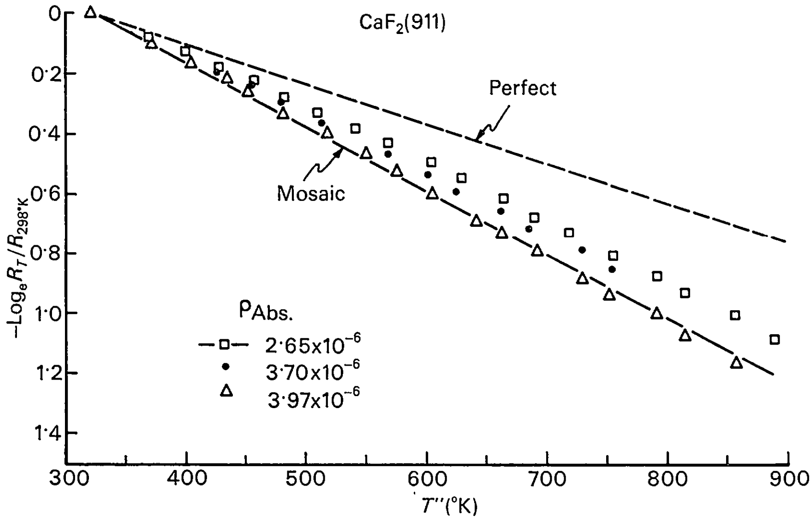

Fig. 1. Plot of the logarithm of the ratio of the integrated intensities at elevated temperatures with respect to that at 298°K *vs.* the reduced temperature (Paskin, 1957) for the 911 reflection of CaF_2. The dashed and solid straight lines are for ideally perfect and ideally mosaic crystals respectively with $M_{\text{slope}} = 1{\cdot}62\ P_{\text{slope}}$ (see text for discussion). The experimental points are for real crystals at various stages of deformation as indicated by their experimentally determined absolute integrated intensities at room temperature, ϱ_{obs}.

crystal that is at one extreme perfect, and at the other, imperfect, and in actual fact may lie somewhere in between. The temperature dependence of the intensity for the imperfect crystal is given by the usual Debye–Waller factor exp $[-2M]$. For the perfect crystal one expects to replace $F^2 e^{-2M}$ of the kinematic case by $|F|\,e^{-M}$ for the Darwin case. This is correct as shown experimentally by Okkerse (1962) and Batterman (1962, 1964) and theoretically by Ohtsuki (1964). However, it is not correct to assume that the integrated intensity of the perfect crystal Darwin reflection should behave as e^{-M}. This would only be true if absorption processes were negligible.

For high orders this is not the case and an absorption term must be included. This term involves a temperature dependent part because of its implicit dependence on $|F|\,e^{-M}$ (Hirsch & Ramachandran, 1950). In fact, as the absorptive process becomes more important, the Darwin solution must reduce to the kinematic result because beam attenuation in the crystal by scattering becomes less important and this is the basis of kinematic theory.

We show in Fig. 1 the theoretical curves of the temperature dependence of the CaF_2 911 reflection. The perfect crystal is surprisingly linear in the range considered. The mosaic curve has a slope 1·62 times the perfect value, not twice the value as one might naively expect.

To make the point more explicit, if one measured the temperature dependence of the 911 reflection from CaF_2 assuming the crystal was imperfect when indeed it was ideally perfect, an error of about 25% would be made using the slope to determine the Debye–Waller factor. The curve would be quite linear and give no hint that something was amiss. Of course, the temperature dependence of a crystal which was neither dynamic nor kinematic would be very difficult to predict. A careful measurement of the absolute intensity is essential to determine the degree of extinction. It can be seen in the Figure that as deformation is increased, and the room temperature integrated intensities approach the mosaic value, the temperature dependence approaches the exp $[-2M]$ type of behavior.

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DISCUSSION

Hart: It is advisable to point out the difference between the various methods. The Pendellösung technique measures only coherent scattering whereas those relating to intensity measurement involve other scattering (Compton and internal scattering, for instance).

Batterman: Yes, if the corrections for these features are not made properly, obviously they would be a source of error.