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On the Use of Neutron Spin-Echo to Separate Inelastic Scattering from Elastic Scattering at High Energy Resolution

BY J. B. HAYTER, M. S. LEHMANN, F. MEZEI* AND C. M. E. ZEYEN

Institut Laue–Langevin, 156 X, 38042 Grenoble CEDEX, France

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Abstract

Generally the measured intensity of a Bragg peak or of elastic diffuse scattering contains an inelastic component (thermal diffuse scattering, low-lying phonon branches). Theoretical corrections for such effects are only possible in the limited number of cases where appropriate data are available. An experimental correction is difficult because the high energy resolution imposed reduces the beam intensity in a conventional experiment. In the case of neutron diffraction, the spin-echo technique proposed by Mezei [*Z. Phys.* (1972), **255**, 146–160] for neutron spectroscopy can be used as a filter for inelastic scattering without significant loss in elastic intensity. The application of the technique to an elastic neutron-scattering experiment is described, and it is shown that for a neutron wavelength of 1·5 Å an energy resolution of better than 50 μeV can be obtained. With this energy band-pass, scattering even from very soft phonons or magnons can be avoided when studying critical scattering near phase transitions. Simple estimates also imply that more than 90% of the TDS contribution can be removed even for soft materials.

Introduction

In recent years emphasis has been put on precise determination from diffraction data of atomic positions and thermal-motion parameters. The aim has been to determine charge density distribution by combining data obtained with both X-ray and neutron radiation, or to study the atomic distribution arising from disorder or thermal motion. Likewise there is a growing interest in the study of elastic diffuse scattering and its relationship to structural disorder and phase transitions. The problem of the separation of inelastic scattering arises mainly in cases where the elastic scattering of interest occurs in the vicinity of a reciprocal lattice point, that is to say close to or under a Bragg peak. This is the case for diffuse scattering from lattice distortions due to defects for example. Similar problems arise when critical scattering has to be measured near a structural phase transformation in the presence of a soft excitation. A main obstacle to a successful outcome of such studies is the occurrence of thermal diffuse scattering (TDS). If squared structure amplitudes are observed, the total effect from TDS can be expressed as (Cochran, 1969; Willis & Pryor, 1975)

$$|F(\mathbf{H})|_o^2 = |F(\mathbf{H})|^2(1+\alpha),$$

where $|F(\mathbf{H})|_o$ is the observed structure amplitude with lattice vector $\mathbf{H}$ (corrected for other effects such as absorption and extinction), $|F(\mathbf{H})|$ is the structure amplitude we aim to obtain, and α gives the TDS contribution.

The estimation of α has been discussed extensively (for a review see Willis & Pryor, 1975). The main contribution to α comes from scattering processes where low-energy (acoustic) phonons are created by or scatter the radiation, and we then approximate α by (Cochran, 1969)

$$\alpha = \frac{K_B T}{NV\rho} \sum_{\mathbf{q}} J(\mathbf{q}), \tag{1}$$

where the sum is over all wavevectors $\mathbf{q}$ of phonons for which scattering can take place, K_B is the Boltzmann constant, T the absolute temperature, N the number of unit cells of volume V in the crystal and ρ the density. $J(\mathbf{q})$ can be expressed as

$$J(\mathbf{q}) = \sum_j \frac{[(\mathbf{q}+\mathbf{H}).\mathbf{e}_j(\mathbf{q})]^2}{\omega_j^2(\mathbf{q})}, \tag{2}$$

where $\mathbf{e}_j(\mathbf{q})$ is a unit vector in the direction of polarization of the mode with frequency ω_j, and the sum is over the acoustic phonons. To do the calculation a series of approximations are normally made. One common approach is to assume an isotropic solid (Nilsson, 1957; Cooper, 1971) with $\omega(\mathbf{q}) = v|\mathbf{q}|$ where v is a mean velocity. We can then write

$$J(\mathbf{q}) \simeq \frac{|\mathbf{H}|^2}{v^2|\mathbf{q}|^2}. \tag{3}$$

* Permanent address: Central Research Institute for Physics, Budapest, Hungary.

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(1) and (3) show the common features of TDS. The contribution is proportional to $|\mathbf{H}|^2 = (2 \sin\theta/\lambda)^2$ so that neglect of TDS will tend to bias the thermal parameters (Cooper & Rouse, 1968). The effect is proportional to T (assuming no changes in physical behaviour of the crystal with temperature) so it can be lowered by cooling. This however also decreases the thermal parameters, so that over a wide range of temperature the relative error in the parameters is constant. Finally, we notice from (3) that $J(\mathbf{q})$ peaks for $\mathbf{q} \to 0$, and as the origin of the vector $\mathbf{q}$ is the end-point of the lattice vector $\mathbf{H}$ a significant contribution from TDS will be found inside the Bragg peak.

