

4.2. Disorder diffuse scattering of X-rays and neutrons

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4.2.1. Scope of this chapter

Diffuse scattering of X-rays, neutrons and other particles is an accompanying effect in all diffraction experiments aimed at structure analysis with the aid of so-called elastic scattering. In this case the momentum exchange of the scattered photon (or particle) includes the crystal as a whole; the energy transfer involved becomes negligibly small and need not be considered in diffraction theory. Inelastic scattering processes, however, are due to excitation processes, such as ionization, phonon scattering *etc.* Distortions as a consequence of structural changes cause typical elastic or inelastic diffuse scattering. All these processes contribute to scattering, and a general theory has to include all of them. Hence, the exact treatment of diffuse scattering becomes very complex. Fortunately, approximations treating the phenomena independently are possible in most cases, but it should be kept in mind that difficulties may occasionally arise.

A separation of elastic from inelastic diffuse scattering may be made if detectors sensitive to the energy of radiation are used. Difficulties may sometimes result from small energy exchanges, which cannot be resolved for experimental reasons. The latter is true for scattering of X-rays by phonons which have energies of the order of 10^{-2} – 10^{-3} eV, a value which is considerably smaller than 10 keV, a typical value for X-ray quanta. Another equivalent explanation, frequently forwarded in the literature, is the high speed of X-ray photons, such that the rather slow motion of atoms cannot be ‘observed’ by them during diffraction. Hence, all movements appear as static displacement waves of atoms, and temperature diffuse scattering is pseudo-elastic for X-rays. This is not true in the case of thermal neutrons, which have energies comparable to those of phonons. Since thermal diffuse scattering is discussed in Chapter 4.1, this chapter is mainly concerned with the elastic (or pseudo-elastic other than thermal) part of diffuse scattering.

The full treatment of the complicated theoretical background for all other kinds of diffuse scattering lies beyond the scope of this article. It is also impossible to refer to all papers in this wide and complicated field. Different theoretical treatments of one and the same subject are often developed, but only some are given here, in most cases those which may be understood most easily – at least to the authors’ feeling. As shown in this chapter, electron-density fluctuations and distribution functions of defects play an important role for the complete interpretation of diffraction patterns. Both quantities may best be studied in the low-angle scattering range, which occasionally represents the only Bragg peak dealing with the full information of the distribution function of the defects. Hence, many problems cannot be solved without a detailed interpretation of low-angle diffraction.

Disorder phenomena in magnetic structures are not specifically discussed here. Magnetic diffuse neutron scattering and special experimental techniques themselves constitute a large subject. Many aspects, however, may be analysed along similar lines as given here. For this particular topic the reader is referred to textbooks of neutron scattering, where the theory of diffraction by magnetic materials is generally included (see, *e.g.*, Lovesey, 1984).

Glasses, liquids or liquid crystals show typical diffuse diffraction phenomena. Particle-size effects and strains have an important influence on the diffuse scattering. The same is true for dislocations and point defects such as interstitials or vacancies. These defects are mainly described by their strain field which influences the intensities of sharp reflections like an artificial temperature factor: the Bragg peaks diminish in intensity, while the diffuse scattering increases predominantly close to them. These phenomena are less important from a structural point of view, at least in the case of

metals or other simple structures. This statement is true as long as the structure of the ‘kernel’ of defects may be neglected when compared with the influence of the strain field. Whether dislocations in more complicated structures meet this condition is not yet known.

Radiation damage in crystals represents another field of diffuse scattering which cannot be treated here explicitly. As long as point defects only are generated, the strain field around these defects is the most important factor governing diffuse scattering. Particles with high energy, such as fast neutrons, protons and others, generate complicated defect structures which have to be treated with the aid of the cluster method described below, but no special reference is given here because of the complexity of these phenomena.

Diffuse scattering related to phase transitions, in particular the critical diffuse scattering observed at or close to the transition temperature, cannot be discussed here. In simple cases a satisfactory description may be given with the aid of a ‘soft phonon’, which freezes at the critical temperature, thus generating typical temperature-dependent diffuse scattering. If the geometry of the lattice is maintained during the transformation (no breakdown into crystallites of different cell geometry), the diffuse scattering is very similar to diffraction phenomena described in this article. Sometimes, however, very complicated interim stages (ordered or disordered) are observed demanding a complicated theory for their full explanation (see, *e.g.*, Dorner & Comes, 1977).

Commensurate and incommensurate modulated structures as well as quasicrystals are frequently accompanied by a typical diffuse scattering, demanding an extensive experimental and theoretical study in order to arrive at a satisfactory explanation. A reliable structure determination becomes very difficult in cases where the interpretation of diffuse scattering has not been incorporated. Many erroneous structural conclusions have been published in the past. The solution of problems of this kind needs careful thermodynamical consideration as to whether a plausible explanation of the structural data can be given.

