



DIFFRACTION - SINGLE CRYSTAL, MAGNETIC

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The analysis of crystal structure and magnetic ordering is usually based on diffraction phenomena caused by the interaction of matter with X-rays, neutrons, or electrons. Even though electron microscopy can achieve atomic resolution, more detailed information on the 3dim. atomic arrangement of crystals with its symmetry and chemical bonding as well as magnetic structures and spin densities requires diffraction methods. The basic theory of diffraction is the same for all types of radiation. Complementary information is achieved due to the different character of X-rays, neutrons and electrons, and hence their different interactions with matter and further practical aspects.

Considering only X-rays and thermal neutrons one finds that their wavelengths are similar ($0.5 \text{ \AA} < \lambda < 2.4 \text{ \AA}$). While the electromagnetic X-ray radiation yields the total electron density distribution, the nuclear scattering of neutrons probes the density distribution of the nuclei and the magnetic neutron scattering the spin density of unpaired electrons.

X-ray diffraction using conventional laboratory equipment and/or synchrotron installations is the most important method for structure analyses. The purpose of this paper is to discuss special cases, for which, in addition to this indispensable part, neutrons are required to solve structural problems. Even though the huge intensity of modern synchrotron sources allows in principle the study of magnetic X-ray scattering the investigation of magnetic structures is still one of the most important applications of neutron diffraction.

2. Reciprocal Lattice and Ewald Construction

Diffraction (or Bragg scattering) means coherent elastic scattering of a wave by a crystal. The experimental information consists of the scattering function $S(\mathbf{Q}, \omega = 0)$ with no change of the energy or wavelength of the diffracted beam. For an ideal crystal and an infinite lattice with the basis vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, there is only diffraction intensity $I(\mathbf{H})$ at the vectors

$$\mathbf{H} = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^* \quad (1)$$

of the reciprocal lattice. h, k, l are the integer Miller indices and $\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*$, the basis vectors of the reciprocal lattice, satisfying the two conditions

$$\mathbf{a}_1^* \cdot \mathbf{a}_1 = \mathbf{a}_2^* \cdot \mathbf{a}_2 = \mathbf{a}_3^* \cdot \mathbf{a}_3 = 1 \text{ and } \mathbf{a}_1^* \cdot \mathbf{a}_2 = \mathbf{a}_1^* \cdot \mathbf{a}_3 = \mathbf{a}_2^* \cdot \mathbf{a}_1 = \dots = 0,$$

or in terms of the Kronecker symbol with i, j and $k = 1, 2, 3$

$$\delta_{ij} = 0 \text{ for } i \neq j \text{ and } \delta_{ij} = 1 \text{ for } i = j \text{ with } \delta_{ij} = \mathbf{a}_i^* \cdot \mathbf{a}_j^*. \quad (2)$$

The basis vectors of the reciprocal lattice can be calculated from those of the unit cell in real space

$$\mathbf{a}_i^* = (\mathbf{a}_j \times \mathbf{a}_k) / V_c, \quad (3)$$

where \times means the cross product, and $V_c = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$ is the volume of the unit cell.

Here is a compilation of some properties of the reciprocal lattice:

- The reciprocal lattice vectors are perpendicular to those in real space: $\mathbf{a}_i^* \perp \mathbf{a}_j$ and \mathbf{a}_k .
 - The lengths of the reciprocal lattice vectors are $|\mathbf{a}_i^*| = 1/V_c \cdot |\mathbf{a}_j| \cdot |\mathbf{a}_k| \cdot \sin \angle(\mathbf{a}_j, \mathbf{a}_k)$.
 - Each point hkl in the reciprocal lattice refers to a set of planes (hkl) in real space.
 - The direction of the reciprocal lattice vector \mathbf{H} is normal to the (hkl) planes and its length is reciprocal to the interplanar spacing d_{hkl} : $|\mathbf{H}| = 1/d_{hkl}$.
 - Duality principle: The reciprocal lattice of the reciprocal lattice is the direct lattice.
- From the positions of the nodes of the reciprocal lattice obtained by diffraction experiments one can determine directly the parameters of the unit cell of a crystal.

Although somewhat abstract, the concept of the reciprocal space provides a practical tool to express geometrically the condition for Bragg scattering in the so-called Ewald construction. In this way the different diffraction methods can be discussed.

