

4.2. Disorder diffuse scattering of X-rays and neutrons

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4.2.1. Introduction

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 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. Static distortions as a consequence of structural changes cause typical elastic diffuse scattering. Many structural phenomena and processes contribute to diffuse scattering, and a general theory has to include all of them. Hence the exact treatment of diffuse scattering becomes very complex.

Inelastic scattering is due to dynamical fluctuations or ionization processes and may become observable as a 'diffuse' contribution in a diffraction pattern. A separation of elastic from inelastic diffuse scattering is generally possible, but difficulties may result from small energy exchanges that 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, values which are 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. Phonon-related or thermal diffuse scattering is discussed separately in Chapter 4.1, *i.e.* the present chapter is mainly concerned with the elastic (or pseudo-elastic other than thermal) part of diffuse scattering. A particularly important aspect concerns diffuse scattering related to phase transitions, in particular the critical diffuse scattering observed at or close to the transition temperature. 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 (*i.e.* there is no breakdown into crystallites of different cell geometry), the diffuse scattering is very similar to diffraction phenomena described in this chapter. 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).

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 occupancies, 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 important subject shall not be included here for the following reason: real three-dimensional crystals generally exhibit diffuse scattering by defects and/or disordering effects that 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.

As shown in this chapter, electron-density fluctuations and distribution functions of defects play an important role in the complete interpretation of diffraction patterns. Both quantities may best be studied in the low-angle scattering range. Hence many problems cannot be solved without a detailed interpretation of low-angle diffraction (also called small-angle scattering).

Disorder phenomena in magnetic structures are also not specifically discussed here. Magnetic diffuse neutron scattering and special experimental techniques constitute a large subject by themselves. Many aspects, however, may be analysed along similar lines to those given here.

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.

Commensurate and incommensurate modulated structures and quasicrystals frequently show a typical diffuse scattering, a satisfactory explanation of which demands extensive experimental and theoretical study. 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.

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 a full understanding of the crystal chemistry of a given structure.

The study of disorder in crystals by diffuse-scattering techniques can be performed with X-rays, neutrons or electrons. Each of these methods has its own advantages (and disadvantages) and they often can (or have to) be used in a complementary way (*cf.* Chapter 4.3 of this volume). Electron diffraction and microscopy are usually restricted to relatively small regions in space and thus supply information on a local scale, *i.e.* local defect structures. Moreover, electron-microscopy investigations are carried out on thin samples (films), where the disorder could be different from the bulk, and, in addition, could be affected by the high heat load deposited by the impinging electron beam. X-rays and neutrons sample larger crystal volumes and thus provide thermodynamically more important information on *averages* of the disorder. These methods are also better suited to the analysis of long-range correlated cooperative disorder phenomena. On the other hand, electron microscopy and diffraction often allow more direct access to disorder and can therefore provide valuable

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information about the underlying model, which can then be used for a successful interpretation of X-ray and neutron diffuse scattering. Basic aspects of electron diffraction and microscopy in structure determination are treated in Chapter 2.5 of this volume.

There is no comprehensive treatment of all aspects of diffuse scattering. Essential parts are treated in the textbooks by James (1954), Wilson (1962), Wooster (1962), Krivoglaz (1969, 1996*a,b*), Schwartz & Cohen (1977), Billinge & Thorpe (1998), Schweika (1998), Nield & Keen (2001), Fultz & Howe (2002), Frey (2003) and Welberry (2004); handbook articles have been written by Jagodzinski (1963, 1964*a,b*, 1987), Schulz (1982), Welberry (1985) and Moss *et al.* (2003), and a series of relevant papers has been collected by Collongues *et al.* (1977).

Finally, we mention that different symbols and ‘languages’ are 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 ‘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 the techniques used in diffuse-scattering work. In this article we try to preserve the most common symbols. In particular, the scattering vector will be denoted as \mathbf{H} , which is more commonly used in crystallography than $\mathbf{Q} = 2\pi\mathbf{H}$.

4.2.2. Basic scattering theory

4.2.2.1. General

Diffuse scattering results from deviations from the identity of translationally 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 that are not located in distinct spots in reciprocal space. 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, many authors use the term ‘incoherent’ systematically for the diffuse scattering away from the Bragg peaks when all diffuse maxima or minima are due to structure factors of molecules or atoms only. 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 neither can be abandoned.

In neutron diffraction, the term ‘incoherent scattering’ refers to scattering by uncorrelated nuclear spin orientations or by a random distribution of isotopes of the same element. 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 that 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 constant, 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 also true 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 the 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 as 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

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

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

where N is the number of scattering nuclei of same chemical species; \mathbf{k} , \mathbf{k}_0 are the wavevectors after/before scattering and $\omega = 2\pi\nu$.

The integrations over space may be replaced by summations in disordered crystals, except in 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 an *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 using the four-dimensional Fourier transforms of G and G_s , respectively: