DIFFUSE SCATTERING AND DISORDER IN CRYSTALS

H. BOYSEN, F. FREY and H. JAGODZINSKI
Institut f. Kristallographie und Mineralogie,
Universitaet Muenchen, 8 Munchen 2, Theresienstr. 41, FRG

I. Diffuse Scattering in Crystals

The so called kinematical theory of diffraction starts with the assumption that the crystal is periodic in space and time. Obviously, all experiments in diffraction use finite crystals which have to be chosen rather small in electron diffraction, but should be pretty large in neutron diffraction. It is this finite size that gives rise to diffuse scattering depending on the radiation used. Very early after the discovery of X-ray diffraction by v. Laue and coworkers it has been recognized that the actual sizes of crystallites scattering coherently is much smaller than the crystal as such. This break down of translational symmetry in space is even more important for the periodicity in time, since the particle size of a phonon is much smaller than the average size of crystallites in the mosaic crystal. This size effect causes a broadening of the line profiles of Bragg-peaks, and determines the line width of the phonon dispersion branches as measured by neutron diffraction or other spectroscopical methods.

Very early experiments in X-ray diffraction showed diffuse scattering, which was correctly interpreted in terms of the thermal motion of atoms. Consequently Debye tried the first theoretical approach to the diffraction problem of thermal motion by assuming independent movements of atoms in space and time. He predicted a decrease in intensities of Bragg-peaks as a function of diffraction angles accompanied by a corresponding increase of a diffuse background scattering. The later introduction of atomic movements correlated in space and time resulted in a more precise description of the diffuse scattering in reciprocal space. For simple substances such as KCl Laval (1939) could show that the thermal diffuse scattering is essentially determined by the low frequency part of the 3 acoustical branches which may be calculated with the aid of the elastic constants. This was indeed one of the first examples using diffuse scattering for the determination of physical properties of crystals.

In 1928 Mauguin observed diffuse layer lines in oscillation photographs of biotite mica, and interpreted them correctly as being caused by disorder without giving the final solution in terms of the well known generalized stacking faults. In the following years more examples of diffuse scattering have been found, but the first attempts of a semi-quantitative or qualitative interpretation have been published independently by Guinier, Hendricks & Teller and Wilson in 1942. Guinier's paper on the Guinier-Preston-zones and their diffuse scattering was an important contribution for understanding the age hardening of alloys, while Hendricks & Teller outlined the diffraction theory of one-dimensionally disordered crystals with interactions of nearest neighbours. Finally Wilson's paper treated the transformation from hexagonal to cubic close packed structures. A qualitative application to Co, mica, clay minerals and others has been given. All the cases mentioned above are characterized by diffuse streaks in reciprocal space. The theoretical solution given by Guinier started with a single two-dimensionally ordered Cu-cluster replacing Al-atoms, while the other three authors constructed the partial partition functions of planar defects entering the diffraction problem.

Obviously, the intensities of diffuse scattering should depend on the difference of the scattering potential between bulk and defect atoms, and they should also be proportional to the concentration of the defects. A periodic array in one (chains) or two (planes) directions leads to a concentration of diffuse scattering into planes (layers) or chains (streaks) in reciprocal space such that the sum of dimensionality of order and diffuse scattering is 3. For this reason the intensity of diffuse scattering is considerably larger for disorder in low dimensions (large defects). A single point defect can hardly be detected using diffraction methods. Consequently a large quantity of
defects is needed which is characterized by its distribution function. Unfortunately, this distribution function cannot be random in most cases because of the strain fields surrounding the defects. Now, the non-periodic parts of the distribution function determine the dimensionality of the diffuse scattering in reciprocal space. It will be shown below that in diffraction strain fields surrounding the defects. Now, the non-periodic parts of the distribution function determine ordered, or a random distribution of defects. The distribution cannot be random in most cases because of the distribution function. Unfortunately, this distribution function cannot be random in most cases because of the dimensionality of the diffuse scattering in reciprocal space. It will be shown below that in diffraction strain fields surrounding the defects. Now, the non-periodic parts of the distribution function determine ordered, or a random distribution or defects. The ordered case may be better described in terms of a modulated structure. Since the distribution function of defects is generally anisotropic the classification in terms of dimensions of the strongly disordered directions seems to be useful for the treatment of diffuse scattering.

Theoretical solutions of the diffraction problem can either be done by constructing the correlation functions of all cell occupations, or by introducing a random distribution of clusters. The latter method is advantageous, if a good approximation is obtained with a few representative clusters and their a priori probabilities. Otherwise the calculation of correlation functions should be tried. Obviously, both methods may lead to complicated formulae, if the number of different cell occupations becomes too large. In order to get a semiquantitative interpretation of diffuse scattering it is often useful to calculate the diffraction of an periodic array of single (averaged) clusters, e.g. domains, distributions of vacancies etc. This means in reciprocal space that each cell is divided into subcells corresponding to the supercell of the periodic array of clusters. As has been shown by Jagodziński et al. (1968), it is possible to try a structure determination with the aid of a convergent set of density and displacement functions (periodic), which are expanded into a Fourier-series. Now, it may easily be shown that the calculation of static and dynamic displacements practically leads to the same diffuse scattering in X-ray diffraction. Therefore, a careful discussion of these displacements may lead to a dynamic interpretation, but normally a unique solution can only be given with the aid of inelastic neutron diffraction. This statement is strongly supported by the following argument. Diffuse scattering caused by lattice defects is at least partially localized, this means that the momentum transfer of the scattered photon (or particle) takes place at least partly onto the defect. Consequently we have to take into account an energy transfer to the defect which in turn gives rise to inelastic scattering. This statement is specifically valid in the case of phase transformations.

In the following the difficulties in measuring and interpreting diffuse intensities will be outlined. Some simple diffraction problems are discussed in order to elucidate the applicability of experimental and theoretical methods to some very different examples of diffuse scattering. Although a quantitative interpretation seems to be difficult, the final results yield much more understanding of the complicated behaviour of crystals than the solution of the ordered structure alone. Both are necessary to clarify the complex correlations between statics and dynamics of crystal structures.