We consider the reciprocal lattice of a crystal and choose its origin 000. In Fig. 1 the wave vector \mathbf{k}_0 (defined in the crystallographers' convention with $|\mathbf{k}_0| = 1/\lambda$) of the incident beam is marked with its end at 000, its origin being called P. We now draw a sphere of radius $|\mathbf{k}_0| = 1/\lambda$ around P passing through 000. Now, if any point hkl of the reciprocal lattice lies on the surface of this Ewald sphere, then the diffraction condition for the (hkl) lattice planes is fulfilled: The wave vector of the diffracted beam \mathbf{k} (with its origin also at P) for the set of planes (hkl) , is of the same magnitude as \mathbf{k}_0 ($|\mathbf{k}| = |\mathbf{k}_0|$) and the resulting vector diagram satisfies $\mathbf{k} = \mathbf{k}_0 + \mathbf{H}$. Introducing the scattering angle 2Θ (and hence the Bragg angle Θ_{hkl}), we can deduce immediately from $2|\mathbf{k}| \cdot \sin \Theta = |\mathbf{H}|$ the Bragg equation:

$$2d_{hkl} \cdot \sin \Theta_{hkl} = \lambda. \quad (4)$$

In the case of single crystal diffraction a rotation of the crystal and therefore also of the corresponding reciprocal lattice (which is rigidly attached to the crystal) is often used to set the diffraction conditions for the measurement of intensities $I(\mathbf{H})$.

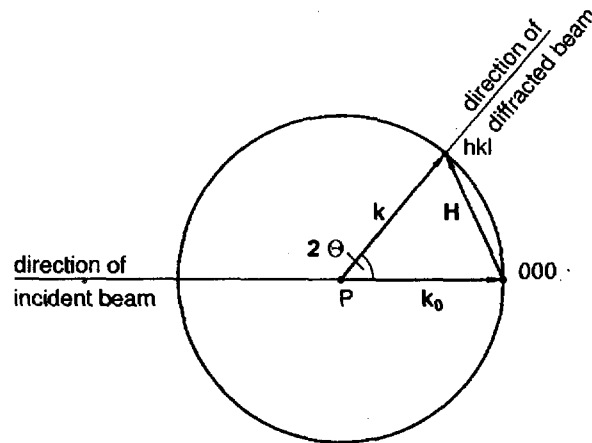


Fig. 1. Ewald construction, in reciprocal space, showing the diffraction condition for the hkl reflection.

If $|\mathbf{H}| > 2/\lambda$ (then $d_{hkl} < \lambda/2$) the reflection hkl cannot be observed. This condition defines the so called limiting sphere, with center at 000 and radius $2/\lambda$: only the points of the reciprocal lattice inside the limiting sphere can be rotated into diffraction position. Vice versa if $\lambda > 2d_{\max}$, where d_{\max} is the largest interplanar spacing of the unit cell, then the diameter of the Ewald sphere is smaller than $|\mathbf{H}|_{\min}$. Under these conditions no node of the reciprocal lattice can intercept the Ewald sphere. That is the reason why diffraction of visible light (wavelength $\cong 5000 \text{ \AA}$) can never be obtained from crystals. λ_{\min} determines the amount of information available from a diffraction experiment. In ideal conditions λ_{\min} should be short enough to measure all points of the reciprocal lattice with significant diffraction intensities.

For a real crystal of limited perfection and size the infinitely sharp diffraction peaks (delta functions) are to be replaced by broadened line shapes. One reason can be the local variation of the orientation of the crystal lattice (mosaic spread) implying some angular splitting of the vector \mathbf{H} . A spread of interplanar spacings $\Delta d/d$, which may be caused by some inhomogeneities in the chemical composition of the sample, gives rise to a variation of its magnitude $|\mathbf{H}|$. The ideal diffraction geometry on the other hand is also to be modified. In a real experiment the primary beam has a finite divergence and wavelength spread. The detector aperture is also finite. A gain of intensity, which can be accomplished by increasing the angular divergence and wavelengths bandwidth, has to be paid for by some worsening of the resolution function and hence by a limitation of the ability to separate different Bragg reflections. All of these influences can be studied by the Ewald construction.

