

Effect of n -beam Interaction*

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Abstract

Weak spurious intensities arising from the n -beam interaction (the multiple diffraction) often obscure the existence of screw axes or glide planes. It is pointed out that the n -beam interaction may also introduce significantly different intensities to a set of crystallographically equivalent reciprocal lattice points. These problems can be solved by making ψ scanning measurements and, more definitely, by a comparison with the simulation based on the Soejima-Okazaki-Matsumoto (1985) formalism; some examples are shown. Since the influence on the intensity reaches 10% for strong reflections and more for weaker ones, a careful examination is essential for the accurate determination of F values.

1. Introduction

It is well established that the n -beam interaction may lead to a wrong conclusion on the space group because it gives apparent intensities to some Bragg reflections which are otherwise absent as a result of screw axes or glide planes. The problem was quantitatively analysed by Soejima *et al.* (1985) using a simulation based on the kinematical theory. The procedure was so easily understood, and the results were in such good agreement with experiment, that a further examination of the n -beam problem was undertaken. An experiment on KMnF_3 (Okazaki *et al.* unpublished) showed that the effect can be observed for every reflection and that even fine details of the ψ scanning pattern can be reproduced by the simulation.

In the present paper the analysis of the n -beam effect is discussed from another point of view. In some cases, the intensities of a set of reflections which are expected to be equivalent are significantly different. If the difference is genuine, we should choose a lower space group for the structure. On the other hand, if not genuine, the difference can be attributed to absorption, extinction, thermal diffuse scattering, or the n -beam effect. It is shown in the following that the measurement of ψ scanning about the scattering vector and a comparison with the simulation are useful in confirming the crystal symmetry. As a sample material, Nb_3Sn of A15 structure with the space group $Pm\bar{3}n$ (Matthias *et al.* 1954) and with a large absorption coefficient (191 cm^{-1} for $\text{Mo K}\alpha$) is chosen. It will also be pointed out that the effect of n -beam interaction can be significant for every reflection. In the literature, the effect on

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stronger reflections has not been discussed seriously, though it must be important when we try to determine an accurate electron density distribution. A discussion on this problem is also given.

2. Methods

The effect of n -beam interaction at the reciprocal lattice point h can be described by summing the effects of independent three-beam interactions, because the reflectivity is small. The following formula is an extension of equation (A.2) given by Soejima *et al.* (1985):

$$(I_h)_{\text{obs}}/rI_0 = N_h \left\{ 1 - r \left(\sum_i N_{\text{opi}} + \sum_i N_{\text{coi}} \right) \right\} + r \sum_i N_{\text{opi}} N_{\text{coi}}, \quad (1)$$

where I_0 denotes the incident intensity, and r an effective reflectivity including absorption and extinction. It is assumed that the value of r is the same for different reflections, while the N_h are normalised to the largest among them:

$$N_h = |F_h|^2 Lp. \quad (2)$$

In equation (1) conventional notation is used. The subscripts op and co indicate the operative and cooperative points respectively; they are related to each other by

$$h = h_{\text{op}} + h_{\text{co}}. \quad (3)$$

The calculation has been carried out using a PDP-11 computer at intervals of 0.1° in ψ .

The ψ scanning measurements have been made on an Enraf-Nonius CAD4 diffractometer with graphite monochromatised Mo $K\alpha$ radiation. The specimen used was a sphere 0.3 mm in diameter and mounted on top of a glass capillary. Since the effect of the p factor on the n -beam intensity is found not to be very significant, the effect of incident beam polarisation is not taken into account.

3. ψ Scanning: Experiment and Simulation

The intensity data were collected for one octant of the reciprocal lattice; the number of reflections is 584. Contrary to the known space group $Pm3n$, all the reflections have significant intensities, larger than twice the standard deviation; this suggests that the n -beam effect is observed. It is also found that the data are hardly consistent with the cubic symmetry; i.e. the intensities of a set of reflections that should be equivalent from the symmetry are significantly different in most cases. In order to examine whether or not these features are genuine, the ψ scanning measurements and the calculation have been made.

Fig. 1 shows the ψ scanning pattern of 220 of Nb_3Sn for (a) the experiment and (b) the calculation. The overall agreement between them is obvious. A modulation of the baseline in Fig. 1a can be attributed to anisotropy in the absorption effect, resulting from the fact that the specimen is not exactly spherical. The peaks on the baseline are due to Umweganregung, corresponding to the last term on the right-hand side of equation (1), while the dips are due to Aufhellung, corresponding to the second term. Since the intensity of 220 is as small as 1/50 of the strongest, Umweganregung

is predominant as seen in Fig. 1*a*. The calculation is carried out with the intensity data of all the observed reflections collected on the CAD4 diffractometer.

