



Diffraction- powder, amorphous, liquid

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1. Introduction

Van Hove brought together in one simple equation the static structure factor, which we measure in diffraction experiments, and the collective excitations, which we measure in inelastic experiment. In 1954 Van Hove derived a general expression for the intensity, $I(\mathbf{Q}, \varepsilon)$, of neutrons scattered by any assembly of nuclei. The number of neutrons scattered per incident neutron can be written as:

$$I(\bar{\mathbf{Q}}, \varepsilon) = \frac{1}{h} \frac{k'}{k} \sum_{j,k} b_j b_k \int_{-\infty}^{\infty} \langle e^{-i\bar{\mathbf{Q}} \cdot \bar{\mathbf{r}}_k(0)} e^{i\bar{\mathbf{Q}} \cdot \bar{\mathbf{r}}_j(t)} \rangle e^{-i\varepsilon t} dt \quad (1)$$

Where $h\mathbf{Q} = h(\mathbf{k} - \mathbf{k}')$ is the neutron momentum transfer and $k = |\mathbf{k}|$ and $k' = |\mathbf{k}'|$ are neutron wave vector magnitudes before and after scattering process ($k = 2\pi/\lambda$). The $\mathbf{Q} = \mathbf{k} - \mathbf{k}'$ is known as scattering vector, b_j, b_k – scattering lengths of the nuclei placed at $\mathbf{r}_j(t), \mathbf{r}_k(t)$ -positions at time t , ε energy loss by neutron in the scattering process. The brackets $\langle \dots \rangle$ denote an average over all possible starting times for observation of the system which is equivalent to an average over all possible thermodynamic state of the sample.

Assuming that the scattering lengths of all atoms in the sample are the same ($b_j = b_k = b$) van Hove's neutron scattering law (Eq.1) can be written as

$$I(\bar{\mathbf{Q}}, \varepsilon) = \frac{Nb^2}{h} \frac{k'}{k} \sum_{j,k} b_j b_k \int_{-\infty}^{\infty} G(\bar{\mathbf{r}}, t) e^{-i\bar{\mathbf{Q}} \cdot \bar{\mathbf{r}}(0)} e^{-i\varepsilon t} d^3r dt \quad (2)$$

$G(\mathbf{r}, t)$ is time dependent pair-correlation function. This function is equal to the probability of an atom being at the origin of a co-ordinate system at time zero and atom being at position \mathbf{r} at time t .

$$G(\bar{\mathbf{r}}, t) = \frac{1}{N} \sum_{j,k} \langle \delta(\bar{\mathbf{r}} - [\bar{\mathbf{r}}_k(0) - \bar{\mathbf{r}}_j(t)]) \rangle \quad (3)$$

N is the number of atoms in the sample.

Eq.1 allows us to see that $I(\mathbf{Q}, \varepsilon)$, is proportional to the space and time Fourier transforms of the time dependent pair correlation function. The $I(\mathbf{Q}, \varepsilon)$, is simply the Fourier transform of a function that gives the probability of finding two atoms a certain distance apart. By inverting Eq.1 information about both structure and dynamics of condensed matter may be obtained from scattering law.

2. Diffraction

Diffraction is the principal technique for determining the atomic and molecular structure of materials. Important application of Van Hove's Eq.1 is the scattering law for diffraction. Even though diffraction is predominantly an elastic process ($\epsilon=0$) neutron diffractometer actually integrate over the energies of scattered neutrons. Diffraction is a coherent elastic process therefore Eq.1 has use the coherent neutron scattering amplitude, b_{coh} . The integration over ϵ gives another Dirac delta function, $\delta(t)$. For diffraction the pair correlation function, $G(\mathbf{r},t)$, has to be determined at $t=0$. For a crystal containing a single isotope

$$I(\bar{Q}) = b_{\text{coh}}^2 \sum_{j,k} \langle e^{i\bar{Q}(\bar{r}_j - \bar{r}_k)} \rangle \quad (4)$$

Where the atomic positions \mathbf{r}_j and \mathbf{r}_k are evaluated at the same instant. If the atoms are stationary thermal averaging in Eq.4 can be removed. In reality the atoms oscillate about their equilibrium positions \mathbf{r}_j and \mathbf{r}_k and only spend a fraction of their time at these positions. When this is taken into account, the thermodynamic average introduces another factor, called the Debye-Waller factor. The Eq.4 then becomes

$$I(\bar{Q}) = b_{\text{coh}}^2 \sum_{j,k} e^{i\bar{Q}(\bar{r}_j - \bar{r}_k)} e^{-\frac{1}{2}Q^2 \langle u^2 \rangle} \quad (5)$$

Where $\langle u^2 \rangle$ is the average of the square of the displacement of an atom from its equilibrium position. This procedure includes the effect of atomic vibrations in the diffraction cross section. $I(Q)=S(Q)$ is also called the structure factor. This equation is the basis of any crystallographic analysis of neutron diffraction data. For materials containing different nuclei and (or) magnetic moments one can find proper formula in e.g G. Bacon's revue.

3. Atomic structure of materials.

Determining the structure of materials remains the most powerful way to understand that material's properties. The standard tools of crystallographer are single crystal and powder diffraction. X-ray diffraction is basic tool for determining space groups and lattice spacing, while for liquids and amorphous materials their extended range of scattering vector \mathbf{Q} gives neutron the advantage. Forty years ago powder diffraction could not be used for solving a new crystal structure, but only for determination the presence of known crystalline phase in powders of unknown compositions. Nowadays it is possible after H. M. Rietveld developed a workable approach for resolving the ambiguities of most powder diffraction patterns. The technique known as Rietveld refinement is widely used in structure analysis of polycrystalline materials.

3.1. Ideal periodic crystals; powder

The density of scattering power, $\rho(\mathbf{r})$, is function of position, \mathbf{r} , within a matter. In crystal the function has to be periodic and it needs to repeat infinitely in all directions in order to match the

repetition of the unit cell of crystal.

$$\rho(\mathbf{r}) = \frac{1}{V_c} \sum_{\mathbf{h}} F_{\mathbf{h}} \exp[-i(\bar{\mathbf{Q}}_{\mathbf{h}} \cdot \bar{\mathbf{r}})] \quad (6)$$

where V_c is the unit cell volume, $F_{\mathbf{h}}$ is the amplitude of the Fourier component and $\mathbf{Q}_{\mathbf{h}} = 2\pi(\mathbf{a}^*h + \mathbf{b}^*k + \mathbf{c}^*l)$. $\mathbf{Q}_{\mathbf{h}}$ is perpendicular to \mathbf{h} plane in crystal. The \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* are the reciprocal lattice vectors.

A property of Fourier series is that they can be "inverted". In crystallography this transformation goes from the real space to the reciprocal-space description. Thus the inverse Fourier transform of Eq.6 gives the amplitude in terms of the scattering density.

$$F_{\mathbf{h}} = \int_{V_c} \rho(\bar{\mathbf{r}}) e^{i(\bar{\mathbf{Q}}_{\mathbf{h}} \cdot \bar{\mathbf{r}})} d\bar{\mathbf{r}} = \sum_{j=1}^n f_j e^{i(\bar{\mathbf{Q}}_{\mathbf{h}} \cdot \bar{\mathbf{r}}_j)} \quad (7)$$

The coefficient f_j is called the scattering factor of the atom. If $F_{\mathbf{h}}$ are known, one can calculate the scattering density $\rho(\mathbf{r})$.

The van Hove equation for elastic-scattering intensities is the convolution of Eq.7 with itself

$$S(\bar{\mathbf{Q}}_{\mathbf{h}}) \equiv I_{\mathbf{h}} = F_{\mathbf{h}} F_{\mathbf{h}}^* = \sum_{j,k} f_j f_k^* e^{i\bar{\mathbf{Q}}_{\mathbf{h}} \cdot (\bar{\mathbf{r}}_j - \bar{\mathbf{r}}_k)} \quad (8)$$

$I_{\mathbf{h}}$ is measured scattering intensity at $\mathbf{Q}=\mathbf{Q}_{\mathbf{h}}$. Elastic scattering experiments directly measure the $|F_{\mathbf{h}}|^2$, the squares of the magnitudes of the structure factors.

Since for elastic scattering the initial and final wave vector are equal in magnitude $k=k'$, all the possible \mathbf{k}' fall on the surface of the sphere with radius $2\pi/\lambda$, commonly called the Ewald sphere. Polycrystalline material, powder, consists of multitude of small crystals, therefore the Ewald construction for a single crystal has to be modified. The main problem with this technique is that only for very simple structures are the diffraction peaks in a powder pattern sufficiently separated to allow measurement of individual peak intensities. The peaks are usually so heavily overlapped that extraction of individual peak intensities is impossible, and the magnitudes of most of the individual structure factor are unknown.

About thirty years ago H. M. Rietveld suggested a solution to this problem. He recognised that a mathematical expression could be written to represent the observed intensity I_c at every position \mathbf{Q} in a powder diffraction pattern:

$$I_c(\bar{\mathbf{Q}}) = I_b(\bar{\mathbf{Q}}) + \sum I_{\mathbf{h}}(\bar{\mathbf{Q}}) \quad (9)$$

This expression has contribution from the background $I_b(\mathbf{Q})$ and from each $\mathbf{Q}_{\mathbf{h}}$ that are in the vicinity of \mathbf{Q} . Real powder pattern has line broadening, so diffraction from the planes labelled by \mathbf{h} contributes not only at $\mathbf{Q}_{\mathbf{h}}$ but at all nearby \mathbf{Q} . In the Rietveld method one models the observed pattern by considering the factors that effect both the affect both line shape and its intensity. The adjustable parameter are then refined by a non-linear least-square process. The $|F_{\mathbf{h}}|^2$ parameters obtained from the fit are a reconstruction of the real $|F_{\mathbf{h}}|^2$; the parameters for line broadening and anisotropy provide information about particle size, structural defects and other phenomena that

distort the ideal Bragg pattern.

In order to solve unknown crystal structure it is possible now to do Rietveld refinement simultaneously for X-ray and neutron powder diffraction patterns . If the refinement produces calculated pattern that match both a neutron powder pattern and a X-ray powder pattern, that

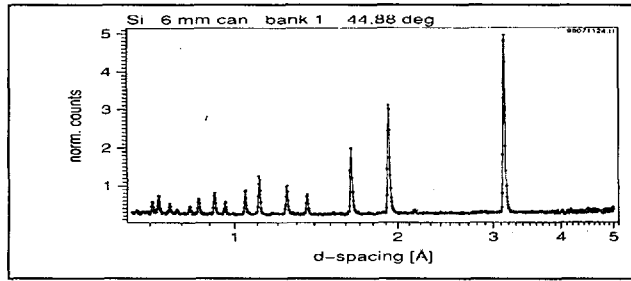


Fig. 1. Neutron diffraction diagram of polycrystalline Si (W. Kokelmann, Rotax, ISIS, 1999) Points-experimental results, curve- fit using GSAS programme.

model is more likely to be correct. Powder diffraction has become a standard technique for the detection and identification of crystalline phases, for quantitative determination of their volume fraction in mixed-phase sample. It is also being used more often to solve problems of structure determination and refinement that have long time been the exclusive domain of single crystal diffraction. Powder diffraction is used also to characterised the composition (stoichiometry), the structural disorder, microstructure e.g. microstrain and domain size of any crystalline material.

3.1.2 Neutron diffraction from disordered materials

Materials can have varying degrees of disorder.

The neutron diffraction technique can be used to measure the structure of atoms and molecules in disordered materials.

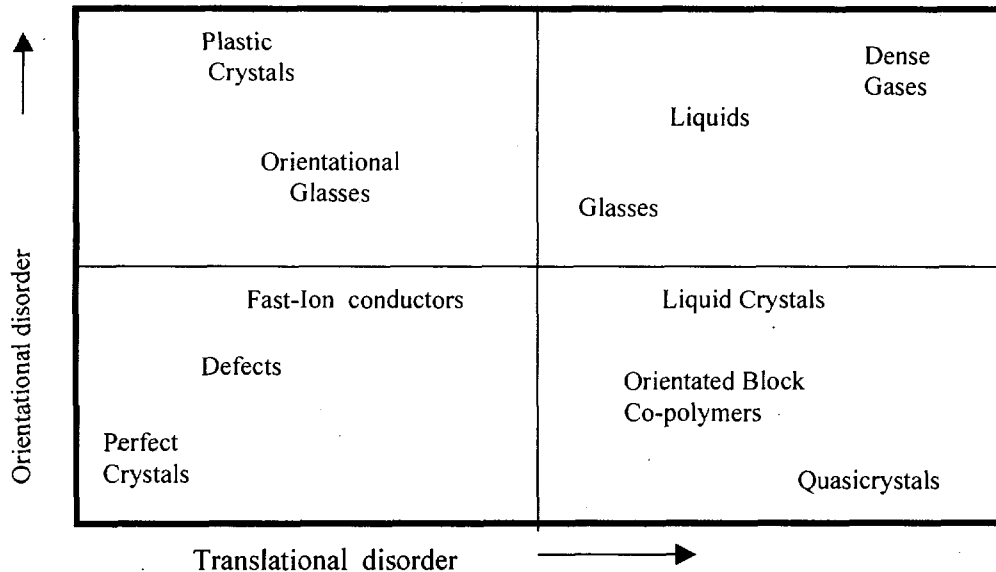


Fig. 2 Materials have varying degrees of disorder (C. Benmore)

Although there is no long-range order in a liquid there is still short range ordering over a few atoms or molecule lengths. Glasses can also have medium range ordering over a several atomic lengths. The measured diffraction pattern is related to the positions of the atoms relative to each other in the liquid or glass.

In diffraction experiments intensity as a function of scattering vector \mathbf{Q} is investigated. For a polycrystalline solid $S(\mathbf{Q})$ shows many Bragg peaks appearing at $\mathbf{Q}_h = \mathbf{k} - \mathbf{k}'$ (see e.g. Fig.1). For liquids and amorphous solid $S(\mathbf{Q})$ is a continuous function, which goes to one as $\mathbf{Q} \rightarrow \infty$.

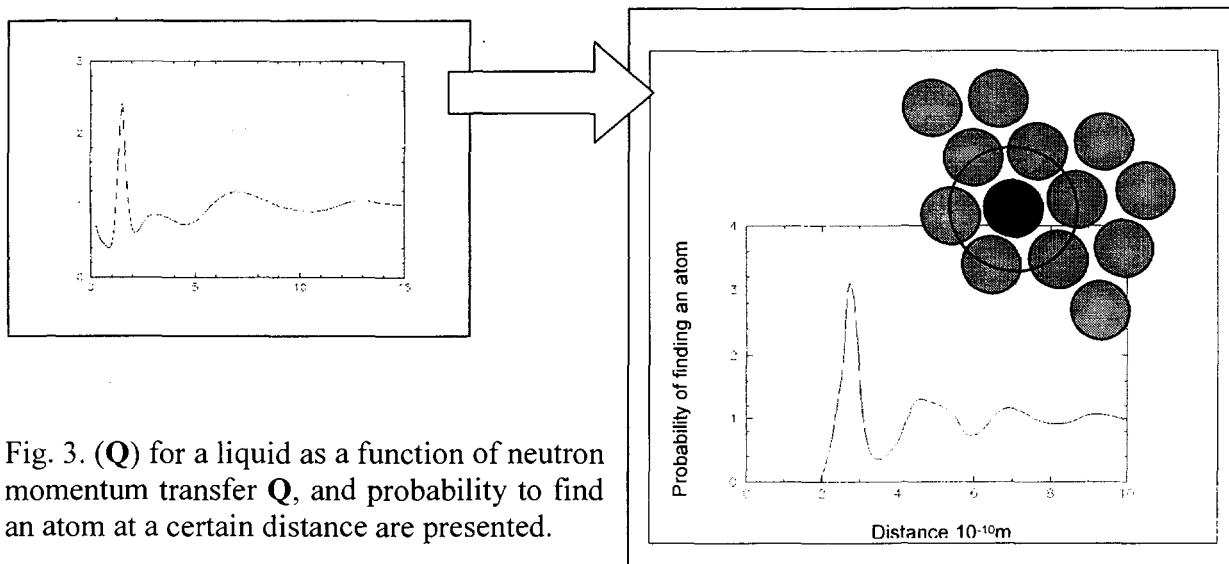


Fig. 3. $S(\mathbf{Q})$ for a liquid as a function of neutron momentum transfer \mathbf{Q} , and probability to find an atom at a certain distance are presented.

The angular dependence of the energy integrated intensity $S(\mathbf{Q})$ reflects the spatial arrangements of atoms $\rho(r)$ of the atoms (the $\rho(r)$ is the density function). In Fig. 3 schematic $S(\mathbf{Q})$ is presented for liquid state when only short range order is present. Fluids or amorphous solid shows usually only an indication of peaks in $S(\mathbf{Q})$ as one can see in Fig.3. For a gas phase $S(\mathbf{Q})=1$, which reflects lack of correlation between atoms.

Whenever disorder affects the crystalline structure of material extra diffuse scattering appears in diffraction pattern. There are different type of disorder in a real crystal e.g. displacement disorder or (and) substitution disorder. A very simple model of so called "mean periodic structure" of disordered lattice was developed. Due to disorder, the whole crystal does not contribute coherently to the diffraction line as in a case of a perfect periodic structure. Bragg peaks remain sharp and well defined, only their intensity being affected by the disorder. An attenuation of the Bragg maximum by the "effective" Debye-Waller factor contains both static and dynamical contributions. An extra scattering, so-called diffuse scattering is distributed rather uniformly in the reciprocal space of crystal. The diffuse scattering is a consequence of disorder of the perfect periodic structure of a crystal. Diffuse scattering usually contributes to background of diffraction pattern of polycrystalline materials. Neutron diffuse scattering is nowadays investigated in order to determine different types of disorder in solids.

There are books and reviews describing scattering of radiation in periodic media. Usually they contain description of X-rays and neutron diffraction techniques and their applications in determination of crystal and magnetic structure of different materials.

3. Very high resolution powder diffraction.

There are two methods used in diffraction technique of polycrystalline materials. Both of them are using Bragg's law.

$$\lambda = 2 d_{hkl} \sin \theta \quad (10)$$

where (hkl) are the Miller indices associated to the interplanar d-spacing, λ is neutron wavelength and 2θ is the scattering angle (the angle between \mathbf{k} and \mathbf{k}').

In the first method the constant wavelength, λ , is used and the angular distribution of monochromatic neutrons from the sample is measured. The double axis neutron spectrometer (DAS) used in this study is very similar to this used in X-rays traditional diffraction and even formulae for intensities of scattered radiation are almost the same for two radiation.

In the time of flight (TOF) method pulsed neutron beam is scattered on polycrystalline sample and the intensity of the scattered neutrons at a fixed angle 2θ is measured as a function of time.

As it was mentioned earlier the high-resolution neutron diffraction is essential for crystal structure investigations when only polycrystalline material is available. Nowadays the best resolution $\Delta d/d = 5 \times 10^{-4}$ (d-lattice spacing) was achieved with TOF, HRPD diffractometer at ISIS neutron spallation source. A scheme of the HRPD is presented in Fig.4.

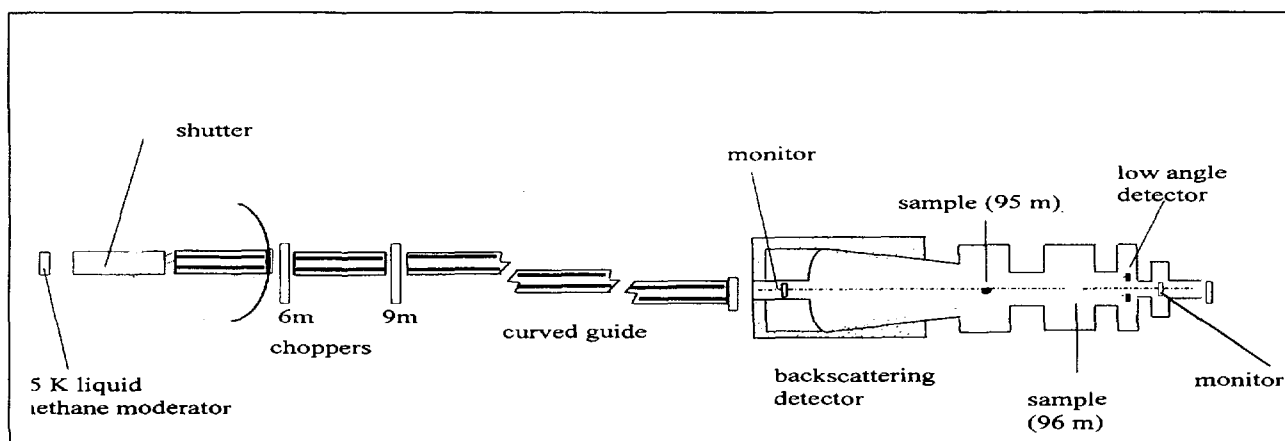


Fig. 4. Scheme of the HRPD diffractometer at ISIS (ISIS User Book)

As it was shown the TOF method is unique for investigation of structure with very large periodicity e.g. a modulated magnetic structures.

In Fig. 5. example of diffraction on such a study is presented. In Fig.5 the neutron diffraction pattern of polycrystalline BiFeO_3 , containing the (101) and (003) magnetic reflections obtained by using different neutron diffractometers: (a) the TOF-HRPD diffractometer at, ISIS, Rutherford-Appelton Laboratory and (b) the DAS are presented. Each pattern was received using the best resolution achieved nowadays. Such high-resolution diffraction diagram is only possible to receive when "ideal polycrystalline material" is available. Information on the magneto-electric coupling effect in BiFeO_3 can only be obtained when the intensity of the maxima in the span (101) (see Fig. 5a) can be determined.

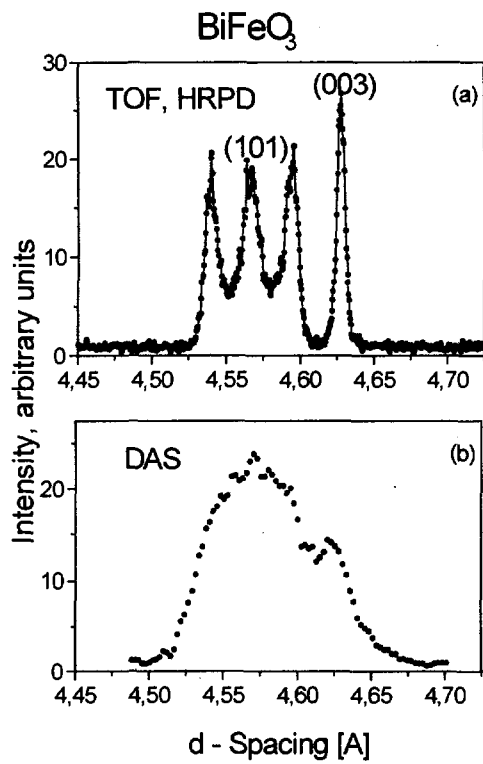


Fig.5 Magnetic neutron diffraction maxima of BiFeO₃ (ferroelectric antiferromagnet).

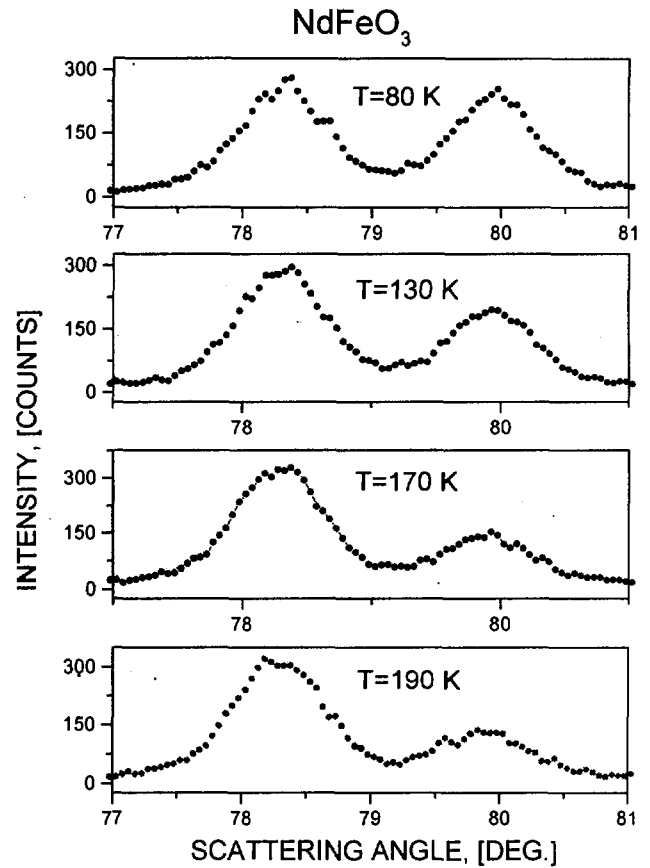


Fig. 6. Neutron diffraction experiment (DAS). The intensity ratio of the two maxima is changing in the reorientation process of magnetic moments of Fe³⁺ ions (I.S., E. Steichele, A. Hewat)

High-resolution neutron diffraction (DAS) was also used for investigation of reorientation of magnetic moment of Fe³⁺ ions in NdFeO₃. The results are presented in Fig. 6.

High resolution neutron diffraction permits also to investigate many phenomena in material science such as phase transitions, magneto-electric effect, GMR, reorientation phase transitions etc.

Neutron powder diffraction is applied also for texture and strain determination in polycrystalline materials. There are many advantages of neutron technique over conventional stress and texture measurement techniques:

- as a non-destructive non-contacting method applicable to nearly all crystalline materials, it can provide sub-surface information not obtainable by any other technique.
- it is much faster than conventional destructive methods
- because the stress state is not disturbed by the measurement, complicated corrections to the data are not required.

A special TOF diffractometer at ISIS, ENGIN, was constructed for a stress and texture investigation.

4. Summary

Abs. Neutron powder diffraction is a unique tool to observe all possible diffraction effects appearing in crystal. High-resolution neutron diffractometers have to be used in this study. Analysis of the magnetic structure of polycrystalline materials requires the use of high-resolution neutron diffraction (λ/d (where d is the interplanar distance)) in the range of large interplanar distances. As distinguished from the double axis diffractometers (DAS), which show high resolution only at small interplanar distances, TOF diffractometry offers the best resolution at large interplanar distances.

(time-of-flight)

General Texts

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