JOHNSON: For the segmented body approach to these almost rigid bodies, we find it practically always necessary, for neutron diffraction studies, to do the best to subtract out the effect of internal vibrations as determined from some normal mode analyses. Also we intend now to put the skewness tensor into this type of calculation. It will not tell us any more about correlation of motion between atoms but will give a cleaner separation of libration from translational effects.

ZACHARIASEN: My comments are on anomalous dispersion effects. The real part $\Delta f'$ cannot be disentangled from the form factor curves used; the imaginary part $\Delta f''$ only shows up in acentric crystals when measuring reflexions H and $\bar{H}$. The accuracy which you get from refinement depends on $\Delta f''$ and this, at present, is best derived from empirical anomalous absorption values given. $\Delta f''$ is only as good as these tables, unless you are dealing with very light atoms when other contributions come in, but still, in my opinion, more reliable than Cromer's calculations. It should be realized that the effect of $\Delta f''$ is very appreciable.

I have recently made measurements on KH_2PO_4 with Mo $K\alpha$ radiation. The reflections are of three types:

(i) Those which have no contributions from K or P but only from O, where no dispersion is observed.

(ii) Those where K and P cooperate completely; here the anomalous dispersion term comes in as the sum of the two $\Delta f''$ and amounts to only about 2% because the reflections are very strong.

(iii) Those where K and P are in opposition. Those reflections are very weak and the difference between the two $\Delta f''$ may amount to as much as 20% of the total.

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Instruments and Techniques Required for Accurate Relative Intensities from Powder Specimens

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For the purpose of accurate intensity measurements the use of transmission specimens is recommended. Apart from special advantages with respect to certain features *e.g.* surface roughness, they allow the measurement of the orientation distribution over a large range, using off-symmetry azimuth values. Correction for preferred orientation should then be possible, provided a simple texture model – a cylindrico-symmetrical needle-type texture – can be assumed. Some computing schemes for carrying out the elimination of the texture parameters are discussed.

The techniques referred to in the title can be considered from different viewpoints. For instance, one may ask which of the existing routine techniques is most suitable for attaining a high accuracy? Quite generally, the field can be restricted to counter methods – though it is perhaps worth mentioning that, apart from properties of available film, the fundamental reason for this restriction is the unfortunate spectral film sensitivity rather than any foreseeable limit of reproducibility. Between the different counter diffractometers, there is little essential variation. All are based on the Bragg–Brentano principle, so there seems to be no choice left.

One may ask, then, if the requirement of high accuracy would make it desirable to apply techniques not used routinely at present. We think this may be true with regard to (1) transmission-type diffractometry, in particular when used (2) to measure intensities at off-symmetry azimuths of the specimen plane.

(1) Transmission geometry means the use of a thin slab of powder specimen permitting the diffracted beam to emerge from the back. Though proposed originally as a direct consequence of the application of curved monochromators to counter diffractometry, the transmission specimen has independent merits.

In the first place, the surface layers of a transmission-type specimen contribute no more to the diffracted intensity than corresponds to the volume they occupy, whereas in reflexion-type specimens their contribution can be predominant. Here 'surface-layer' means the layer – with a thickness at least of the order of the average particle diameter – which can be suspected to show systematic deviations from the average distribution of crystallite orientation and (in the case of mixtures) of composition.

Secondly, the effect of surface roughness is much less in transmission than in reflexion, because of the much smaller angle between surface normal and X-ray beam. This is important in the investigation of strongly absorbing powders.

The transmission-type specimen has some obvious disadvantages. Depending upon the material under hand, a slab of uniform thickness may be more difficult to fashion than a reflexion specimen, and it will usually require a binding agent and/or a support. Also the transmission geometry is clearly unfavourable for large Bragg angles. In many cases, however, the use of Mo K radiation will yield sufficient information at low to medium angles.

The need for a focusing monochromator in transmission geometry is not a disadvantage, because the complication and the (not very large) loss of intensity are compensated by the spectral purification and the increased resolving power.