Two ways of correcting for TDS are open. The α can be calculated by integration over $J(\mathbf{q})$. This requires knowledge of the dynamic characteristics of the material to obtain $\omega_j(\mathbf{q})$ and $\mathbf{e}_j(\mathbf{q})$, as well as a knowledge of instrumental resolution. The necessary dynamical quantities are only available for a limited number of compounds. Removal of TDS by experimental techniques is another possibility, and the normal way would be to perform an energy analysis of the diffracted beam. This has been achieved for X-rays with Mössbauer resonance techniques to filter out the radiation which has changed energy (O'Connor & Butt, 1963; Butt & O'Connor, 1967) and can be done for neutrons by employing a standard triple axis spectrometer, where the inelastically scattered radiation is removed by the analyser crystal of the spectrometer. Unfortunately in the latter case a sufficient energy resolution is obtained only by drastically sacrificing beam flux, which renders the method impractical for the determination of Bragg intensities even with a high flux beam reactor as source. In addition the estimate of elastic intensities is then affected by the wavelength band-pass of the analyser crystal, and this can well introduce errors comparable to the TDS eliminated. Elastic diffuse scattering which is still detectable at some distance from a Bragg peak [such as, for example, Huang scattering (Peisl, 1975)] may in certain cases be discriminated from inelastic contributions by classical three-axis methods (Burkel, Von Guerard, Metzger, Peisl & Zeyen, 1979). However, in general such experiments require further improved energy resolution to eliminate inelastic scattering. In order to filter out TDS in the case of neutron diffraction a different approach is therefore needed. The experiment should fulfil the following conditions:

1. The intensity impinging on the crystal should be sufficiently high to ensure reasonable measurement times.

2. A strict requirement on energy resolution should not impose any restriction on the elastic resolution function, so that the elastic scattering process is either identical to the case where no energy resolution is demanded or is independently adjustable.

We believe that these conditions can be met by the neutron spin-echo technique (Mezei, 1972) and we describe below the possible experimental arrangement. We shall consider a neutron wavelength of 1·5 Å. Although this is somewhat longer than is generally acceptable for high-resolution diffraction work, this is at present the shortest wavelength for which the experiment proposed is certainly feasible. The limitation arises from the necessity to use polarizing mirror techniques. In the light of the significant progress made in these techniques in recent years (Mezei & Dagleish, 1977; Saxena & Schoenborn, 1977; Gukasov, Ruban & Bedrizova, 1977) we do not believe the present wavelength limitation is significant.

A spin-echo filter diffractometer

The experimental arrangement is shown in Fig. 1. A spin polarizer P_1 and analyser P_2 have been added to a three-axis diffractometer together with magnetic guide fields H_1, H_2 and four $\pi/2$ spin-turn coils. The polarizer and analyser operate by mirror reflection and do not in principle affect the beam distribution. Hence they may be incorporated into the diffractometer geometry as a simple, fixed offset in monochromator/sample and sample/analyser angles. If neutron supermirrors are used (Mezei & Dagleish, 1977) this offset angle will be of the order 0·7° at 1·5 Å. In addition a vertically focusing crystal analyser can be placed before the detector in order to concentrate the beam on the detector surface, as the distances in the diffractometer have been increased by the addition of the guide fields. This analyser works in a mirror mode, and should not affect the wavelength band-width. In certain diffuse scattering cases it can be used to further reduce this band-width if necessary.

We will follow a neutron through an elastic scattering process. After it has left the polarizer P_1 its spin $\frac{1}{2}$ will be aligned with the magnetic guide field H_1. At the first $\pi/2$ spin-turn coil we turn the neutron spin so that it is orthogonal to the guide field, which for simplicity we shall assume is orthogonal to the horizontal plane.

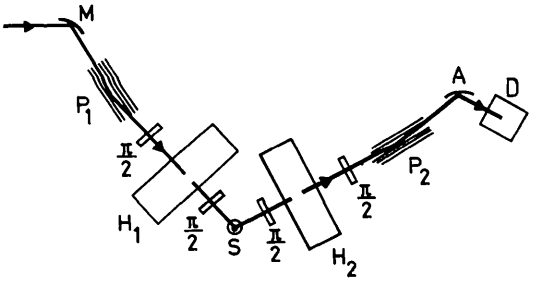

Fig. 1. Schematic arrangement of a spin-echo filter on a three-axis diffractometer, M: focusing crystal monochromator, A: focusing crystal analyser, P_1, P_2: spin polarizer and analyser, D: detector, S: sample, $\pi/2$: spin-turn coils, $\mathbf{H}_1$, $\mathbf{H}_2$: guide-fields.