3. Structure Factor and Bragg Intensities

3.1. Nuclear Scattering

In kinematical approximation, assuming that the magnitude of the incident wave amplitude is the same at all points in the specimen (this implies a small sample size, weak scattering intensities, no multiple diffraction and neglecting of absorption), the diffracted intensity is proportional to the square of the amplitude of the scattered wave for each individual reflection; it can be regarded as a weight ascribed to the reciprocal lattice nodes

$$I(\mathbf{H}) \sim |F(\mathbf{H})|^2.$$

The structure factor $F(\mathbf{H})$, in terms of the Fourier transform, contains the complete information on the distribution of the scatterer density in the unit cell

$$F(\mathbf{H}) = \sum_j b_j \exp[2\pi i(\mathbf{H} \cdot \mathbf{r}_j)] \cdot T_j(\mathbf{H}) = |F(\mathbf{H})| \cdot \exp[i\varphi(\mathbf{H})]. \quad (5)$$

In the case of nuclear scattering of neutrons the structure factor has the dimension of a length, as has the scattering length $b_j(\mathbf{H}) = b_j = \text{const. of nucleus } j$. $T_j(\mathbf{H})$ is the Debye-Waller factor which takes into account dynamical and static displacements of the nucleus j from its average position \mathbf{r}_j in the unit cell

$$\mathbf{r}_j = x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3. \quad (6)$$

With the fractional co-ordinates x_j , y_j and z_j ($0 \leq x_j < 1$, $0 \leq y_j < 1$, $0 \leq z_j < 1$) the scalar product in the exponential function can be written as

$$\mathbf{H} \cdot \mathbf{r}_j = hx_j + ky_j + lz_j. \quad (7)$$

Important: The measured Bragg intensities $I(\mathbf{H})$ from diffraction experiments yield only the modules of the structure factors, $|F(\mathbf{H})| \propto \sqrt{I(\mathbf{H})}$, and not their phases $\varphi(\mathbf{H})$ (see Eq. 5), which would be required for the inverse Fourier transform of the data (Fourier synthesis) to give directly the arrangement of the atoms in the unit cell. The lack of the phase information is known as the phase problem of crystallography.

In a diffraction experiment normally only relative Bragg intensities are measured. A SCALE factor is assumed to be rigorously the same for all reflections of one data set. For merely nuclear neutron scattering and single crystals the integrated relative intensities are given by

$$I(\mathbf{H}) = \text{SCALE} \cdot L \cdot A \cdot |F(\mathbf{H})|^2. \quad (8)$$

The Lorentz factor L is instrument specific. The absorption correction A depends on the geometry and linear absorption coefficient of the sample.

The geometrical diffraction conditions and hence the reciprocal lattice yield the periodicity of a crystal. The $|F(\mathbf{H})|^2$ values associated as weights to the nodes of the reciprocal lattice give the diffraction symbol and hence valuable information on the space group symmetry. Here systematic absences (zero structure factors) can be related to the choice of a non-primitive Bravais lattice, or to the presence of non-symmorphic symmetry operations (symmetry operations with translation components).

3.2. Magnetic Scattering

The dipolar interaction between the neutron magnetic moments and the magnetic moments of atoms (and nuclei) \mathbf{m}_j leads to the magnetic neutron scattering in addition to the nuclear contribution. In the case of an ordering of the magnetic moments over the whole crystal (periodic magnetic structure) the magnetic structure factor is given by

$$F_M(\mathbf{H}) = \sum b_{Mj}(\mathbf{H}) \cdot \exp[2\pi i(\mathbf{H} \cdot \mathbf{r}_j)] \cdot T_j(\mathbf{H}) \quad (9)$$

with the magnetic scattering amplitude

$$b_{Mj}(\mathbf{H}) = (e^2 \gamma / 2m_e c^2) \cdot f_{Mj}(\mathbf{H}) \cdot \sigma \cdot \mathbf{m}_{\perp j}(\mathbf{H}). \quad (10)$$