Obviously, there is a close relationship between thermodynamics and diffuse scattering in disordered systems, representing a stable or metastable thermal equilibrium. From the thermodynamical point of view the system is then characterized by its grand partition function, which is intimately related to the correlation functions used in the interpretation of diffuse scattering. The latter is nothing other than a kind of ‘partial partition function’ where two atoms, or two cell occupations, are fixed such that the sum of all partial partition functions represents the grand partition function. This fact yields the useful correlation between thermodynamics and diffuse scattering mentioned above, which may well be used for a determination of thermodynamical properties of the crystal. This subject could not be included here for the following reason: real three-dimensional crystals generally exhibit diffuse scattering by defects and/or disordering effects which are not in thermal equilibrium. They are created during crystal growth, or are frozen-in defects formed at higher temperatures. Hence, a thermodynamical interpretation of diffraction data needs a careful study of diffuse scattering as a function of temperature or some other thermodynamical parameters. This can be done in very rare cases only, so the omission of this subject seems justified.

For all of the reasons mentioned above, this article cannot be complete. It is hoped, however, that it will provide a useful guide for those who need the information for the full understanding of the crystal chemistry of a given structure.

There is no comprehensive treatment of all aspects of diffuse scattering. Essential parts are treated in the textbooks of James (1954), Wilson (1962), Wooster (1962) and Schwartz & Cohen (1977); handbook articles are written by Jagodzinski (1963,

1964a,b, 1987), Schulz (1982), Welberry (1985); and a series of interesting papers is collected by Collongues *et al.* (1977).

Many differences are caused by different symbols and by different ‘languages’ used in the various diffraction methods. Quite a few of the new symbols in use are not really necessary, but some are caused by differences in the experimental techniques. For example, the neutron scattering length b may usually be equated with the atomic form factor f in X-ray diffraction. The differential cross section introduced in neutron diffraction represents the intensity scattered into an angular range $d\Omega$ and an energy range dE . The famous scattering law in neutron work corresponds to the square of an (extended) structure factor; the ‘static structure factor’, a term used by neutron diffractionists, is nothing other than the conventional Patterson function. The complicated resolution functions in neutron work correspond to the well known Lorentz factors in X-ray diffraction. These have to be derived in order to include all techniques used in diffuse-scattering work.

4.2.2. Summary of basic scattering theory

Diffuse scattering results from deviations from the identity of translational invariant scattering objects and from long-range correlations in space and time. Fluctuations of scattering amplitudes and/or phase shifts of the scattered wavetrains reduce the maximum capacity of interference (leading to Bragg reflections) and are responsible for the diffuse scattering, *i.e.* scattering parts which are not located in reciprocal space in distinct spots. Unfortunately, the terms ‘coherent’ and ‘incoherent’ scattering used in this context are not uniquely defined in the literature. Since all scattering processes are correlated in space and time, there is no incoherent scattering at all in its strict sense. (A similar relationship exists for ‘elastic’ and ‘inelastic’ scattering. Here pure inelastic scattering would take place if the momentum and the energy were transferred to a single scatterer; on the other hand, an elastic scattering process would demand a uniform exchange of momentum and energy with the whole crystal.) Obviously, both cases are idealized and the truth lies somewhere in between. In spite of this, a great many authors use the term ‘incoherent’ systematically for the diffuse scattering away from the Bragg peaks, even if some diffuse maxima or minima, other than those due to structure factors of molecules or atoms, are observed. Although this definition is unequivocal as such, it is physically incorrect. Other authors use the term ‘coherent’ for Bragg scattering only; all diffuse contributions are then called ‘incoherent’. This definition is clear and unique since it considers space and time, but it does not differentiate between incoherent and inelastic. In the case of neutron scattering both terms are essential and cannot be abandoned.

In neutron diffraction the term ‘incoherent’ scattering is generally used in cases where no correlation between spin orientations or between isotopes of the same element exists. Hence, another definition of ‘incoherence’ is proposed for scattering processes that are uncorrelated in space and time. In fact there may be correlations between the spins *via* their magnetic field, but the correlation length in space (and time) may be very small, such that the scattering process appears to be incoherent. Even in these cases the nuclei contribute to coherent (average structure) and incoherent scattering (diffuse background). Hence, the scattering process cannot really be understood by assuming nuclei which scatter independently. For this reason, it seems to be useful to restrict the term ‘incoherent’ to cases where a random contribution to scattering is realized or, in other words, a continuous function exists in reciprocal space. This corresponds to a δ function in real four-dimensional space. The randomness may be attributed to a nucleus (neutron diffraction) or an atom (molecule). It follows from this definition that the scattering need not be continuous, but

may be modulated by structure factors of molecules. In this sense we shall use the term ‘incoherent’, remembering that it is incorrect from a physical point of view.