In Fig. 1*b*, the assignment of dominant pairs of the operative and cooperative points are given for some peaks and dips. For example, the peak marked $201-02\bar{1}$ consists of a single dominant contribution of a pair of the operative 201 and cooperative $02\bar{1}$ points. When there is more than one pair dominant, they are all given. The largest peak is at the mirror point and is due to the strongest 020 and its equivalent 200. For the dips, either the operative or the cooperative point is very weak: 100 and 300 are prohibited, while 620 and 260 are negligible. These features are consistent with equation (1).

The fitting of the peak-height-to-baseline ratio to the experimental data gives an r value of 0.02. The value of another parameter $\Delta\lambda/\lambda$, the relative width of the wavelength of the incident beam, is empirically taken to be 0.01.

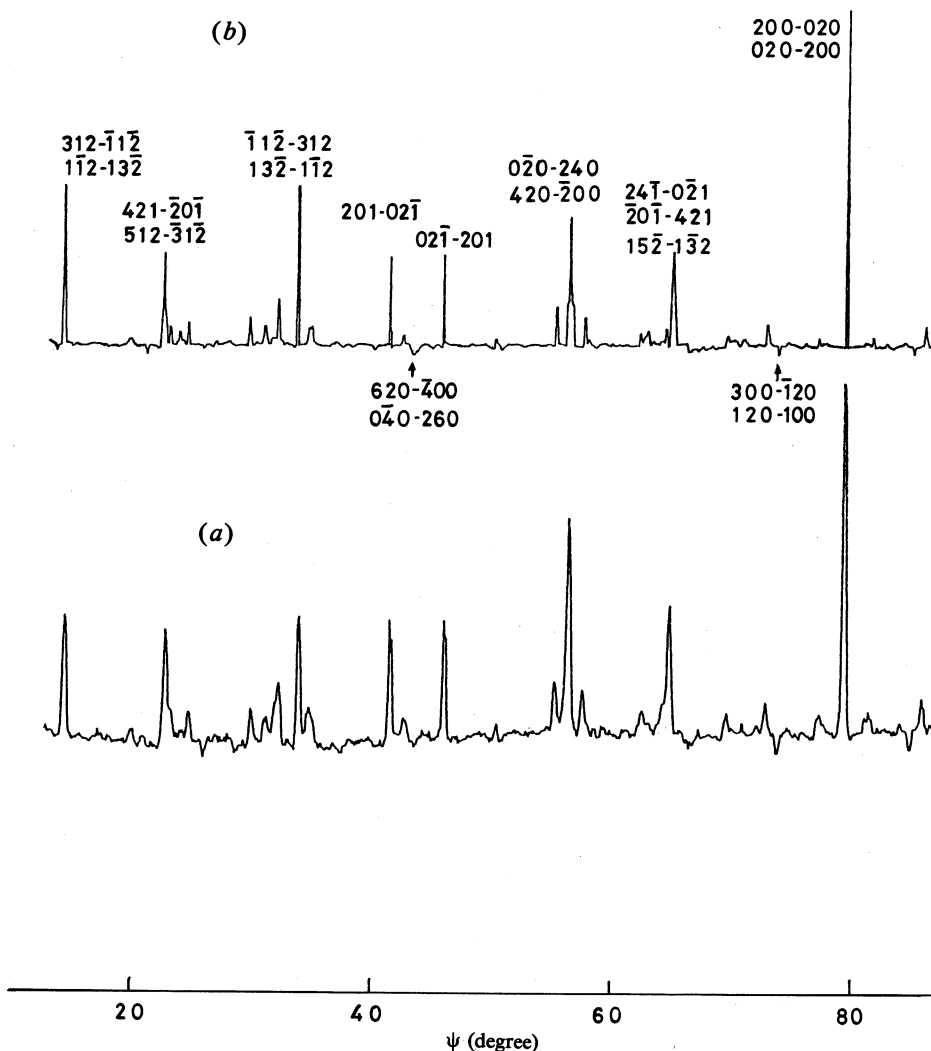


Fig. 1. The ψ scanning patterns of 220 of Nb_3Sn : (a) experiment with Mo K α and (b) calculation. The assignment of the operative and cooperative points is given for some peaks and dips.

