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The Intensities of Multiple Diffraction Effects

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The effects of simultaneous reflections on the intensities of reflections used in crystal structure analysis have been discussed by Zachariasen (1965) and by Moon & Shull (1964) for cases where only secondary extinction need be considered.

In the present investigation the intensities of a number of reflections from a variety of crystals have been monitored in the course of azimuthal scans about the **S** vectors (θ constant). These include several space group 'forbidden' reflections (of the type 010 in $P2_1$, *etc.*) and others of weak to medium intensity. Measurements were made with a PAILRED automatic diffractometer using crystal monochromatized Mo K and Cu K radiations. The 'mosaic' crystals investigated included ammonium oxalate, anthrone, Ca_2VO_4Cl, 1,2-*trans*-cyclohexanedicarboxylic acid and L-alanyl, D-alanyl-2,5-diketopiperazine. The effects observed vary widely from crystal to crystal and are often difficult to explain in terms of secondary extinction alone. Although in a few cases the incidence of simultaneous diffraction effects was surprisingly low, it is evident that the intensities of very weak reflections are often systematically overestimated because of simultaneous diffraction effects.

The effects of unit-cell size, incident beam divergence, X-ray wavelength and other variables on the magnitudes of simultaneous diffraction effects will be discussed. Results observed with highly perfect crystals will be compared with those encountered when ordinary imperfect crystals are used.

References

ZACHARIASEN, W. H. (1965). *Acta Cryst.* **18**, 705.
MOON, R. M. & SHULL, C. G. (1964). *Acta Cryst.* **17**, 805.

[*Owing to illness, Professor Post was unable to supply a text of his contribution, which is therefore reproduced here in abstract form only. The discussion after this paper follows.*]

DISCUSSION

AHMED: How will errors due to multiple reflexions appear in difference maps? Will there be systematic features or do you expect merely random effects?

POST: I favour elimination of errors where recognized. Their effect on difference maps may be predictable but the inverse process of deducing their origin from study of the difference map may not be feasible.

HAMILTON: In this matter, it should be noted that even if errors in intensities are random, they tend to pile up near atomic positions and also in between atoms.

HIRSHFELD: Have you examined the correlation between the width of these enhancement peaks and the path of the second reciprocal lattice point through the Ewald sphere?

POST: Moon & Shull have carried out such calculation and also, in an unpublished thesis at Brooklyn Polytechnic, Williamson examined α-quartz, potassium and ammonium sulphate for double diffraction and the overwhelming importance of angular divergence is evident. He used a Fankuchen double-crystal monochromator, the assembly providing a beam of divergence of ~ 10 sec in both directions. He not only eliminated many peaks from the double-diffraction pattern but the average decrease in half-width was of the order of 30. The calculations of Moon & Shull referred to indicate that they correspond very closely to the simple geometrical considerations.

FISCHER: (*a*) The influence of both systematic and accidental Renninger effect on the structure factors is higher than one might expect: The structure of Na_2BeF_4 has been refined based on an equi-inclination diffractometer with

(i) 'normal' intensity measurements,
(ii) measurements avoiding double reflexion.

The ratio of weighted R-factors, R(i):R(ii), was 1·6:1·0 (F. Weber, Ph. D. Thesis, Frankfurt, 1967).

(*b*) In pre-computing possible double reflexion situations for a diffractometer, it is vital to take into account the divergence of the primary beam. Otherwise there is considerable danger of missing many Renninger interactions. For the equi-inclination technique, a FORTRAN program has been written by F. Weber (*Z. Kristallogr.*, in press). For the Eulerian-cradle-type diffractometer, a similar program will soon be available from V. Schramm, Saarbrücken.

COPPENS: (*a*) I have similar comments concerning a neutron diffraction refinement of cyanuric acid where the *h2l* reflexions were mainly affected. The influence on the y parameters was of the order of a few thousandths of an Å, but this could be significant for detailed studies.

(*b*) We have had cases where we could not find multiple reflexions on rotation although the extinction was severe – perhaps this was due to using a very narrow beam.

POST: I do not quite agree with that conclusion. For detection of multiple reflexions, it is often necessary to use a very slow angular motion on account of the Lorentz factors for the second reflexion. There may be only a momentary glimpse of the condition. Since extinction is, in a sense, a three-beam situation, its presence and the occurrence of

multiple reflexions are likely to co-exist or reflect two aspects of the internal structure.

MASLEN: Can you comment on the broad modulation observable in the Si curve in addition to the sharp peaks?

POST: The specimen referred to had been ground and had a fairly substantial mosaic spread, probably mainly in the surface layers. Moon & Shull have carried out calculations and we have examined two cases. It appears possible to explain the widths observed on the basis of those geometrical considerations, at least for mosaic crystals. For perfect crystals, the situation is of course different.

WEISS: Now is probably the time for crystallographers to accept, at the beginning of a crystal study, that multiple diffraction effects exist, and are important, and to seek to satisfy themselves as to their magnitude in the specific case they have on hand. One way which would be useful would be to look for their effect on space-group forbidden reflexions.

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The Correction of Measured Structure Factors for Thermal Diffuse Scattering

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Correction of X-ray intensities for thermal diffuse scattering (TDS) is necessary, though difficult in practice. Existing calculations for the TDS correction are reviewed and the hitherto neglected resolution function, $R(\mathbf{q})$, of the diffractometer is discussed. It is concluded that overcorrection for inelastic scattering results when $R(\mathbf{q})$ is ignored. Computation of accurate corrections requires a knowledge of the elastic constants of the material, experimental measurement of $R(\mathbf{q})$ for several reflexions and considerable machine programming and computing time.

1. Introduction

I undertook to give this paper with some reluctance, since my periods of interest in accurate measurement of structure factors and in lattice dynamics have scarcely overlapped. Consideration of both at the same time has proved to be a useful exercise however, and has convinced me that the correction of X-ray intensities for thermal scattering is both necessary, and difficult in practice. I am therefore advocating a tedious correction which I never applied to my own data!

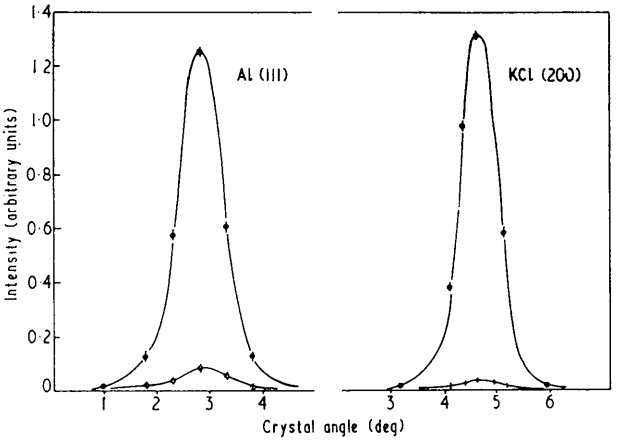

Fig. 1. Bragg intensity and diffuse intensity determined by the method of Butt & O'Connor (1967). Reproduced from their paper.

The theory of X-ray scattering by lattice vibrations has been reviewed elsewhere (Cochran, 1966; Smith, 1966) and will not be considered in detail. Bragg scattering is the process in which the X-ray photon is scattered without change of energy, so that the wavelength is unaltered. This scattering is superimposed on a background of Compton scattering and possibly fluorescence scattering which we do not consider since the intensity varies slowly in reciprocal space and is easily subtracted off. Thermal scattering is the process in which the incident radiation is scattered inelastically, the incident photon exchanging one or more quanta of vibrational energy (phonons) with the crystal. The change in energy (or wavelength) of the scattered radiation is only a few parts per million, ordinarily negligible. It is however enough to distinguish elastically and inelastically scattered radiations when the technique of Mössbauer spectroscopy is used (Butt & O'Connor, 1967). Fig. 1 shows the elastically and inelastically scattered components from Al (111 reflexion) and from KCl (200 reflexion). The intensity of thermal scattering is seen to be by no means negligible, even for these low-angle reflexions. Fig. 1 can be misleading: to gain intensity the experiment had to be done with poor geometrical resolution and as a result the inelastic and elastic components appear equally 'peaked' at a reciprocal lattice point, which is not at all the case.

Lattice vibrations can be distinguished as acoustic modes, for which the (circular) frequency $\omega_j(\mathbf{q})$ is proportional to the wave number q for small values of q,