The neutron spin will now be lying in the horizontal plane, and will therefore precess around the guide field with the Larmor frequency

$$\Omega_L = \frac{4\pi\mu_n}{h} H = 2{\cdot}303 \times 10^2 H \text{rad.s}^{-1},$$

where μ_n is the neutron magnetic moment and h is Planck's constant. H is measured in A m^{-1}. In this manner we have assigned to each neutron an internal clock. After a passage of d(m) in a uniform field the number of precession turns for a neutron with wavelength λ (Å) is

$$N = \frac{2\mu_n m}{h^2} \lambda \int_0^d H\,\mathrm{d}l = \frac{\lambda}{1{\cdot}08 \times 10^2} \int_0^d H\,\mathrm{d}l,$$

where m is the neutron mass, and the neutron velocity (which is inversely proportional to λ) has been used to calculate the time spent in the precession region.

Before the scattering process takes place we turn off the precession by bringing the spin back to the vertical direction with a $\pi/2$ spin-turn coil. This is to avoid problems in the sample region due to field inhomogeneities caused by the sample Eulerian cradle. After the sample the $\pi/2$ turn process is repeated, but this time the guide-field is oriented so that the spin precesses in the sense opposite to that in the first arm. If the two guide-fields are identical, and if the neutron velocity is unaltered on scattering, then on arrival at the last spin-turn coil the net accumulated number of spin-turns is zero. Clearly neutrons with different velocities execute different numbers of turns, but because of the field reversal at half way the start and end spin-configurations for all neutrons are identical. This is the principle of neutron spin-echo focusing (Mezei, 1972). We can finally turn the spin back to vertical with the last $\pi/2$ spin-turn coil, and the neutron will pass the spin analyser P_2, which is identical to the polarizer.

If the neutron undergoes an inelastic process the velocity changes at the sample, the number of spin-turns executed in the two arms are different, and the vertical spin component, P_Z, before the analyser is changed. Use of a sufficiently large number of spin-turns will eventually completely randomize the spin distribution of inelastically scattered neutrons and bring the mean Z-spin component for these neutrons to zero. An analysis of the P_Z component will then reveal the proportion of inelastic scattering events occurring, and we can thus filter out this part of the observations.

The energy resolution of the filter

Following Mezei (1972) the Z component of a neutron just before the final analyser will be

$$P_Z = \cos(2\pi N_1 - 2\pi N_2). \tag{4}$$

N_1 and N_2 are the number of precessions of the neutron in the two identical guide fields

$$N_1 = \frac{1}{1{\cdot}08 \times 10^2} \lambda \int_0^d H\,\mathrm{d}l \tag{5}$$

and

$$N_2 = \frac{1}{1{\cdot}08 \times 10^2} (\lambda + \Delta\lambda) \int_0^d H\,\mathrm{d}l,$$

where $\Delta\lambda$ is the wavelength change of the neutron upon scattering by the sample. For $\Delta\lambda$ small this is given by $\Delta\lambda/\lambda \simeq -\omega/2E$ where E is the incoming neutron energy and ω the energy change on scattering. $\int_0^d H\,\mathrm{d}l$ is the line integral of the field magnitude along a neutron path of length d.

P_Z can then be written as

$$P_Z = \cos\left(2\pi N_1 \frac{\Delta\lambda}{\lambda}\right)$$

$$= \cos\left(\frac{\pi N_1}{E}\omega\right). \tag{6}$$

To obtain the final value of P_Z seen by the analyser we have to integrate over all possible energy transfers ω and the incoming neutron wavelength band $f(\lambda)$

$$\langle P_Z \rangle = \frac{1}{\int f(\lambda)\,\mathrm{d}\lambda \int \mathrm{d}\omega S(\omega)} \int f(\lambda)\mathrm{d}\lambda$$

$$\times \int \mathrm{d}\omega S(\omega) \cos\left(\frac{\pi N_1}{E}\omega\right)\mathrm{d}\omega, \tag{7}$$

where $S(\omega)$ is the scattering function of the sample. For a sharp wavelength band $f(\lambda)$ and small energy transfers ω, (7) can be written in the following simpler form:

$$\langle P_z \rangle = \frac{1}{\int_{-\omega}^{\infty} S(\omega)\,\mathrm{d}\omega} \int_{-\infty}^{\infty} S(\omega) \cos\left(\frac{\pi N_1}{E}\omega\right)\mathrm{d}\omega. \tag{8}$$

Our remaining task is to calculate how big N_1 must be in practice for realistic suppression of TDS. For the purpose of numerical estimation we shall take $S(\omega)$ at a lattice point as a Bragg peak $\delta(\omega)$ superimposed on a Lorentzian distribution of thermal diffuse scattering, $L(\omega)$:

$$S(\omega) = (1 - \tau)\,\delta(\omega) + \tau L(\omega), \tag{9}$$

where

$$L(\omega) = \frac{1}{\pi} \frac{\omega_0}{\omega_0^2 + \omega^2}, \tag{10}$$

with half-width at half-height ω_0, τ being the relative intensity of the TDS. Equations (8)–(10) then give

$$\langle P_z \rangle = (1 - \tau) + \tau \exp\left(-\frac{\pi N_1}{E}\omega_0\right).$$

The exponential term represents contributions from inelastically scattered neutrons where the velocity change and the total number of spin-turns are insufficient to randomize the spin distribution for these neutrons. We shall require that this term be <1%, giving, for the worst case, where τ would be equal to 1:

$$\exp\left(-\frac{\pi N_1}{E}\omega_0\right) \leq 0{\cdot}01, \tag{11}$$

so that

$$N_1 \geq 1{\cdot}47\frac{E}{\omega_0}. \tag{12}$$

N_1 gives the number of spin-turns necessary to more than 99% randomize the Lorentzian distribution with half-width ω_0; and we have then obtained a filter that is effective for scattering process with $\omega > \omega_0$. The term ω_0 is the effective energy resolution.

Taking $E_0 = 36$ meV corresponding to 1·5 Å neutrons and arriving at a resolution $\omega_0 = 50$ μeV then gives $N_1 > 1056$ precessions. From (5) this corresponds to a field integral of $7{\cdot}6 \times 10^4$ A delivered by H_1 and H_2 which may be easily achieved with a magnet producing $2{\cdot}39 \times 10^5$ Am^{-1} (3 kOe) over 0·32 m. The measured polarization will then be given to better than 1% by

$$\langle P_z \rangle = 1 - \tau, \tag{13}$$

where τ is the fraction of TDS having an energy transfer > 50 μeV.

For a given diffractometer setting and constant guide-fields $H_1 = H_2$, spin-echo intensities I^E and $\bar{I}^E$ are measured with the current in the last $\pi/2$ coil respectively positive and negative. The polarization is then

$$\langle P_z \rangle = \frac{I^E - \bar{I}^E}{I^E + \bar{I}^E} P_1 P_2, \tag{14}$$

where P_1 and P_2 are the polarizer and analyser efficiencies. Further details are given by Hayter (1978). Comparing $\langle P_z \rangle$ observed this way with $\langle P_z \rangle$ when the spin-echo filter is turned off and using (13) we can estimate the TDS for each point in the crystallographic scan.

Finally we shall estimate for a soft crystal the amount of TDS not removed by the filter when measuring structure amplitudes. We shall use the approximation of a spherical scan (Pryor, 1966), which gives a correction factor

$$\alpha(\mathbf{q}) = \frac{|\mathbf{H}|^2 K_B T q}{2\pi^2 v^2 \rho}, \tag{15}$$

where q is the limit of the scan. The data used are from a study of hexamethylenetetramine (Dolling, Pawley & Powell, 1973). The average value of the slope of the acoustic-phonon dispersion relations is 15 meV/Å^{-1}. With $\omega_0 = 50$ μeV the spin-echo filter will be effective for q larger than $q_e = 3{\cdot}3 \times 10^{-3}$ Å^{-1}. A typical scan range covering a good part of the TDS is $\Delta\theta = 1{\cdot}4°$ corresponding to a maximum q, q_m, of 0·1 Å^{-1}. The amount of TDS not removed is then given as $\alpha(q_e)/\alpha(q_m) = q_e/q_m = 0{\cdot}03$, so even for soft materials we can remove more than 90% of the thermal diffuse scattering.

Conclusion

A method for removal of inelastic components in neutron diffraction experiments has been proposed. This method uses precessions of the magnetic spin of the neutron for estimates of energy changes, and energy analysis of the diffracted beam should therefore be decoupled from the elastic resolution function. This means that the neutron flux on the sample crystal can be kept at reasonable values and that methods for estimates of intensities are comparable with standard diffraction methods.

Presently the method is only applicable for wavelengths equal to and longer than 1·5 Å. This of course reduces its applicability in many cases of interest in structure analysis. It is, however, applicable to a wide range of studies where observations of pure elastic scattering is needed.

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