International Tables for Crystallography (2010). Vol. B, Section 5.3.6, pp. 659–660.

Extinction effects can be safely neglected in the case of scattering by very small crystals; more precisely, this is possible when the path length of the neutron beam in the crystal is much smaller than $\Delta = V_c/\lambda F$, where λ is the neutron wavelength and F/V_c is the scattering length per unit volume for the reflection considered. Δ is sometimes called the 'extinction distance'.

A very important fact is that extinction effects also vanish if the crystal is imperfect enough, because each plane-wave component of the incident beam can then be Bragg-reflected in only a small volume of the sample. This is the extinction-free case of 'ideally imperfect crystals'. Conversely, extinction is maximum (smallest value of y) in the case of ideally perfect non-absorbing crystals.

Clearly, no significant extinction effects are expected if the crystal is thick but strongly absorbing, more precisely if the linear absorption coefficient μ is such that $\mu\Delta \gg 1$. Neutron diffraction usually corresponds to the opposite case ($\mu\Delta \ll 1$), in which extinction effects in nearly perfect crystals dominate absorption effects.

Extinction effects are usually described in the frame of the mosaic model, in which the crystal is considered as a juxtaposition of perfect blocks with different orientations. The relevance of this model to the case of neutron diffraction was first considered by Bacon & Lowde (1948). If the mosaic blocks are big enough there is extinction within each block; this is called *primary extinction*. Multiple scattering can also occur in different blocks if their misorientation is small enough. In this case, which is called *secondary extinction*, there is no phase coherence between the scattering events in the different blocks. The fact that empirical intensity-coupling equations are used in this case is based on this phase incoherence.

In the general case, primary and secondary extinction effects coexist. Pure secondary extinction occurs in the case of a mosaic crystal made of very small blocks. Pure primary extinction is observed in diffraction by perfect crystals.

The parameters of the mosaic model are the average size of the perfect blocks and the angular width of their misorientation distribution. The extinction theory of the mosaic model provides a relation between these parameters and the extinction coefficient, defined as the ratio of the observed reflectivity to the ideal one, which is the kinematical reflectivity in this context.

In conventional work, the crystal structure factors of different reflections and the parameters of the mosaic model are fitted together to the experimental data, which are the integrated reflectivities and the angular widths of the rocking curves. In many cases, only the weakest reflections will be free, or nearly free, from extinction. The extinction corrections thus obtained can be considered as satisfactory in cases of moderate extinction. Nevertheless, extinction remains a real problem in cases of strong extinction and in any case if a very precise determination of the crystal structure factors is required.

There exist several forms of the mosaic model of extinction. For instance, in the model developed by Kulda (1988*a*,*b*, 1991), the mosaic blocks are not considered just as simple perfect blocks but may be deformed perfect blocks. This has the advantage of including the case of macroscopically deformed crystals, such as bent crystals.

A basically different approach, free from the distinction between primary and secondary extinction, has been proposed by Kato (1980*a*,*b*). This is a wave-optical approach starting from the dynamical equations for diffraction by deformed crystals. These so-called Takagi–Taupin equations (Takagi, 1962; Taupin, 1964) contain a position-dependent phase factor related to the displacement field of the deformed crystal lattice. Kato proposed considering this phase factor as a random function with suitably defined statistical characteristics. The wave amplitudes are then also random functions, the average of which represent the coherent wavefields while their statistical fluctuations represent the incoherent intensity fields.

Modifications to the Kato formulation have been introduced by Al Haddad & Becker (1988), by Becker & Al Haddad (1990, 1992), by Guigay (1989) and by Guigay & Chukhovskii (1992, 1995). Presently, it is not easy to apply this 'statistical dynamical theory' to real experiments. The widely used methods for extinction corrections are still based on the former mosaic model, according to the formulation of Zachariasen (1967), later improved by Becker & Coppens (1974*a*,*b*, 1975).

As in the X-ray case, acoustic waves produced by ultrasonic excitation can artificially induce a transition from perfect to ideally imperfect crystal behaviour. The effect of ultrasound on the scattering behaviour of distorted crystals is quite complex. A good discussion with reference to neutron-scattering experiments is given by Zolotoyabko & Sander (1995).

The situation of crystals with a simple distortion field is less difficult than the statistical problem of extinction. Klar & Rustichelli (1973) confirmed that the Takagi–Taupin equations, originally devised for X-rays, can be used for neutron diffraction with due account of the very small absorption, and used them for computing the effect of crystal curvature.