The intensities of 220, 202 and 022 are 21.4, 26.5 and 21.2 respectively. The difference is significant though they should be equivalent from the symmetry. In Fig. 2 the experimental ψ scanning patterns of these reflections are shown. The intensity measurement on the diffractometer is made at $\psi = 0$. Since the ψ coordinate depends on the relative orientation between the crystal and the diffractometer axes, the position $\psi = 0$ on the ψ scanning pattern is not the same for a set of equivalent reflections. Properly shifting the pattern along the ψ coordinate, we find, as shown in Fig. 2,

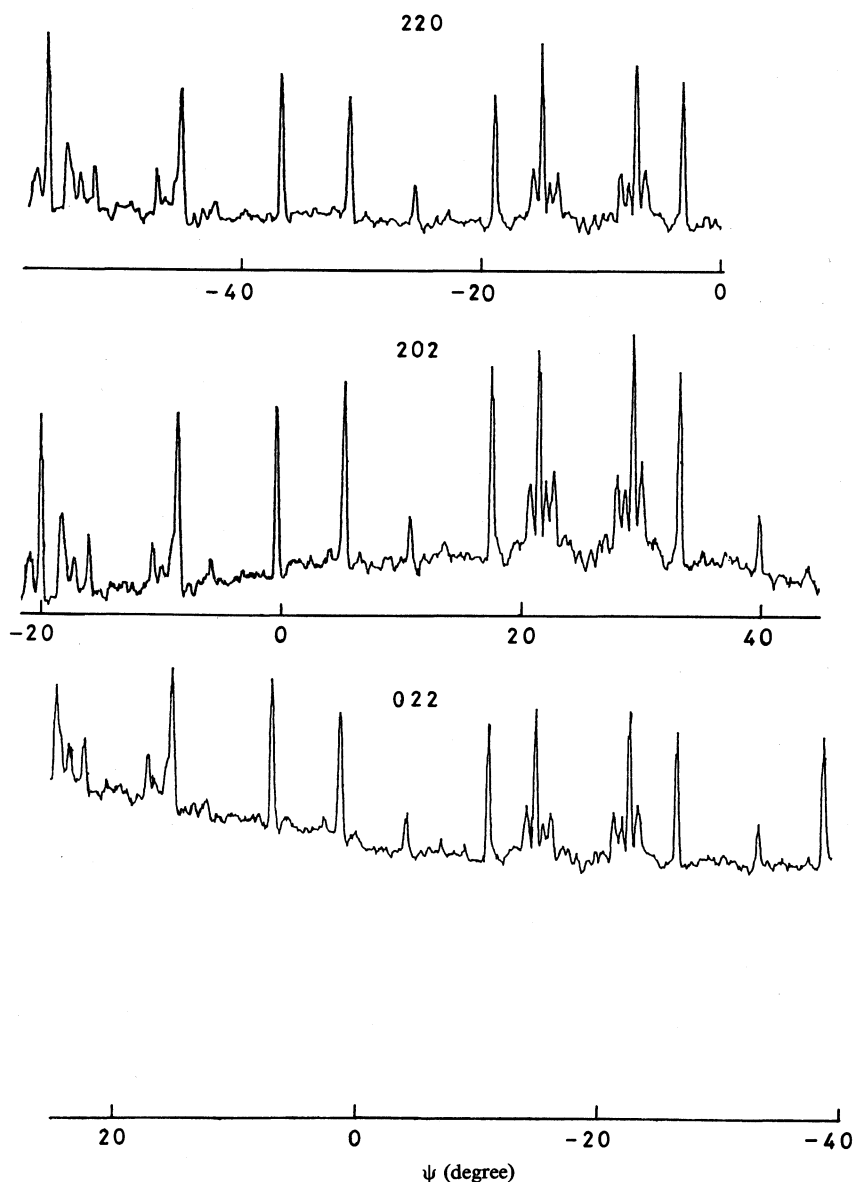


Fig. 2. The ψ scanning patterns of 220, 202 and 022. The ψ coordinates are adjusted for clarity. The modulation of the baseline is attributed to the absorption effect. The abscissas, and the ordinates, for 220 and 202 are shifted (see text).