$\frac{1}{2}\sigma$ is the neutron spin operator and $\mathbf{m}_{\perp j}(\mathbf{H})$ the projection of the magnetic moment \mathbf{m}_j onto the scattering plane (hkl). The magnetic form factor $f_{Mj}(\mathbf{H})$ is the Fourier transform of the normalised magnetisation density $M_j(\mathbf{r})$ of the atom or ion j

$$f_{Mj}(\mathbf{H}) = \int_V M_j(\mathbf{r}) \cdot \exp[2\pi i(\mathbf{H} \cdot \mathbf{r})] \cdot d\mathbf{r} \quad (11)$$

$$\text{with } f_M(0) = \int_V M_j(\mathbf{r}) \cdot d\mathbf{r} = 1.$$

This is a function of the reciprocal lattice vector \mathbf{H} , whereas the atomic scattering factor f_j of X-ray diffraction

$$f_j(|\mathbf{H}|) = \int_V \rho_j(\mathbf{r}) \cdot \exp[2\pi i(\mathbf{H} \cdot \mathbf{r})] \cdot d\mathbf{r}, \quad (12)$$

for a spherical electron density $\rho_j(\mathbf{r})$, depends only on the modules of \mathbf{H} .

The intensity of magnetic and nuclear neutron scattering is of the same order of magnitude. For unpolarised neutrons the Bragg intensity of nuclear and magnetic neutron diffraction is simply an incoherent superposition

$$I(\mathbf{H}) = I_N(\mathbf{H}) + I_M(\mathbf{H}) \sim |F_N(\mathbf{H})|^2 + |F_M(\mathbf{H})|^2. \quad (13)$$

For polarised neutrons on the other hand the coherent superposition gives

$$[|F(\mathbf{H})|^2]^\pm = |F_N(\mathbf{H}) \pm F_M(\mathbf{H})|^2 \quad (14)$$

with the interference terms $\pm 2 \cdot |F_N(\mathbf{H}) \cdot F_M(\mathbf{H})|$ according to the two possible directions of polarisation (+ and -). In measuring the flipping ratio at superimposed Bragg reflections, that means the ratio of the intensities for the two polarisations up and down, even small magnetic structure factors can be determined quite accurately.

The analysis of a magnetic structure starts with the determination of its periodicity with respect to that of the crystal structure. The identification of magnetic reflections is usually accomplished by a careful comparison of powder diagrams recorded below and above the magnetic phase transition temperatures. A more detailed study of the scattering vectors, e.g. for incommensurate structures, may require also single crystal experiments. The nuclear structure factors $F_N(\mathbf{H})$ can be calculated from the known crystal structure. In this way the SCALE factor of the data set can be obtained and the absolute values of the magnitudes of the magnetic structure factors $|F_M(\mathbf{H})|$ can be determined. The individual orientations of the magnetic moments \mathbf{m}_j with respect to the basis vectors of the crystal lattice and their magnitudes are then to be calculated.

4. Contrast Variation

Neutron diffraction can be used for an experimental distinction of atoms/ions with almost equal X-ray scattering amplitudes. In the case of mixed systems it is furthermore possible to determine a fractional site occupation. Another application of neutron diffraction is the determination of accurate atomic parameters (positional and thermal parameters, site occupations) of lighter elements in the presence of heavy ones.

The contrast in conventional X-ray diffraction is directly related to the ratio of the number of electrons Z_j of the different atoms or ions j involved. The atomic scattering factor f_j in the structure factor formula, which represents the Fourier transform of the atomic electron density distribution, is proportional to Z_j ($f_j = Z_j$ for $\sin\theta/\lambda = 0$). Standard X-ray techniques can hardly differentiate between atoms/ions of a similar number of electrons, and only an average structure - including a total occupation probability of mixed occupied sites - may be obtained in such cases.

For neutrons the atomic scattering factor f_j is replaced by the nuclear scattering length (or coherent scattering amplitude) b_j , which is of the same order of magnitude for all nuclei but varies from nucleus to nucleus in a non systematic way. b_j values, which can be either positive or negative, depend on the isotopes and nuclear spin states of the element j . A nucleus of an isotope with spin I may have two different neutron scattering lengths: one for the combined spin state $J = I + 1/2$ and one with $J = I - 1/2$. An important and fundamental example is provided by the simplest of all nuclei, the proton with spin $I = 1/2$. The two spin states, $J = 1$ (triplet) and $J = 0$ (singlet), with statistical weights $3/4$ and $1/4$ respectively, have the scattering lengths for a *free* proton:

$$b_H^s = -23.7 \text{ fm}, b_H^l = +5.38 \text{ fm}, b_{\text{freeH}} = 1/4 b_H^s + 3/4 b_H^l = -1.89 \text{ fm (with } 10^{-15} \text{ m} = 1 \text{ fm)}.$$

The value for the *bound* proton in a crystal structure, which is to be used in the structure factor calculations, amounts to $b_H = 2 \cdot b_{\text{freeH}} = -3.741 \text{ fm}$.