II. Basic Concepts

Type and strength (quality and quantity) of scattering by an assembly of atoms, molecules, ... depend on the interaction of the used radiation with kind and conformation of the single constituents and on the disposition of the scattering centers in space and time described by correlation functions. In particular, diffuse scattering is due to deviations from the identity of originally translational invariant particles and from the long range correlations (in space and time) at least in averaged sense. This includes intramolecular disorder of molecules occupying perfect lattice sites, substitutional disorder, deviations from a perfect spatial arrangement or all together, possibly being time dependent.

Fluctuations of scattering amplitudes corresponding to different scattering centers and/or phase shifts of the scattered waves reduces the maximum capacity of interference (“Bragg reflections”). Nevertheless, the remaining part of scattered waves does also interfere coherently causing a comparably lower and usually not well located “diffuse” scattering. This point gives rise to some confusion in literature; taking as an example a binary alloy (solid solution without any order) one can define a mean (e.g. X-ray-) amplitude: \( f = c_1 f_1 + c_2 f_2 \), where \( c_1 \), \( c_2 \) and \( f_1, f_2 \) are the concentrations and the single scattering amplitudes, respectively. \( f^2 \) determines the Bragg scattering, the difference \( f^2 - P^2 \) (\( P = c_1 f_1^2 + c_2 f_2^2 \)) remains for diffuse scattering. In neutron scattering different isotopes have different scattering amplitudes (“lengths”) usually called \( b \) which is equivalent to \( f \) apart from the sin \( \theta/\lambda \) dependence. Considering an element consisting of two randomly distributed isotopes we have exactly the same formalism in deriving \( b^2 \) and \( b^2 \) which are usually called coherent and incoherent, respectively. The last term, however, is misleading because the isotope scattering is in fact completely coherent, too. To avoid a new terminology and because isotope scattering is not of interest in the context of this article we join the usual terminology. Real incoherent X-ray scattering like fluorescence or Compton scattering remains also out of consideration.

Using the symbol \( h_{\alpha\beta} \) as common for \( f \) and \( b \) the scattered intensity in any kind of problem can be written as proportional to a double differential cross section (per solid angle \( d\Omega \) and energy window \( d(\delta h_{\alpha\beta}) \)):
\[
Q = |Q| = 4\pi \sin \theta /\lambda; \quad S_{\text{coh}}/S_{\text{inc}} \quad \text{are the coherent/incoherent scattering functions, respectively, which contain all the information about the sample.}
\]

The other factors characterize the interaction \((b_{\text{coh}}, b_{\text{inc}})\) and the used radiation \((k_f, k_i)\) which correspond to the space-time-pair correlation function \(G(r, t)\) and refers to scattering by one and the same particle at different times. It provides a lot of information about the movement of an individual particle (e.g. translational or rotational diffusion processes) and gives in some respect complementary results to the analysis of the coherent scattering. A discussion is beyond the scope of this article.

Coming back exclusively to the first part of (1) all subscripts "coh" are omitted hereafter - we find by Fourier transformation to the self-correlation function \(G(r, t)\) and refers to scattering by one and the same particle at different times. It provides a lot of information about the movement of an individual particle (e.g. translational or rotational diffusion processes) and gives in some respect complementary results to the analysis of the coherent scattering. A discussion is beyond the scope of this article.

Rewriting formula (3) into a form more familiar for X-ray people one gets:

\[
\frac{d\sigma}{d\Omega} = \sum_{m=1}^{M} \sum_{n=1}^{M} b_m^* b_n e^{iQ(r_m - r_n)}
\]

\(M\) denotes the total number of atoms, \(r_m, r_n, r_r\) are an arbitrary vector in real space, a basic lattice vector and a vector related to the origin of a cell, respectively \((r_m = r_n + r_r)\). With the structure factor \(F_r = \sum b_k e^{iQr}\), (4) can be written as:

\[
\frac{d\sigma}{d\Omega} = \sum_{n=1}^{N} \sum_{n'=1}^{N} F_n^* F_{n'} e^{iQ(r_n - r_{n'})}
\]

In a static disorder problem one has to average over all cells \(N\), i.e. \(F_n^* F_{n'}\) will be replaced by \(F_n^* F_{n'}^*\). When the defects show no long range order \(F_n\) and \(F_{n'}\) are independent except for \(\Delta r = (r_n - r_{n'})\) being small (short range order only). Therefore one can write:

\[
F_n - F_{n'}^* = F_n - F_{n'}^* = |F|^2 \quad \text{for large } \Delta r
\]

\[
\frac{d\sigma}{d\Omega} \sum_{n,n'} \sum_{n,n'} |F|^2 e^{iQ(r_n - r_{n'})} + \sum_{n,n'} (F_n^* F_{n'} - |F|^2) e^{iQ(r_n - r_{n'})}
\]

The first part in (6) refers to all cells and produces therefore sharp Bragg reflections with intensity proportional to \(|F|^4\). Because relatively few neighbours contribute to constructive interferences in the second term this scattering is diffuse. In case of complete disorder this second part reduces to a sum over \(n = n'\) or \(I_{\text{diff}} = N |(F)^2 - |F|^2|\). The general formula (6) is valid for all kinds of time averaged problems. The general way is to evaluate from a disorder model \(|F|^2\) and \(|F|^2\) and compare these with measured diffuse intensities by least squares methods. The reverse way ("Fourier method"), carried out in Patterson space, is much more cumbersome.