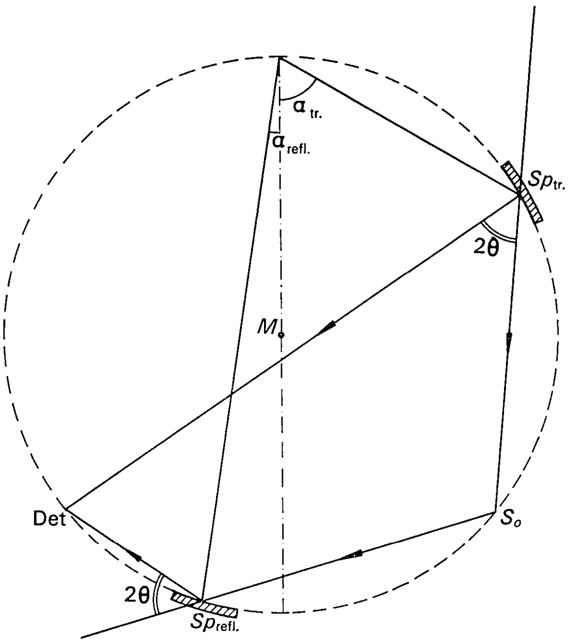

Fig. 1. Geometry for transmission-type (S_{ptr}) and for reflexion-type (S_{prefl}) specimens. S_o = source (virtual in the case of transmission); Det = detector. The circle is a focusing circle; α is the angle between normal of reflecting plane and normal of specimen plane.

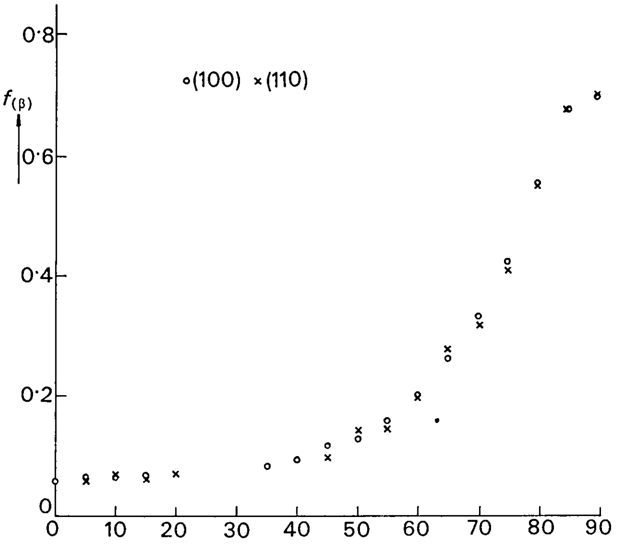

Fig. 2. Measured distribution of (100) and (110) lattice plane normals in an α-Cd(OH)$_2$ powder specimen. Values for $\alpha < 30°$ have been obtained in reflexion, the others in transmission.

Still, on the whole, the advantages mentioned above may be considered as, if not far-fetched, at least difficult to prove; in several cases (low absorption, small particles) they are certainly not important. The reason for which we think transmission geometry deserves serious consideration is closely connected with the second technique and, more generally, with preferred orientation.

This latter effect has thus far been treated as a nuisance which has to be completely eliminated if one is to obtain a high degree of accuracy. Now a texture-free transmission specimen is by no means easier to prepare than a reflexion specimen. On the other hand, 'complete elimination' is, for many substances, next to impossible in any specimen whatsoever. What is even more important, the degree of elimination is hardly ever measured by a direct test for preferred orientation. Instead, the agreement of measured intensities with some sort of structure model is often taken as a proof of the absence of texture. We think that a much more firm base for the reliability of the data can be obtained by actually measuring preferred orientation; this is possible through the use of transmission geometry for (2).

(2) Measurement of diffracted intensity at off-symmetry azimuths (meaning specimens not coinciding with a bissectrix of the diffraction angle). Essentially similar measurements are, of course, made in instruments for measuring texture. One might consider the use of such instruments for the present purpose. It is doubtful, however, if their use will be entirely satisfactory. This may be the case for simple cubic compounds with patterns resembling those of metals. More complex patterns, however, require a resolving power not usually available in these instruments.

In the latter case, the measurement will usually have to be made on lines with small Bragg angles, because in complex patterns only among these are found the lines of sufficient intensity and sufficient separation from neighbours to allow this type of measurement. From this small θ-value it follows that only a very small part of the orientation distribution can be investigated in reflexion. The angle α between the surface normal and a given diffraction vector can take values between $\pm(\theta-\beta)$ in reflexion, β being the minimum angle allowed between specimen and beam, which is in practice of the order of 5 degrees. This is shown in Fig. 1, depicting a fixed focusing circle with fixed source and detector slits (for a given θ).

The same Figure shows the situation for transmission. It appears that the angle α now varies between $\pm(\pi/2-\theta+\beta)$, which for small θ covers a large part of the full range. The two techniques combined yield complete coverage except for twice an arc of 2β.