The natural isotope mixture and a statistical spin state distribution lead to the commonly used general formula $b_j = \alpha \cdot b_{j\alpha} + \beta \cdot b_{j\beta} + \gamma \cdot b_{j\gamma} + \dots$ with the sum of the different isotope fractions $\alpha + \beta + \gamma + \dots = 1$ ($b_{j\alpha}$, $b_{j\beta}$, $b_{j\gamma}$ are the individual scattering lengths of the

different isotopes of the element j). The natural nickel isotopes, for instance, have extremely different coherent scattering amplitudes:

$$b(^{58}\text{Ni}) = +14.4 \text{ fm}, \quad b(^{60}\text{Ni}) = +3.0 \text{ fm}, \quad b(^{61}\text{Ni}) = +7.6 \text{ fm}, \\ b(^{62}\text{Ni}) = -8.7 \text{ fm}, \quad b(^{64}\text{Ni}) = -0.37 \text{ fm}$$

resulting in an overall scattering length $b_{\text{Ni}} = +10.34 \text{ fm}$.

Neutron experiments frequently make use of compounds containing single isotope elements, like fully deuterated samples. Incoherent scattering due to a statistical distribution of isotopes and nuclear spin states is not discussed here. It may influence the effective absorption and the background conditions of neutron diffraction studies.

A special possibility of contrast variation, the combination of X-ray and neutron diffraction information, is demonstrated for the example of the intermetallic compounds $(\text{Mn}_{1-x}\text{Cr}_x)_{1+\delta}\text{Sb}$, with $0 \leq x \leq 1$ [1]. This mixed system is of special interest due to its magnetic properties: competing magnetic interactions with isotropic ferromagnetic behaviour for $\text{Mn}_{1+\delta}\text{Sb}$ and an uniaxial antiferromagnetic structure for $\text{Cr}_{1+\delta}\text{Sb}$. It crystallises in the hexagonal NiAs-type structure (space group: $P6_3/mmc$) with some additional partial occupation (≤ 0.14) of the interstitial site 2(d):

$$2(a) - 0,0,0; 0,0,1/2 \quad \text{and} \quad 2(d) - 2/3,1/3,1/4; 1/3,2/3,3/4,$$

Conventional X-ray diffraction cannot differentiate between chromium ($Z_{\text{Cr}} = 24$) and manganese ($Z_{\text{Mn}} = 25$) on these sites but yields important information on their overall occupation probabilities $M = (\text{Mn}, \text{Cr})$: $M_a M_d \text{Sb}$, where M_a stands for the occupation probability of site 2(a) and M_d for that of site 2(d). The Sb position is assumed to be fully occupied, thus serving as an internal standard.

The corresponding nuclear scattering lengths of neutron diffraction are extremely different with a negative sign for manganese: $b_{\text{Cr}} = +3.52 \text{ fm}$ and $b_{\text{Mn}} = -3.73 \text{ fm}$.

Remember: A positive value of b_j means that there is a phase shift of 180° between the incident and scattered neutron waves as a consequence of predominant potential scattering. The few negative b_j values - no phase change - result from resonant scattering.