The general behaviour of the TDS will be described in the lowest approximation by:

\[
I_{\text{diff}} \geq N \sum_{k} b_k^2 |1 - e^{-2\beta_k \cos(\theta/\lambda^2)}|
\]

where \(\beta_k\) denotes the temperature factor. Formula (7) describes a continuous isotropic scattering which increases with scattering angle. In practice it is difficult to extract information about thermal parameters from the diffuse background, this can easier be done by analysis of the Debye-Waller factors affecting the Bragg peaks. As a result of a more rigorous lattice
dynamical treatment one derives expressions for the TDS which usually are called phonon scattering. By the interaction of the incident radiation with the vibrations of the whole crystal lattice one or more energy quanta (phonons) can be exchanged. Separating one specific lattice wave (direction $\mathbf{q}$, wavelength $A = \frac{1}{|\mathbf{q}|}$, frequency $\omega$, displacement direction of a vibrating atom $\mathbf{e}(0)$) the scattered intensity in the high temperature approximation is given by:

$$ I_{1PH} = \frac{1}{V_c} \sum_{k} \left| F_{dyn} \right|^2 \delta(Q - H \pm \mathbf{q}) $$

(8)

where:

$$ F_{dyn} = \sum_{k} \frac{b_k}{\sqrt{m_k}} e^{-\frac{2\pi\hbar^2}{\alpha^2}(Q \cdot \mathbf{e})} e^{\mathbf{H} \cdot \mathbf{r}_k} $$

(9)

($H$ is a reciprocal lattice vector, $m_k$ the mass of the $k$th atom). This scattering by one wave is exactly located at points $\pm \mathbf{q}$ around each reciprocal lattice point and is fully coherent. Because generally not only one wave, but many waves with different values $q_1, \ldots$ are excited, this scattering becomes diffuse in an X-ray pattern or in a (two axes) neutron diffractometer recording. As can be seen from (8) and (9) the intensity of TDS is determined by three essential factors: the Debye-Waller factor takes care of the intensity reduction due to the roughening of the crystal lattice by all the other lattice modes; the $1/\alpha^2$ term is responsible for the enhanced TDS due to low frequency modes, e.g. the long wavelength acoustic modes around the Bragg peaks; the scalar product $(Q \cdot \mathbf{e})$ dominates the observability of satellite scattering similar to the extinction rules in conventional structure analysis. Although static modulation wave(s) in a crystal may be of completely different origin the points mentioned above are still valid (except for the $1/\alpha^2$ term). In case of domains a crystal may be visualized as modulated by a rectangular wave. In consequence, satellite scattering of higher order may occur, which is, most frequently, diffuse due to the limited size of domains and due to (static) fluctuations of the domain distribution. The analysis of this pattern requires very accurate measurements of position, width, integrated intensity and background of the subsidiary peaks. Because X-ray pictures cannot decide between elastic or inelastic nature of a satellite, additional experiments (with neutrons) are needed to determine whether $\omega = 0$ or not. A temperature dependence of diffuse scattering, however, is generally not decisive with respect to a static or a dynamic origin of a modulation.

Some new aspects are related to the so called plastically crystalline state which refers to orientational disorder of molecules in a crystal. Diffuse scattering may arise due to static orientational disorder or only local order between different orientational states which can be treated in frame of the general formalism (6) or due to thermal motions. Apart from the normal modes mentioned above, transitions between the different states may occur by statistical diffusion like jumps. This behaviour can be analysed by observation of quasielastic neutron scattering.

When crystals undergo transitions between different states of order (here, for example, a transition between a completely orientational disorder to a state with preferred orientations, there may arise a critical increase of diffuse scattering very close to the transition point due to preceding large fluctuations. In conclusion it should be mentioned that the separate discussion of static and thermal disorder in frame of classical lattice dynamics is an approximation only. Any defect modifies vibrational frequencies and displacement patterns. This problem becomes very complicated in case of cooperating defects where new phenomena like localized states occur. A discussion of this topic goes far beyond the scope of this article.

### III. Methods

Regarding the main characteristics of diffuse scattering

- weak in comparison with Bragg scattering
- anisotropically and inhomogeneously distributed in reciprocal space
- elastic, inelastic or quasielastic in origin

frequently related to more than one structural element

special care has to be taken on the following points:

1. type of experiment: X-rays-neutrons (or other)

2. strong sources

3. best choice of wavelength

4. monochromatic, focusing techniques

5. sample environment and background reduction

6. resolution, scanning procedure and data analysis:

these points will be considered separately in sec. IV.

Starting an investigation of a disorder problem by analysis of the diffuse scattering an overall picture should first be recorded by X-ray diffraction experiments; several sections through reciprocal space help to define the problem. For this film methods are preferable: cameras with relatively short distances crystal–film avoid long exposure times. Unfortunately there are some disorder problems which cannot be attacked with X-ray methods. X-rays are rather insensitive to elucidate disorder problems, where hydrogen atoms are involved, light in presence of heavy atoms play the dominant role, or when the disorder is intimately related to elements differing only scarcely in X-ray scattering amplitudes (e.g. AI/Si/Mg). In these cases neutrons have to be used at an early stage.
Suspecting a remarkable part of the diffuse scattering not to be of static origin concomitant purely elastic, inelastic or quasielastic neutron experiments have to be planned from the very beginning.

Because the diffuse scattering is usually very weak, strong radiation sources are needed, whereas the background level should be as low as possible at the same time. Coming to the background problem latter on some short remarks should be done on the sources. Even a normal modern X-ray tube is a stronger source than a reactor with the highest available flux. For this reason most experimental work which can be done with X-rays should be done. Generally the characteristic spectrum will be used, but there are special applications, where the white spectrum is of interest (see below). With view on rotating anodes one should not only keep in mind the power, but also the flux density, because there is little merit from a broad focus in diffuse scattering work. One can suppose that also synchrotron sources will play an important role in this type of research in the near future.

Comparing film and diffractometer (X-ray) methods, film techniques are highly recommended at an early stage. Diffractometer scans should be carried out after a careful analysis of the overall distribution of diffuse intensity in reciprocal space. In case of powder diffractometer experiments, for example, preferred orientations/textures could lead to a complete mis-identification of the problem. Single crystal experiments are preferable in some respect, because diffuse phenomena in a powder diagram may be analysed only after having got an idea about the disorder and only in special cases (see sec. VIh). Nevertheless powder investigations give quick supporting information (e.g., superlattice peaks, split reflections, lattice strains, domain size effect, ...).