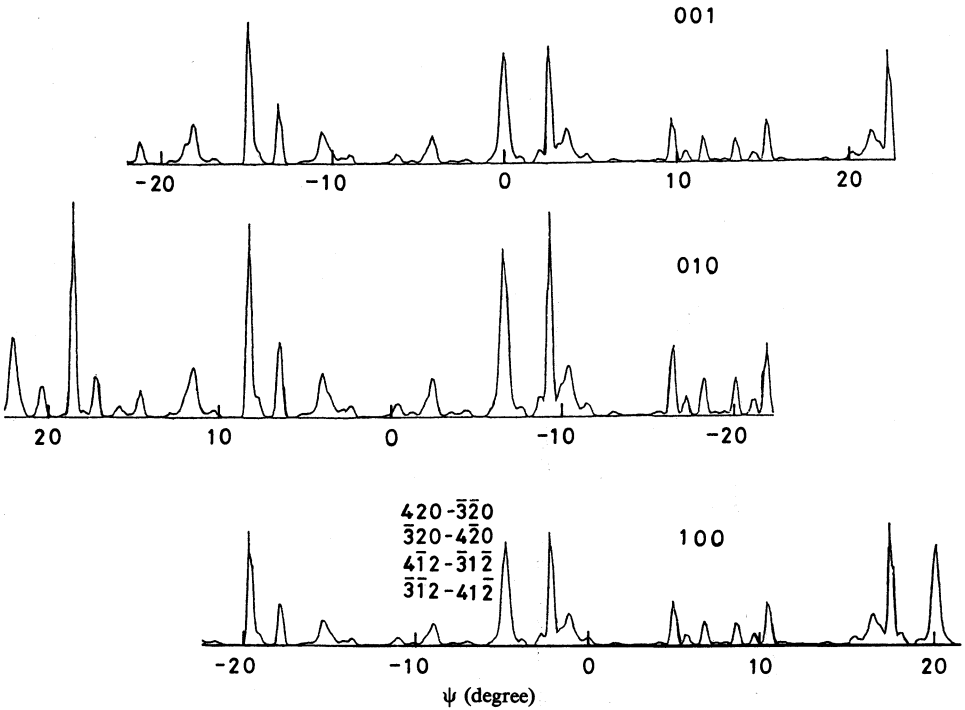


Fig. 3. The ψ scanning patterns of 001, 010 and 100. It is obvious that the intensity of 001 integrated at $\psi = 0$ is more than ten times as strong as those of the others.

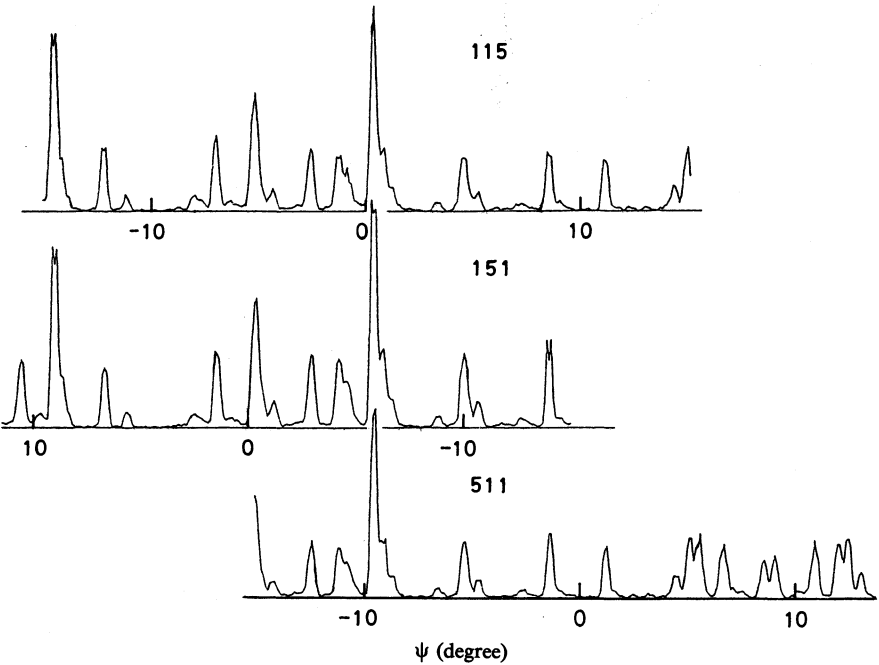


Fig. 4. The ψ scanning patterns of 115, 151 and 511.

that the patterns of the three reflections are identical. The higher intensity of 202 is mainly due to the fact that $\psi = 0$ for this reflection is at the tail of one of the highest peaks. For the other reflections the positions $\psi = 0$ are free from those peaks. The identity of the ψ scanning patterns is strong support for the symmetry that results in the equivalence of the relevant reflections.

Two examples of reflections prohibited by N glides are shown in Figs 3 and 4 for 001 and 115 respectively, together with those of equivalent reflections. Since the height of the baseline is zero and free from modulation, a comparison of the height is easier in these cases. The ψ coordinates are arranged so that the equivalence of the pattern is readily seen. In Fig. 3 the situation is shown in which 001 is 1/25 of the strongest, while 100 and 010 are very much weaker. The position of $\psi = 0$ for 001 is just the position of one of the highest peaks; the assignment on the basis of the simulation is given in the figure. In Fig. 4 the height at $\psi = 0$ for 511 is obviously lower than those for 115 and 151. The observed intensity for these three reflections are 0, 6.0 and 5.0 respectively. A few more examples, for instance 003, 130, etc. have been examined; all have shown that the crystal has cubic symmetry, though the conventional intensity data do not suggest it.