In Figs. 2 and 3, some results are shown of measurements which we made on a specimen of α-Cd(OH)$_2$. This hexagonal compound was available in the form of a fine-grained powder, with platy crystals parallel to (001). Preferred orientation was enhanced expressly (so as to test the relation between distributions of different net plane normals) by smoothing a mixture of the powder with petroleum jelly on cellophane. Prism reflexions such as 100 and 110 show a high peak at the expected position $\alpha = 90°$. The curves in Fig. 3 have a maximum at a lower angle. For these planes (101) and (111), the angle with (001) is 56·67 and 69·20°, respectively. The actual maxima occur at angles which are some 5–10° higher.

Subsequent calculation based on a needle-type texture (see below) showed that this systematic error is real. Afterwards we discovered that its cause was an unexpected deviation of the texture axis from the surface normal. The former dips about 5° in the direction in which the last smoothing stroke during specimen preparation has taken place!

This effect illustrates the necessity to have a rigorously defined texture axis of symmetry. Further experiments are envisaged, where we plan to use a fast specimen spinner – as used to suppress particle statistics – for this purpose.

Finally something should be said about the method of correction for preferred orientation. We have not actually carried out such a correction. Indeed the above experiments were used only to test the theory of texture. Several aspects of the actual problem were encountered, however.

(*a*) Absorption. For a plane-parallel specimen this effect is entirely determined by a single parameter: μt, t being the thickness. The formulae are well known and they present no difficulty except some care for the singularity at $\alpha = 0$. The parameter can either be measured (which we did) or treated as an extra unknown. The support, if not extremely thin, may require introduction of an extra parameter.

(*b*) Texture model. A general orientation distribution is an arbitrary function of no less than three variables (the Euler angles). Fortunately, cylindrical symmetry such as obtained by a specimen spinner reduces the number of variables to two. Even so, complete determination of this function is a huge task. Nevertheless, for cubic compounds, which admit no further simplification, this is necessary. As stated above, the measurement may in these cases be feasible with a texture goniometer, because of the simple nature of the pattern.

The problem has been dealt with in a very thorough manner by Roe & Krigbaum (1964). They showed that it can be solved – in principle at least – by expanding the function in a series of conjugated Legendre functions. The distribution of a given crystallographic direction, being cylindrically symmetrical about the texture axis, can be developed in a series of zonal Legendre functions. The coefficients of the latter – obtained from direct measurement of this distribution – are related to those of the first-mentioned series by linear relations. From the measurement of a sufficient number of net plane normal distributions, the complete distribution can be derived.

In powder diffraction, one is often faced with a more favourable situation; namely, when the powder consists of particles in the form of either plates or needles. One may assume that in such cases the azimuth defining the crystal orientation for a given needle axis, or plate normal, is distributed evenly over its range of 2π. We shall call this, for simplicity, a needle-type distribution.

If moreover, the texture has an axis of cylindrical symmetry, the resulting orientation distribution is now a function of merely one variable. This is clear from the fact that it is entirely determined, for instance, by the distribution $f(\beta')$ of the polar angle β' of the needle-axis (or plate normal) – that is, the angle it makes with the texture axis. The polar distribution $g(\chi)$ of any other direction (making an angle φ with the needle axis) can be expressed in the form of an integral:

$$g(\chi) = \frac{1}{\pi}\int_0^{\pi} f(\beta')d\gamma;$$

$$\cos\beta' = \cos\chi\cos\varphi + \sin\chi\sin\varphi\cos\gamma\,, \qquad (1)$$

where β' is the polar angle of a point on a small circle, with its centre at a distance χ from the pole. This point is further defined by an azimuth angle γ which is zero and π at the intersections of the small circle with the meridian passing through its centre.

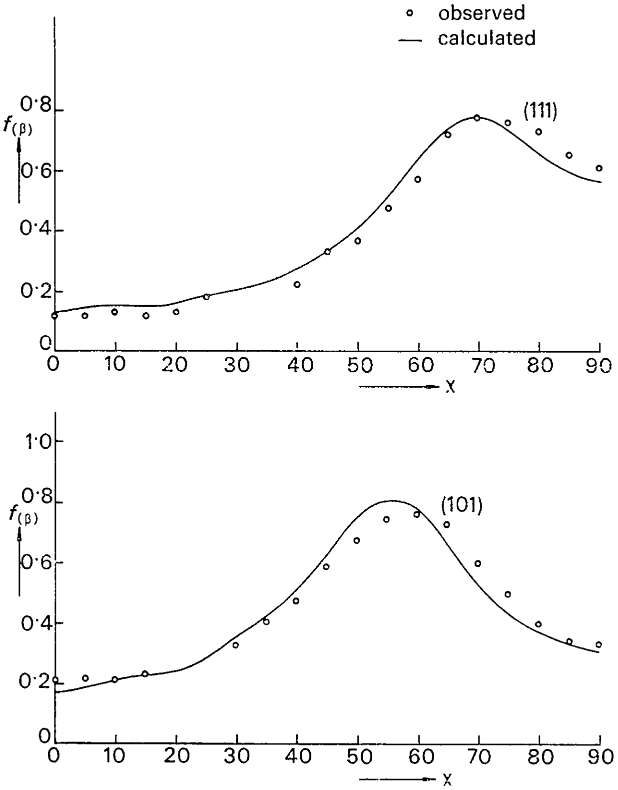

Fig. 3. Measured and calculated distributions of (111) and (101) planes. Drawn line: calculated from Fig. 2, assuming that texture axis = surface normal, or $\chi = \alpha$.