Before starting an experiment of any kind one should specify the best adapted wavelength. This is important, firstly, with respect to the problem to be solved: e.g., point defects cause diffuse scattering falling off with increasing Q, short range ordering between clusters show broad peaks corresponding to large d-spacings, lattice relaxation processes induce a broadening of the interferences (Huang-scattering) and (static) modulation waves with long periods give rise to satellite scattering close to the Bragg peaks. In all these cases a long wavelength is preferable. On the other hand, if diffuse phenomena are structured in a sense that broad peaks are observable up to high Q-values or diffuse streaks/planes have to be recorded up to high Q in order to decide between different models, a short wavelength is needed. The choice of wavelengths secondly affects the accuracy with which an experiment can be carried out: generally, experiments with shorter wavelengths have lower angular ($\Delta Q$) and energy resolution. Thirdly, special attention must be paid to absorption phenomena, in particular, when an absorption edge of an element is close to the used wavelength. Strong fluorescence scattering may completely obscure weak diffuse scattering phenomena. The generally lower absorption of neutrons of any wavelength makes absolute measurements easier than with X-rays. Further the use of longer wavelengths is advantageous, when main contributions can be recorded with wavelengths exceeding the Bragg cut-off $Q = 2d_{\text{max}}$ of the sample. Then a "contamination" by Bragg-scattering can be avoided. The aspect of long wavelengths is also profitable from another point: the contribution of the TDS increases with Q. Thus, if most of a static diffuse intensity can be observed within the first reciprocal cell(s) the TDS becomes very small.

Highly monochromatic radiation should be used in order to eliminate broadening effects due to the wavelength spread. Focusing monochromators help to overcome a lack of luminosity. Moreover, a focusing technique, in particular, a focusing camera geometry is very helpful for deciding between geometrical broadening and "true" diffuseness. We cannot give a comprehensive listing of all useful focusing techniques which can be found in the literature. We just like to mention a method, which is used with good success in our laboratory. In the monochromatic convergent beam the sample is placed with its selected axis lying in the scattering plane. The specimen is fully embedded in the incident beam, which is focused onto the film (Jagodzinski, 1968). By this procedure the influence of the sample size will be suppressed. E.g., in an oscillation photograph a high resolution perpendicular to diffuse layer lines may thus be achieved (cf. sec. V). Frequently used in recent times are standing crystal techniques in combination with monochromatic radiation. By the so called monochromatic Laue-technique or the focusing Noromosic-technique (Jagodzinski & Korekawa, 1973) heavily overexposed photographs—with respect to Bragg scattering—allow for sampling of diffuse intensity, if a crystal is oriented in such a way that there is a well defined section between the Ewald sphere and the diffuse phenomenon under consideration. By putting together single Noromosic photographs standing Weissenberg patterns can be simulated.

A serious and important problem is the careful suppression of the background. Incoherent background scattering being an inherent property of the sample occurs as continuous blackening in case of fluorescence, as scattering at high 20-angles due to Compton scattering, or as "incoherent" inelastic effects. Protecting the film by a thin Al or Ni foil is of some help against fluorescence, but attenuates the diffuse intensity also. Scratching the film emulsion after the exposure from the "front" side of the film is another possibility to reduce the relative amount of the lower energetic fluorescence radiation. Obviously,
energy dispersive counter methods are highly efficient in this case. Air scattering produces a background at low 2θ angles. Evacuation or controlled atmosphere studies need a chamber which in turn gives rise to new spurious scattering. This problem is less serious in neutron work. Mounting of a specimen e.g. on a silica fiber with cement, not well aligned collimators or beam catchers are further "sources". Sometimes a specimen has to be enclosed in an (usually silica glass-) capillary which will always be hit by the incident X-ray beam. Careful and tedious experimental work is necessary in case of low and high temperature investigations which have to be carried out in many disorder problems. Whereas the experimental situation is again less serious in neutron scattering, there are big problems with scattering from walls and containers in X-ray work. Most of the X-ray investigations have therefore been made on quenched samples. Because TDS is dominating at high temperatures, also in presence of a static disorder problem, the quantitative separation can hardly be done in case of a high instrumental background. Calculation and subtraction of the TDS is in principle possible, but very difficult in practice. Recent developments of low- and high-temperature X-ray equipment in our laboratory took special care of the background problem (Adlhart & Huber, 1982; Adlhart et al., 1982).

For quantitative measurements of diffuse intensities diffractometer recording or microdensitometer scanning of photographs are common methods. The scanning direction in either case must be well adapted to the anisotropy of the diffuse phenomenon. Valuable developments with view on diffuse scattering work are linear and area detectors for X-ray and neutron instruments which are commercially available now. Typical inelastic neutron machines are spectrometers which allow for an energy analysis of the diffuse scattered neutrons. Most famous are the so called "Three Axes Spectrometers" (TAS) where the analysis is accomplished by variation of the glancing angle of an "analyser crystal".

A very recent development concerns the use of anomalous X-ray scattering if radiation with a wavelength close to an absorption edge of an element involved in a disorder problem is used. As in case of conventional structural work the corrections to the form factor $f$ may help to identify and separate a specific "marked" atom or cluster of atoms in a surrounding matrix. Currently under progress in our laboratory is, for example, a study of precipitations. Scanning over a diffuse streak with different wavelengths could reveal an anomalous variation of the diffuse intensity. In this type of experiments a strong source with tunable wavelength band is needed.

Finally one should mention a classical method of detecting diffuse intensity at low angles: the small angle scattering technique. This well established method allows for the determination of the characteristics of clusters, polymers,... etc. like volume, molecular weight, conformation,... In recent years this technique also a field of neutron scattering was remarkably improved and used for the study of biological substances and kinetic problems.