The knowledge of the overall occupation probabilities M_a and M_d - from conventional X-ray studies - allows the evaluation of the Cr : Mn ratios of the different sites 2(a) and 2(d) from the corresponding effective scattering lengths determined by neutron diffraction. In the structure analyses based on the neutron data $b_{\text{eff}} = b_{\text{Mn}} \cdot \text{PP}$ is obtained individually for the two sites ($\text{PP}_a = a$ and $\text{PP}_d = d$ stands for refined pseudo occupation probabilities). According to $b_{\text{eff}}(2a) = a[(1-y) \cdot b_{\text{Mn}} + y \cdot b_{\text{Cr}}]$ and $b_{\text{eff}}(2d) = d[(1-z) \cdot b_{\text{Mn}} + z \cdot b_{\text{Cr}}]$ we can calculate $y = [b_{\text{eff}}(2a)/a - b_{\text{Mn}}] / [b_{\text{Cr}} - b_{\text{Mn}}]$ and $z = [b_{\text{eff}}(2d)/d - b_{\text{Mn}}] / [b_{\text{Cr}} - b_{\text{Mn}}]$. The detailed site occupations lead to the general formula $(\text{Mn}_{1-y}\text{Cr}_y)_a (\text{Mn}_{1-z}\text{Cr}_z)_d \text{Sb}$

site 2(a) site 2(d)

corresponding to a chemical composition of $\text{Mn}_{[(1-y)a + (1-z)d]} \text{Cr}_{[ya + zd]} \text{Sb}$. It is evident, that the individual (Cr,Mn) distribution on the two crystallographically different sites 2(a) and 2(d) is not accessible by a chemical analysis. For most of the samples studied, the site 2(a) was found to be fully occupied: $a \approx 1.0$. But the formula $(\text{Mn}_{1-x}\text{Cr}_x)_{1+\delta}\text{Sb}$ used normally is only correct for the special case of equal Cr : Mn ratios on both sites:

$$x = y = z \quad \text{and} \quad 1 + \delta = a + d.$$

The detailed information on the (Cr,Mn) distribution is needed to explain the magnetic properties of these intermetallic compounds, for which only the spins localised on

the 2(a) sites are involved in the magnetic ordering leading to a complex magnetic phase diagram. An overall Cr : Mn ratio from chemical analysis is not sufficient.

In general, a mixed occupation of one crystallographic site with three kinds of scatterers - e.g. Mn, Cr, and "vacancies" - requires at least two independent and sufficiently different experimental data to determine the fractional occupancies.

5. The Hydrogen Problem in Structure Analysis

The determination of the structure parameters of hydrogen atoms is a special problem involving different aspects of X-ray and neutron diffraction. It is obvious that H/D atoms with $Z = 1$ give only a small contribution to the electron density and, therefore, they are hardly visible in X-ray structure analyses. This holds especially when heavy atoms are present. But there is a more general problem: the single electron of H/D is engaged in the chemical bonding and is not localised at the proton/deuteron position. This position, however, is of importance when hydrogen bonds - eventually related to the lattice dynamics or structural phase transitions - are discussed.

X-ray studies of electron densities of simple molecular crystals, for which theoretical calculations for isolated molecules are possible, are of special interest in order to compare experimental and theoretical results for a better understanding of chemical bonding in crystalline solids. Molecular crystals consist normally of light atoms often including hydrogen. A combination with neutron diffraction experiments is important to determine the structure parameters of the H/D atoms properly. More generally, the structure analysis by neutron diffraction yields separately and independently from the X-ray data the structure parameters of all atoms including the mean square displacements due to static and dynamic (even anharmonic) effects. This complete information can be used in a so-called X-N synthesis to obtain experimental electron deformation densities from the measured X-ray Bragg intensities.

One of the most important fields of application of neutron diffraction is the determination of H/D sites and of their Debye-Waller factors. As an example for a study of a variety of hydrogen bonds, where the structure model was established by conventional X-ray analysis and neutron diffraction served especially to localise the hydrogen atoms, the case of fully deuterated $\text{Na}_2\text{S}\cdot 9\text{D}_2\text{O}$ was chosen [2]. Its crystal structure (non-centrosymmetric space group: $P4_122$ or $P4_322$) is dominated by discrete $[\text{Na}(\text{D}_2\text{O})_5]$ and $[\text{Na}(\text{D}_2\text{O})_4]$ spiral chains of $\text{Na}(\text{D}_2\text{O})_6$ octahedra. There are five different water molecules with O-D distances between 0.949 Å and 0.983 Å, and D-O-D angles from 104.6° to 107.5°. These water molecules are involved furthermore in six different O-D...S bridges to the S^{2-} ions. Details of the various O-D...O/S hydrogen bonds were combined with results from Raman spectroscopy from which the uncoupled O-D(H) stretching frequencies could be reasonably well assigned to the nine different O-D(H) groups of the crystal structure.