(*c*) Characterization of a needle-type texture by parameters. From (1) or from the general results of Roe & Krigbaum one derives easily the following relation between the coefficients A_{2n} and B_{2n} of P_n in a development of $f(\chi)$ and $g(\chi)$ in Legendre functions $P_n(\cos\varphi)$:

$$B_{2n}=P_{2n}(\cos\varphi)\,.\,A_{2n}\;. \tag{2}$$

Hence the coefficients A_{2n} would appear to be the most suitable parameters to characterize the texture. Indeed the results of Fig. 2 and 3 were obtained by a spherical harmonic analysis of the curve of Fig. 2, followed by application of equation (2) and subsequent synthesis.

It is doubtful, however, whether this approach is the most appropriate one if a weak texture has to be eliminated from a number of precision intensity measurements. The distribution of Fig. 2 and 3 is probably typical of the rather broad type of maxima to be expected. The calculation mentioned above has shown that many (here 12) terms are needed to obtain a reasonable degree of accuracy. If the texture itself is only weak, a smaller number may be sufficient, but hardly less than 5 or so. It may be advantageous to sacrifice the simple and linear relationship expressed by equation (2), and to define $f(\beta)$ by some parameters more closely adapted to its expected form. As such, one might think of just two parameters, defining height and width of the maximum, respectively. This leads to much more complicated relations between $f(\chi)$ and $g(\chi)$, which would have to be completely available in order to allow the elimination of such a pair of parameters from a set of measurements.

Reference

Roe, R. J. & Krigbaum, W. R. (1964). *J. Chem. Phys.* **40**, 2608.

DISCUSSION

Weiss: It is true that preferred orientation effects can be disentangled given a thin enough transmission specimen, but I suspect that an accuracy of ~1% is required.

De Wolff: The texture must not be too pronounced; there are techniques for reducing it with transmission specimens.

Weiss: Suppose you use Mo $K\alpha$ on a powder specimen of a transition element, such as iron, it is difficult to make your specimen thin enough, when the $1/e$ thickness is only a few thousandths of an inch.

De Wolff: You should aim at a thickness even less than the $1/e$ value.

Milledge: Those directly concerned with the investigation of orientation use special techniques for their detection. Could these be of assistance?

De Wolff: In principle you are correct, but the materials which are usually studied by powder procedures are generally not of simple symmetry and it is difficult to select reflexions sufficiently strong and sensitive to orientation to be effective.

Alexander: For very thin specimens, the statistical grain size problem is very severe. Appropriate specimen preparation and handling is obviously of importance to smooth out the distribution.

De Wolff: With the appropriate specimen movement, the axis of the distribution can be fixed.

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Conversion of Relative Intensities to an Absolute Scale

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The determination of an absolute scale for X-ray intensities involves the experimental evaluation of a number of constants in the intensity equation whose values are not normally required. The absolute intensities so obtained will not be useful, in the present context, unless the overall accuracy can be maintained at about 1% or better. Some of the difficulties which can occur in making the measurements to the necessary accuracy are discussed.

Introduction

If a Bragg reflection from an ideal powder is measured by scanning a slit through it in the usual way, the integrated intensity, *P*, is related to the structure factor, *F*, by the equation:

$$P=\left(\frac{P_0N^2r_0^2lw\lambda^3}{32\pi R^2\mu\omega}\right)\left(\frac{j(1+k\cos^2 2\theta)}{\sin^2\theta\cos\theta\,(1+k)}\right)(F^2)\,. \tag{1}$$

P_0 is the total power in the primary beam, N the number of unit cells per unit volume, r_0 the classical electron radius, λ the wavelength, l and w the length and width of the receiving slit, R the radius of the spectrometer, μ the linear absorption coefficient, ω the angular velocity of the receiving slit, j the multiplicity, K the polarization ratio of the monochromator ($K=\cos^2 2\theta$ if the monochromator reflects as an ideal mosaic), and θ the Bragg angle. Since the factors in