**IV. Data Analysis**

A tentative disorder model can often be guessed from the characteristic features of the diffuse scattering regarding also results from chemical and physical considerations. For a more definite decision a quantitative comparison between calculated and observed intensities is essential, which also serves to derive the magnitudes of the inherent model parameters.

A careful analysis of the data requires the knowledge of the instrumental resolution, which depends on the scattering angle 2θ and implies intensity corrections analogous to the Lorentz factor used in the determination of a structure from the (sharp) Bragg reflections. Resolution is most conveniently described by the resolution function $R(Q - Q_0)$, which is defined as the probability of detecting a photon or neutron with momentum transfer $hQ = h(k - k_0)$ when the instrument is set to measure $Q_0$. $R$ depends on the various collimations, mosaic spreads and the spectral distribution of the source, which are indicated in a schematic drawing of a diffractometer in Fig. 1. If photographic techniques are used, the detector aperture is controlled by the slit width of the densitometer. The form of $R$ is very well known for neutrons and given by Cooper & Nathans (1968a):

$$R(Q - Q_0) = R_0 \exp \left\{ -\frac{1}{2} \sum_{j=1}^{3} \sum_{i=1}^{3} M_{ij} A Q_j A Q_i \right\} \tag{10}$$

![Schematic arrangement of a two axes diffractometer](image)

Fig. 1. Schematic arrangement of a two axes diffractometer. $\eta_0$ and $\eta_{0w}$ denote horizontal/vertical divergences of the collimators and mosaic spreads of the monochromator and the sample, respectively. $\eta_s$ the spectral width of the source.
where Gaussians are assumed for the mosaic distributions and transmission functions leading to expressions for the coefficients $R_o$ and $M_{\omega}$. Although this should be modified to some extent for X-rays the main features for our purposes can be derived by this Gaussian approximation too. $R$ may either be obtained from known divergences or by Bragg peaks (see eq. (11): $d\sigma/d\Omega \to d\sigma(Q-H)$). A normalization with the Bragg peaks is also useful in order to put the diffuse scattering on an absolute scale.

a) Single crystals

The measured intensity is given by the convolution

$$I(Q_0) = \varphi_0 \int d\sigma(Q) \cdot R(Q-Q_0) d^3Q$$  \hspace{1cm} (11)

where $\varphi_0$ is the incident flux on the monochromator. For dynamical disorder the cross section depends also on energy, i.e. there is an additional integration over energy (see eq. (11)), which deserves special attention in the case of neutrons (Cooper & Nathans 1967; Schrader & Boysen, 1984). In general the intensity has to be calculated from (11). In practice, however, some important simplifications can be made, if $d\sigma/d\Omega$ is either very sharp or very broad compared to $R$, i.e. for Bragg peaks, sharp streaks, planes or extended 3-dim. diffuse peaks. In the latter case $d\sigma/d\Omega$ can be taken out of the integral (11). Thus the corresponding "Lorentz factor" is independent of $2\theta$:

$$L_1 = 1$$  \hspace{1cm} (12)

For diffuse planes (in the scattering plane) of very small width it follows

$$L_2 = 1/\sqrt{\beta_1^2 + \beta_2^2 + \eta^2} \cdot \sin^2 \theta$$  \hspace{1cm} (13)

where $\beta_1$ is the effective vertical divergence before the sample, which depends on $\beta_0$, $\beta_1$ and $\eta_1$, but is independent of $2\theta$. By using large vertical divergences ($\beta_1 > \eta_1$), $L_2$ can be kept nearly constant. On a (sharp) diffuse streak the intensity variation is approximately:

$$L_3 = L_2/\sqrt{\beta_1^2 + \eta^2} \cdot \cos^2 \psi \cdot \sin^2 \theta + 4 \eta^2 \cdot \sin^2 \theta \cdot \sin^2 \psi + \alpha_1^2 \sin^2 \theta(\theta + \psi) + \alpha_2^2 \sin^2 \theta(\psi - \theta)^{1.2}$$  \hspace{1cm} (14)

where $\alpha_2$ is the effective horizontal divergence before the sample and $\psi$ is the angle between the scattering vector $Q_0$ and the streak. (14) only applies for characteristic X-ray radiation ($h_0$ small). Otherwise (e.g. white spectrum) a more complicated formula holds. If a TAS is used, $\alpha_2$ and $\beta_2$ have to be replaced by the effective collimations after the sample due to the analyser part. It is clear, however, that in any case a detailed knowledge of all instrumental parameters is needed for an exact evaluation.

Therefore, in order to extract the disorder cross section (and hence the structure factor) it is recommended to use integrated intensities from scans perpendicular to the streak or plane. Then for diffuse planes $L_2^2 = 1$ (13) and for streaks $L_2^2 = L_2$ (14'), which again can be made approximately constant for large $\beta_1$'s. For other scan directions $L^2 = L^2/\sin \alpha$, where $\alpha$ is the angle between the scan direction and the streaks. Since in an usual measurement the integration is done on an angle $\Delta \omega$ via a general $\Delta \omega$: $\mu:\pm 2\theta$ scan, an additional correction factor

$$\Delta \omega/\Delta Q_0 = \sin(\beta + 0)/\kappa \cdot \sin 2\theta$$  \hspace{1cm} (15)

arises, where $\beta$ is the angle between $Q_0$ and the scan direction $\mathbf{Q}_0$ and $g = (\tan \beta + \tan 0)/2 \cdot \tan 0$. For the most frequently used $\omega$- and $1:2$-scans $\beta = 90^\circ$ and $0^\circ$, respectively.