Remember: The scattering lengths of the proton and the deuteron are $b_H = -3.74$ fm and $b_D = +6.67$ fm, respectively. Their magnitudes are comparable to the average of all b_j magnitudes and, therefore, H/D can be considered as "normal" atoms for neutron diffraction. The different signs of b_H and b_D may be of interest in Fourier maps for contrast reasons. Experimental conditions like background and effective absorption are strongly affected by the huge and exceptional incoherent neutron scattering cross section of hydrogen ($\sigma_{\text{inc}}(\text{H}) = 79.7$ barns as compared to $\sigma_{\text{inc}}(\text{D}) = 2.0$ barns). Very often deuterated compounds are preferred in order to profit from the larger b_D value, but mainly to reduce the background from incoherent scattering. This volume-dependent background may become crucial for neutron powder diffraction experiments, for which normally sample volumes of more than 1 cm^3 are required.

The hydrogen problem is of special importance for structural phase transitions driven by proton ordering. As a well known example the ferroelectric transition in KH_2PO_4 (KDP) is presented. A characteristic feature of its crystal structure consists in the PO_4 groups linked by hydrogen bonds. At room temperature KDP crystallises in a tetragonal phase (space group: $I 4_2d$), where the protons in the $\text{O}\cdots\text{H}\cdots\text{O}$ bonds are dynamically disordered. At $T_C = 122$ K, KDP transforms to a ferroelectric phase of orthorhombic symmetry (space group: $Fdd2$) in which the protons order in short asymmetric $\text{O}-\text{H}\cdots\text{O}$ bonds [3].

6. Molecular Disorder

Disordered structures and pseudosymmetries related to dynamical reorientation and/or structural phase transitions are of great current interest. In principal, the dynamical disorder of molecules is due to the fact that the intermolecular bonds are very much stronger than the external ones between the molecular groups and the surrounding crystalline frame. It is obvious that the chemical bonding scheme predicts the symmetry of a crystal structure, and not the other way around. We can state, however, that in the case of an incompatible point group symmetry of a molecule with respect to its site symmetry in the crystal structure, molecular disorder is the necessary consequence. In order to modellize the atomic density distributions correctly in a way to obtain physically meaningful potentials, very accurate Bragg intensities over a large $\sin\theta/\lambda$ range are required. X-ray experiments are generally more restricted than neutron studies because of the $\sin\theta/\lambda$ dependence of the atomic scattering factor f_j .

As an example, related to the H/D problem, the dynamical disorder of the NH_3 group in the cubic high temperature phase of the metal hexamine halide $\text{Ni}(\text{NH}_3)_6\text{I}_2$ (space group: $Fm3m$) is presented. With the NH_3 tetrahedra ($3m$ symmetry) on crystallographic sites of $4mm$ symmetry it is obvious that they must be orientationally disordered. At 19.7 K, $\text{Ni}(\text{NH}_3)_6\text{I}_2$ undergoes a first order phase transition to a probably ordered rhombohedral low temperature modification [4].

Single crystal neutron diffraction studies at 35 K and 295 K [5] revealed a planar proton density distribution perpendicular to the four fold axes. Its four maxima are directed towards the neighbouring iodines according to the influence of $\text{N}-\text{H}\cdots\text{I}$ bonding. This

proton density can be explained as a consequence of a coupled rotational-translational motion of the ammine group.

7. Spin densities in magnetic molecular compounds

Molecular magnetic compounds are of great actual interest due to both, applicational perspectives and fundamental research. The spin density distribution is an essential information for the understanding of the magnetic properties of these materials; it yields the localisation of the magnetic electrons and give rise to the microscopic magnetic interactions. Polarised neutron diffraction on single crystals is presently the most powerful tool for determining the spin densities in molecular compounds [6]. Results obtained from a data treatment by the maximum-entropy reconstruction method are presented for the purely organic ferromagnet, β -4,4,5,5-tetramethyl-2-*p*-(nitro-phenyl)-3-oxido-4,5-dihydroimidazolium 1-oxyl (*p*NPNN) [7].

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