5.3.5. Effect of external fields on neutron scattering by perfect crystals

The possibility of acting on neutrons through externally applied fields during their propagation in perfect crystals provides possibilities that are totally unknown in the X-ray case. The theory has been given by Werner (1980) using the approaches (migration of tie points, and Takagi–Taupin equations) that are customary in the treatment of imperfect crystals (see above). Zeilinger *et al.* (1986) pointed out that the effective-mass concept, familiar in describing electrons in solid-state physics, can shed new light on this behaviour: because of the curvature of the dispersion surface at a near-exact Bragg setting, effective masses five orders of magnitude smaller than the rest mass of the neutron in a vacuum can be obtained. Related experiments are discussed below.

An interesting proposal was put forward by Horne *et al.* (1988) on the coupling between the Larmor precession in a homogeneous magnetic field and the spin–orbit interaction of the neutron with nonmagnetic atoms, a term which was dismissed in Section 5.3.2 because its contribution to the scattering length is two orders of magnitude smaller than that of the nuclear term. A resonance is expected to show up as highly enhanced diffracted intensity when a perfect sample is set for Bragg scattering and the magnetic field is adjusted so that the Larmor precession period is equal to the *Pendellösung* period.

5.3.6. Experimental tests of the dynamical theory of neutron scattering

These experiments are less extensive for neutron scattering than for X-rays. The two most striking effects of dynamical theory for nonmagnetic nearly perfect crystals, *Pendellösung* behaviour and anomalous absorption, have been demonstrated in the neutron case too. *Pendellösung* measurement is described below (Section 5.3.7.2) because it is useful in the determination of scattering lengths. The anomalous transmission effect occurring when a perfect absorbing crystal is exactly at Bragg setting, *i.e.* the Borrmann effect, is often referred to in the neutron case as the suppression of the inelastic channel in resonance scattering, after Kagan & Afanas'ev (1966), who worked out the theory. A small decrease in absorption was detected in pioneering experiments on calcite by Knowles (1956) using the corresponding decrease in the emission of γ-rays and by Sippel *et al.* (1962), Shil'shtein *et al.* (1971) and Hastings *et al.* (1990) directly. Rocking curves of perfect crystals were measured by Sippel *et al.* (1964) in transmission, and by Kikuta *et al.* (1975). Integrated intensities were measured by Lambert & Malgrange (1982). The large angular amplification associated with the curvature of the dispersion surfaces near the exact Bragg setting was demonstrated by Kikuta *et al.* (1975) and by Zeilinger & Shull (1979).

In magnetic crystals, the investigations have been restricted to the simpler geometry where the scattering vector is perpendicular to the magnetization, and to few materials. *Pendellösung* behaviour was evidenced through the variation with wavelength of the flipping ratio for polarized neutrons by Baruchel *et al.* (1982) on an yttrium iron garnet sample, with the geometry selected so that the defects would not affect the Bragg reflection used. The inclination method was used successfully by Zelepukhin *et al.* (1989), Kvardakov & Somenkov (1990) and Kvardakov *et al.* (1990*a*) for the weak ferromagnet $FeBO_3$, and in the room-temperature weak-ferromagnetic phase of hematite, α-Fe_2O_3, by Kvardakov *et al.* (1990*b*) and Kvardakov & Somenkov (1992).

Experiments on the influence of defects in nearly perfect crystals have been performed by several groups. The effect on the rocking curve was investigated by Eichhorn *et al.* (1967), the intensities were measured by Lambert & Malgrange (1982) and by Albertini, Boeuf, Cesini *et al.* (1976), and the influence on the *Pendellösung* behaviour was discussed by Kvardakov & Somenkov (1992). Boeuf & Rustichelli (1974) and Albertini *et al.* (1977) investigated silicon crystals curved by a thin surface silicon nitride layer.

Many experiments have been performed on vibrating crystals; reviews are given by Michalec *et al.* (1988) and by Kulda *et al.* (1988). Because the velocity of neutrons is of the same order of magnitude as the velocity of acoustic phonons in crystals, the effect of ultrasonic excitation on dynamical diffraction takes on some original features compared to the X-ray case (Iolin & Entin, 1983); they could to some extent be evidenced experimentally (Iolin *et al.*, 1986; Chalupa *et al.*, 1986). References to experimental work on neutron scattering by imperfect crystals under ultrasonic excitation are included in Zolotoyabko & Sander (1995).

Some experiments with no equivalent in the X-ray case could be performed. The very strong incoherent scattering of neutrons by protons, very different physically but similar in its effect to absorption, was also shown to lead to anomalous transmission effects by Sippel & Eichhorn (1968). Because the velocity of thermal neutrons in a vacuum is five orders of magnitude smaller than the velocity of light, the flight time for neutrons undergoing Bragg scattering in Laue geometry in a perfect crystal could be measured directly (Shull *et al.*, 1980). The effect of externally applied fields was measured experimentally for magnetic fields by Zeilinger & Shull (1979) and Zeilinger *et al.* (1986). Slight rotation of the crystal, introducing a Coriolis force, was used by Raum *et al.* (1995), and gravity was tested recently, with the spectacular result that some states are accelerated upwards (Zeilinger, 1995).