However, in order to optimize an experiment the scan direction and also the instrumental collimations should be carefully chosen according to the problem in question. If, e.g. the variation of $d\sigma/d\Omega$ is appreciable along a streak, the resolution should be kept narrow in one direction (but may be relaxed in the other to gain intensity) and the scans be performed perpendicular to that direction. On the other hand, if the variation is smooth, the sharpest signal is measured by a scan perpendicular to the streak. In any case a good knowledge of the resolution and its variation with $2\theta$ is helpful. More thorough treatments of resolution are given by Cooper & Nathans (1968a, b) and Izumi (1973) and applied to diffuse peaks by Yessik et al. (1973) and to diffuse streaks and planes by Boysen & Adlhart (1983).

b) Powders

In polycrystalline samples the intensity has to be averaged over all orientations:

$$I(Q_0) = n/4\pi Q_0^2 \cdot \int I(Q) \cdot d(Q) \cdot d^3Q$$  \hspace{1cm} (16)

where $n$ is the number of crystallites. This leads to characteristic modulations of the background according to the dimensionality of the disorder. Although only in very simple cases a model can be obtained from a powder pattern alone, the refinement of a known disorder model can be favourably done with powders, e.g. to follow the temperature dependence or to use neutrons, when no large single crystals are available. A detailed analysis is given by Yessik et al. (1973) for diffuse peaks and by Boysen (1981) for streaks and planes. Quite generally the intensity may be written as

$$I_n(Q_0) = P \cdot \sum \{m(t)A_n \cdot 1/Q_0^2 \cdot \phi_d(Q_0, t)$$  \hspace{1cm} (17)

The index $n$ denotes the dimensionality of the disorder, $t$ is the (shortest) distance from the origin, $m(t)$ the corresponding multiplicity, $A_n$ contains the struc-
ture factor, $P$ the instrumental luminosity and $\phi_n$ describes the characteristic modulation. Assuming Gaussian line shapes of width $D$ for the narrow direction(s):

\[
\phi_0 = \frac{1}{\sqrt{2\pi(M^2 + D^2)}} \exp\left\{-\frac{(Q_0 - \tau)^2}{2(M^2 + D^2)}\right\}
\]

(18a)

\[
\phi_1 = \frac{1}{\sqrt{2\pi(M^2 + D^2)}} \times \int \exp\left\{-\frac{(Q_0 - \sqrt{\tau^2 + q^2})^2}{2(M^2 + D^2)}\right\} dq
\]

(18b)

\[
\phi_2 = \pi Q_0 \left[1 - \text{erf}\left\{(\tau - Q_0)/\sqrt{2(M^2 + D^2)}\right\}\right] + \sqrt{2\pi(M^2 + D^2)} \cdot \exp\left\{-\frac{(Q - \tau)^2}{2(M^2 + D^2)}\right\}
\]

(18c)

The integral in (18b) has to be evaluated numerically. $M$ is connected with the well known dependence of the fwhm of the Bragg peaks $A_{1/2} = U \cdot \sin^2 \theta + V \cdot \cos \theta + W$ (Caglioti et al., 1958) by $M^2 = A_{1/2}^2 (4k + Q_0^2)/32 \cdot \ln 2$. In the case of extended 3-dim. diffuse peaks only the variation $\sim 1/Q_0^2$ remains, i.e. $L_0^2 = 1/\sin^2 \theta$. The characteristic functions $\phi_0$, $\phi_1$, $\phi_2$ are compared in Fig. 2 for equal values of $\tau$ and $D$. Note the difference in the peak shifts and the high angle tails. It should be mentioned that the diffuse intensity relative to a Bragg peak is much larger for powders than for single crystals. Besides, a powder pattern always contains in principle all the information about the sample and might thus induce more thorough single crystal investigations.

Of course the usual corrections for absorption and polarization have to be included in any quantitative analysis, while extinction is mostly negligible. As mentioned in III, the background should be reduced as far as possible. Remaining contributions like incoherent and multiple scattering all vary only slowly with $2\theta$ and can be subtracted by linear interpolation or fitting a smooth curve, or even calculated quantitatively and then subtracted. An empty scan can take care of the instrumental background.

V. Examples

In the last section we present a few examples taken from work carried out in our laboratory, which provide different types of diffuse scattering and, in consequence, different types of disorder. They give a good picture of the various concepts and methods discussed before.

a) $E_2P_1,_{1.6}$

The title compound, $(C_{10}H_{10}N_2)_{1.6}$, consists of a tetragonal framework built by columnar stacks of $E_2P$ molecules, where channels in one direction are left open. In these channels iodine chains are embedded. As found earlier by Endres et al. (1979) the $c$-periods along the unique $c$-axis of the organic matrix and of the chains, are incommensurate with each other at least at room temperature. Disorder phenomena are caused by weak interactions between the

![Fig. 2. Characteristic line shapes of diffuse peaks, streaks, and planes in powder diagrams.](image-url)
iodine chains and between the host structure and the chains. These interactions become stronger with decreasing temperature. Equidistant continuous diffuse planes perpendicular to the c-axis (Fig. 3a) indicated a nearly uncorrelated 1-dim. iodine sublattice. Main structural elements are \( I_3 \) units as can be deduced from the relatively intense 3th, 6th, 9th, ... diffuse layer lines. The statistics which govern the distribution of the I atoms along \( c \) can be determined by a quantitative intensity analysis of the diffuse lines. Therefore, high quality X-ray patterns were taken in a temperature range from 123 to 333 K by the monochromatic focusing Noromosic technique. Using the equi-inclination method the X-rays can be focused on the zeroth and the tenth layer simultaneously thus providing a weak and smooth variation of the resolution volume in reciprocal space. Digital intensity data of the diffuse sheets were then recorded by scanning across the layer lines with a microdensitometer (Fig. 3b). To compare intensity profiles with interference functions due to different models, several careful corrections have to be made: lateral short-range order modulations not mentioned so far have to be averaged out; the intensity must be corrected for the influence of form factor and temperature factor dependence, for absorption and for background; convolution with a normalized resolution function which was determined by measuring Bragg reflections, takes care of instrumental effects. For a more detailed description see Rosshirt et al. (1984). By least squares methods the calculated intensity profiles for three different 1-dim. liquid models were compared with the measured and corrected data. Depending on the particular model 9 or 8 parameters including 3 instrumental parameters were refined. As a result we found a clear decision in favour of an asymmetric distribution function of next nearest \( I_1 \) molecules which is intermediate between a classical Zernike-Prins model and a symmetric Gaussian function. As function of temperature one can determine mean distances and mean square deviations indicating that the binding forces between the iodines within the chains are stronger than v.d. Waals forces and partially of metallic type. We do not want to give here a full description of this problem, but only show that the interpretation of diffuse intensity profiles provides very detailed information. It should not be concealed, however, that the order/disorder problem even in this simple compound is much more difficult: along the chain direction doubled and sixfold superperiods exist as indicated by satellite lattice layers: the organic matrix shows a fourfold superperiod along \( c \); lateral correlations of short range type via interactions host-chain exist. The solution of the disorder problem as a whole must be found step by step.