As mentioned in Chapter 4.1 the theory of thermal neutron scattering must be treated quantum mechanically. (In principle this is true also in the X-ray case.) In the classical limit, however, the final expressions have a simple physical interpretation. Generally, the quantum-mechanical nature of the scattering function of thermal neutrons is negligible at higher temperatures and in those cases where energy or momentum transfers are not too large. In almost all disorder problems this classical interpretation is sufficient for interpretation of diffuse scattering phenomena. This is not quite true in the case of orientational disorder (plastic crystals) where H atoms are involved.

The basic formulae given below are valid in either the X-ray or the neutron case: the atomic form factor f replaces the coherent scattering length b_{coh} (abbreviated to b). The formulation in the frame of the van Hove correlation function $G(\mathbf{r}, t)$ (classical interpretation, coherent part) corresponds to a treatment by a four-dimensional Patterson function $P(\mathbf{r}, t)$.

The basic equations for the differential cross sections are:

$$\frac{d^2\sigma_{\text{coh}}}{d\Omega d(\hbar\omega)} = N \frac{|\mathbf{k}| \langle b \rangle^2}{|\mathbf{k}_0| 2\pi\hbar} \int_{\mathbf{r}} \int_t G(\mathbf{r}, t) \times \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt \quad (4.2.2.1a)$$

$$\frac{d^2\sigma_{\text{inc}}}{d\Omega d(\hbar\omega)} = N \frac{|\mathbf{k}| \langle b^2 \rangle - \langle b \rangle^2}{|\mathbf{k}_0| 2\pi\hbar} \int_{\mathbf{r}} \int_t G_s(\mathbf{r}, t) \times \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt \quad (4.2.2.1b)$$

(N = number of scattering nuclei of same chemical species; \mathbf{k} , \mathbf{k}_0 = wavevectors after/before scattering).

The integrations over space may be replaced by summations in disordered crystals except for cases where structural elements exhibit a liquid-like behaviour. Then the van Hove correlation functions are:

$$G(\mathbf{r}, t) = \frac{1}{N} \sum_{\mathbf{r}_j, \mathbf{r}_j'} \delta\{\mathbf{r} - [\mathbf{r}_j(t) - \mathbf{r}_j(0)]\} \quad (4.2.2.2a)$$

$$G_s(\mathbf{r}, t) = \frac{1}{N} \sum_{\mathbf{r}_j} \delta\{\mathbf{r} - [\mathbf{r}_j(t) - \mathbf{r}_j(0)]\}. \quad (4.2.2.2b)$$

$G(\mathbf{r}, t)$ gives the probability that if there is an atom j at $\mathbf{r}_j(0)$ at time zero, there is an *arbitrary* atom j' at $\mathbf{r}_j'(t)$ at *arbitrary* time t , while $G_s(\mathbf{r}, t)$ refers to the *same* atom j at $\mathbf{r}_j(t)$ at time t .

Equations (4.2.2.1) may be rewritten by use of the four-dimensional Fourier transforms of G , and G_s , respectively:

$$S_{\text{coh}}(\mathbf{H}, \omega) = \frac{1}{2\pi} \int_{\mathbf{r}} \int_t G(\mathbf{r}, t) \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt \quad (4.2.2.3a)$$

$$S_{\text{inc}}(\mathbf{H}, \omega) = \frac{1}{2\pi} \int_{\mathbf{r}} \int_t G_s(\mathbf{r}, t) \exp\{2\pi i(\mathbf{H} \cdot \mathbf{r} - \nu t)\} d\mathbf{r} dt \quad (4.2.2.3b)$$

$$\frac{d^2\sigma_{\text{coh}}}{d\Omega d(\hbar\omega)} = N \frac{k}{k_0} \langle b \rangle^2 S_{\text{coh}}(\mathbf{H}, \omega) \quad (4.2.2.4a)$$

$$\frac{d^2\sigma_{\text{inc}}}{d\Omega d(\hbar\omega)} = N \frac{k}{k_0} [\langle b^2 \rangle - \langle b \rangle^2] S_{\text{inc}}(\mathbf{H}, \omega). \quad (4.2.2.4b)$$

Incoherent scattering cross sections [(4.2.2.3b), (4.2.2.4b)] refer to one and the same particle (at different times). In particular, plastic crystals (see Section 4.2.4.5) may be studied by means of this