5.3.7. Applications of the dynamical theory of neutron scattering

5.3.7.1. Neutron optics

Most experiments in neutron scattering require an intensity-effective use of the available beam at the cost of relatively high divergence and wavelength spread. The monochromators must then be imperfect ('mosaic') crystals. In some cases, however, it is important to have a small divergence and wavelength band. One example is the search for small variations in neutron energy in inelastic scattering without the use of the neutron spin-echo principle. Perfect crystals must then be used as monochromators or analysers, and dynamical diffraction is directly involved. As in the X-ray case, special designs can lead to strong decrease in the intensity of harmonics, *i.e.* of contributions of $\lambda/2$ or $\lambda/3$ (Hart & Rodrigues, 1978). The possibility of focusing neutron beams by the use of perfect crystals with the incident beam spatially modulated in amplitude through an absorber, or in phase through an appropriate patterning of the surface, in analogy with the Bragg–Fresnel lenses developed for X-rays, was suggested by Indenbom (1979).

The use of two identical perfect crystals in nondispersive ($+, -, \|$) setting provides a way of measuring the very narrow intrinsic rocking curves expected from the dynamical theory. Any divergence added between the two crystals can be sensitively measured. Thus perfect crystals provide interesting possibilities for measuring very small angle neutron scattering. This was performed by Takahashi *et al.* (1981, 1983) and Tomimitsu *et al.* (1986) on amorphous materials, and by Kvardakov *et al.* (1987) for the investigation of ferromagnetic domains in bulk silicon–iron specimens under stress, both through the variations in transmission associated with refraction on the domain walls and through small-angle scattering. Imaging applications are described in Section 5.3.7.4. Badurek *et al.* (1979) used the different deflection of the two polarization states provided by a magnetic prism placed between two perfect silicon crystals to produce polarized beams.

Curved almost-perfect crystals or crystals with a gradient in the lattice spacing can provide focusing (Albertini, Boeuf, Lagomarsino *et al.*, 1976) and vibrating crystals can give the possibility of tailoring the reflectivity of crystals, as well as of modulating beams in time (Michalec *et al.*, 1988). A double-crystal arrangement with bent crystals was shown by Eichhorn (1988) to be a flexible small-angle-neutron-scattering device.

5.3.7.2. Measurement of scattering lengths by Pendellösung effects

As in X-ray diffraction, *Pendellösung* oscillations provide an accurate way of measuring structure factors, hence coherent neutron scattering lengths. The equal-thickness fringes expected from a wedge-shaped crystal were observed by Kikuta *et al.* (1971). Three kinds of measurements were made. Sippel *et al.* (1965) measured as a function of thickness the integrated reflectivity from a perfect crystal of silicon, the thickness of which they varied by polishing after each measurement, obtaining a curve similar to Fig. 5.1.6.7, corresponding to equation 5.1.6.8. Shull (1968) restricted the measurement to wavefields that propagated along the reflecting planes, hence at exact Bragg incidence, by setting fine slits on the entrance and exit faces of 3 to 10 mm-thick silicon crystals, and measured the oscillation in diffracted intensity as he varied the wavelength of the neutrons used by rotating the crystal. Shull & Oberteuffer (1972) showed that a better interpretation of the data, when the beam is restricted to a fine slit, corresponds to the spherical wave approach (actually cylindrical wave), and the boundary conditions were discussed more generally by Arthur & Horne (1985). Somenkov *et al.* (1978) developed the inclination method, in which the integrated reflectivity is measured as the effective crystal thickness is varied nondestructively, by rotating the crystal around the diffraction vector, and used it for germanium. Belova *et al.* (1983) discuss this method in detail. The results obtained by this group for magnetic crystals are mentioned in Section 5.3.6. Structure-factor values for magnetic reflections were obtained by Kvardakov *et al.* (1995) for the weak ferromagnet $FeBO_3$.

5.3.7.3. Neutron interferometry

Because diffraction by perfect crystals provides a well defined distribution of the intensity and phase of the beam, interferometry with X-rays or neutrons is possible using ingeniously designed and carefully manufactured monolithic devices carved out of single crystals of silicon. The technical and scientific features of this family of techniques are well summarized by Bonse (1979, 1988), as well as other papers in the same volumes, and by Shull (1986).

X-ray interferometry started with the Bonse–Hart interferometer (Bonse & Hart, 1965). A typical device is the LLL skew-symmetric interferometer, where the L's stand for Laue,

references