\( b) \ CuNSal \)

An example of a disorder problem where satellite and diffuse scattering are intimately connected with one another, both being strongly temperature dependent in addition, provides the compound \( \alpha \) CuNSal, \( Cu(C\cdot H\cdot N\cdot O\cdot Z) \) (Adlhart et al., 1982). This substance undergoes two phase transitions at \( T_1 = 305 K \) (2nd order) and \( T_2 = 241 K \) (1st order), respectively. Above \( T_1 \), in the orthorhombic phase 1, there is a remarkable diffuse streaking in directions parallel \( a^* \) through Bragg reflections with \( l \neq 0 \) (Fig. 4a). This diffuse scattering increases in intensity approaching \( T_1 \) from above. At \( T_1 \) satellites occur at positions \( q = (0.3 \ 0 \ 0) \) again only in sheets with \( l \neq 0 \) (Fig. 4b). These phenomena can be understood by a displacement disorder involving transversal waves with displacement vectors \( e \) parallel to \( c \) (cf. eq. (9)) and increasing amplitudes for \( T \rightarrow T_1 \). At \( T_1 \) one wave with \( A \sim 3 \ a \) condenses. By further cooling (a) the intensity of the satellites increases considerably indicating larger amplitudes of the modulation wave, and (b) below 260 K the satellite positions are shifted continuously to lower \( q \)-values and, simultaneously, (c) the satellite reflections are broadened. That means, approaching the second transition point from above

![Fig. 4a. Selected area of a \( h02 \) normal beam Weissenberg photograph of CuNSal taken at 323 K, CuK\( \alpha \) radiation, 6kW Rigaku rotating anode (from ref. Adlhart et al., 1982 a).](image-url)

![Fig. 4b. Equivalent photograph to Fig. 4a taken at 253 K](image-url)
the modulation wavelength becomes continuously larger indicating an incommensurately modulated structure (phase II) where the correlation length of this modulation decreases. A more detailed analysis shows that the displacement pattern of the modulation is a precursor of the monoclinic structure below 241 K (phase III). In phase III satellite and diffuse scattering vanish completely. Quantitative measurements by diffractometer recording reveal relatively more intense diffuse scattering around the satellites (in phase II) which excludes "normal" TDS being responsible. Normal acoustic lattice modes (\(q \rightarrow 0\) for \(q \rightarrow 0\)) cause diffuse intensity contributions which are approximately proportional to the intensity of the accompanying reflections. A possible explanation for this behaviour are phase fluctuations of the static displacement wave, which produce strong additional diffuse scattering at the satellite positions only. This interpretation, however, is basically due to dynamical excitations, which might be wrong because only X-ray pictures are available. Looking carefully on Fig. 4b also satellites of second order at \(\pm 2q_0\) are observable. By comparing intensities of satellite scattering of first and second order, respectively, with the intensity of main reflections, one can try to decide whether the satellites of 2nd order are diffraction harmonics of a sinusoidal modulated structure only, or anharmonicity effects are responsible. In the latter case deviations of the sinusoidally modulated structure exist towards a more box-like or trapezoidal shape. A clear cut decision could not be done so far. This example shows how various methods, film- and counter techniques, qualitative and quantitative measurements of diffuse streaks and diffuse satellite scattering can be helpful in analysing an ordering problem to a high extent. It shows also, however, that for definite conclusions a neutron experiment would be needed to prove the dynamic character if the picture is correct. Unfortunately this question remained open because the sample material at hand is too small, or in other words, the neutron sources are too weak.

c) \(Ti_{0.8}Sn_{0.2}O_x\)-mixed crystals

Exsolution phenomena are frequently observed in rock forming minerals such as feldspars, pyroxenes, spinels, garnets, rutile and many others. It is well known that the exsolution behaviour depends widely on the prehistory of the minerals, e.g. lunar pyroxenes show a completely different diffuse diffraction pattern than terrestrial ones. Consequently, the diffuse diffraction during exsolution processes may be used as an additional source of information in order to elucidate the prehistory of rocks. Although single crystal work yields more precise information on diffuse scattering, it is often useful to first study the powder pattern. Unfortunately the number of papers studying diffuse scattering of rock forming minerals quantitatively is very small for experimental reasons. Hence we have to discuss this problem with an early paper by Dorner & Jagodzinski (1972) as a simple example.

Exsolution of SnO<sub>2</sub> in rutile TiO<sub>2</sub> has been studied at 1073 K under various pressure conditions 1-3000 kbar and in presence of and without water. For sake of brevity let us restrict here to the exsolution process under normal conditions (1 bar, dry atmosphere). TiO<sub>2</sub> and SnO<sub>2</sub> are isotypic (tetragonal) with slightly different lattice constants. The larger Sn-ion causes an increase of \(a\) (+0.143 Å) and \(c\) (+0.25 Å), respectively. As has been shown by an electron-microscopical study by Stubican & Schultz (1968) there is a lamellar exsolution parallel (001) with an increase of the lamellae-thickness as function of the heat treatment. Fig. 5 shows a series of diffraction-patterns of Ti<sub>0.8</sub>Sn<sub>0.2</sub>O<sub>x</sub> as function of tempering time. The powder quenched to room temperature (Fig. 5a) shows the normal diffraction pattern of an ideal mixed crystal. After a heat treatment of \(2\) h at 1073 K an increase of the diffuse background and a broadening of the (101), (111), (211) reflections can clearly be seen (Fig. 5b), while (110), (200), (210), (220) do not show this effect. From this observation we may conclude that small platelets of SnO<sub>2</sub> are integrigrow with TiO<sub>2</sub> with a congruent plane of intergrowth. Furthermore, a fluctuation of \(c\)-lattice-constants between exsolved SnO<sub>2</sub> and the host takes place, and causes the broadening of all reflections with \(I \neq 0\). After a heat treatment of \(3\) h no change in the width of the \((hk0)\)-reflections could be observed, but there was a distinct splitting of \((hk1)\)-reflections (Fig. 5c), which has been explained in terms of a modulated structured by Stubican & Schultz (1968).

In contrast to this finding a careful study of a high precision photometer record revealed that the "side bands" demanded by these authors are nothing else than the \((hk1)\)-reflections of two types of lamellae accompanying the reflection of the original mixed crystal. This statement is confirmed by the obser-

Fig. 5. Powder diffraction patterns (high resolution densitometer records) of Ti<sub>0.8</sub>Sn<sub>0.2</sub>O<sub>x</sub> annealed at 1073 K; Figs. 1 e correspond to the different annealing times (from above).
vation of a rapid decrease in intensity of this peak with annealing time (Fig. 5d, e). Obviously, there is a large activation energy for forming nuclei of SnO₂ platelets. Once this process has been started the crystallite transforms rapidly. After a heat treatment of 48 h (Fig. 5d) the reflections due to the original mixed crystal, also still visible, have become very weak. Annealing for 144 h (Fig. 5e) shows the end of this preliminary exsolution process. The (100)-reflection, however, shows first signs of the beginning splitting indicating the breakdown of the congruent plane of intergrowth of the two phases. At this stage we have the beginning of the separation of two stable phases. All structural processes observed before represent precipitation or "spinodal decomposition" as they are called by many authors.

From the theoretical point of view the calculation of diffracted intensities may easily be done for the case of congruent planes of intergrowth. Here we have two strictly ordered directions within this plane, and the formulae for 1-dim. disordered crystals can be applied. This was done (Dorner & Jagodzinski, 1972) by introducing a priori-probabilities \((1-x₁)\), \((1-x₂)\) of neighbouring pairs of Sn- and Ti layers. The propagation of order was calculated with the aid of the well known matrix formalism. Furthermore, the authors introduced a phase shift factor taking into account the two different lattice constants of the lamellae. Another important variable in their calculation was the chemical composition of the two types of lamellae which need not meet the compositions of the stable phases at 1073 K. All experimental data were analysed applying a similar procedure as described in sec. IV. The refinement has been done with a special method which cannot be explained here, but it should be pointed out that the agreement between experimental and theoretical curves was excellent. Figure 6 shows a typical example. A major difficulty was the subtraction of the central peak of each reflection group which belongs to virgin crystallites, and cannot be included in the theoretical calculation. The reflection groups (101) and (201) were used for comparison, both groups yielded the same parameters. Differences were observed for short and very long annealing times. This is in agreement with the expectation that the theory of lamellar intergrowth cannot be applied in these limits. Figure 7 shows the increase in thicknesses and chemical compositions of the two types of lamellae as function of annealing time. Surprisingly the purity of both lamellae decreases with annealing time. This strange behaviour may be explained in terms of a balance between the free energies of the volumes and the interfaces of the lamellae.

d) Quartz:

An example of purely dynamical disorder, which has been investigated with (neutron) power diffraction, is given in \(β\)-quartz. With X-rays a system of diffuse streaks running along \([\overline{2}00]\)-directions has been observed by Arnold (1965) (Fig. 8) and interpreted as statistical displacements of Si-O-Si-O-... chains along \(\{001\}\) cooperating in \(\{100\}\) planes. Inelastic neutron scattering experiments by Bauer et al. (1971) revealed its dynamic character. A flat dispersion branch between \(E\) and \(M\) \((=\{300\}\)-direction) softens in energy while approaching the \(x\) \(β\)-transition from below. The diffuse scattering was further studied by integral and elastic neutron powder diffraction (two- and three axes configuration of the instrument, respectively) at higher temperatures up to 1073 K in the \(β\)-phase by Schrader & Boysen (1984) showing that the intensity is essentially independent of temperature and remains of inelastic origin. For a quantitative analysis the dynamic structure factor \(S\) of the corresponding modes has to be calculated, which requires the knowledge of the eigenvectors \(e\)
along the whole $\Gamma-M$-direction. Just above the transition temperature 846 K it has been determined from single crystal inelastic neutron scattering by Boysen et al. (1980) at the Brillouin zone boundary ($M$-point). It may be described as a cooperative rotation of (nearly rigid) SiO$_2$-tetrahedra in Si–O–Si ... chains around axes parallel to [100], while the phase is reversed in adjacent (100) planes. The individual displacements of the atoms in this mode are shown in Fig. 9. By fitting the diffuse background of the powder diagrams a clear distinction could be made between two possible models. An example is shown in Fig. 10, where the Bragg peaks have been removed by fitting them with the static (averaged) structure and subtracting the calculated pattern. Here the characteristic line shape of a diffuse streak in powders as discussed in sec. IV (Fig. 2) is obscured by the superposition of many (41) different streaks. The correct eigenvector has the same displacement pattern along the whole streak within one chain (cooperative in (100) planes) as at the $M$-point, while the phase between adjacent (100) planes changes from 0 to 180$^\circ$ between $\Gamma$ and $M$. The width of the streaks is determined by the (steep) dispersion perpendicular to [100], which is also independent of temperature in the $\beta$-phase.

From these results it is concluded that (100) planes are dynamically decoupled on a unit cell scale, which supports a disorder model of $\beta$-quartz as a space and time average of fluctuating $x_1$, $x_2$-microdomains (Dauphine twins) separated by (100) interfaces, in which the ideal $\beta$-structure is realised.

References