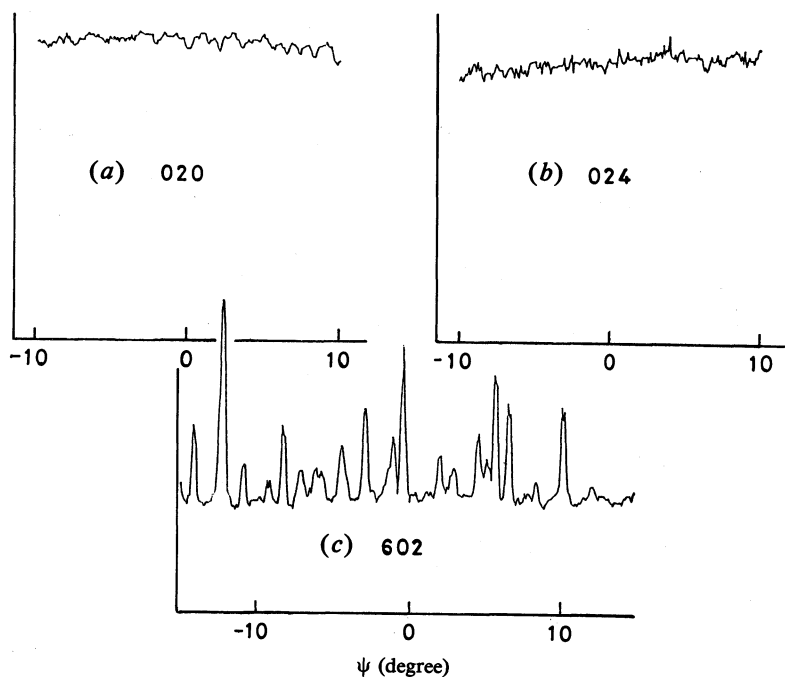


Fig. 5. The ψ scanning patterns of (a) 020, (b) 024 and (c) 602.

4. Discussion

As shown in the preceding section, the ψ scanning patterns of a set of equivalent reflections are found to be identical after adjusting the ψ coordinate. From the original intensity data, in particular in the case of 001, 010 and 100 with the intensities 39.0, 1.4 and 2.8 respectively, it is difficult to imagine that they are equivalent. This adjustment of the ψ coordinate can be evaluated, in principle, from the orientation parameter of the crystal, the UB matrix. It is desirable, in general, that the intensity

measurements of a set of reflections which are supposed to be equivalent are made at the corresponding ψ positions. This will be possible in a future experiment.

It is true that the *n*-beam interaction often makes the space group determination ambiguous. It is to be emphasised, at the same time, that the *n*-beam interaction represents the crystal symmetry; the ψ scanning patterns should therefore be identical for a set of equivalent reflections. This fact will be useful when a detailed examination of the symmetry is attempted. The intensity dataset to be used for the simulation naturally includes the *n*-beam effect. The effect of this on the final ψ scanning pattern is second order; the error will not be much larger than the fluctuation of the observed intensity.

Finally, a general effect of the *n*-beam interaction on the structure factor determination is discussed. Fig. 5 shows ψ scanning patterns of a few more reflections: (a) 020, (b) 024 and (c) 602. The intensity of 020 is largest among 584 reflections; those of 024 and 602 are 1/4 and 1/300 of that for 020. Since 020 is the strongest, only dips are observed on the ψ scanning pattern; for 024, dips are dominant but some peaks are also seen. In the case of 602, the intensity is so weak that dips are hardly observed.

It is to be noted that even for strong reflections the effect of the *n*-beam interaction cannot be neglected; the effect can introduce an error of 10%, and more for weaker reflections. The situation here is entirely common for all other materials examined, including the case of the molecular crystal $C_{12}H_{12}O_5$.

As far as the accuracy of the structure determination is concerned, the present effect is more important for strong reflections. Although the effect may not be significant, by chance, in a conventional measurement usually made at $\psi = 0$, it may result, again by chance, in an intensity variation as much as 10% for individual reflections. The problem in practice is that in many cases it may not be possible to make the ψ scanning measurement for numerous reflections. Therefore, making use of the simulation based on the Soejima–Okazaki–Matsumoto (1985) formalism is to be recommended for correcting the intensity data.

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