Elastic Diffuse Scattering of Neutrons as a Tool for Investigation of Non-magnetic Point Defects

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Valuable information on the interatomic forces and energies in solids can be drawn from scattering experiments on crystals containing randomly distributed defects. However, defect concentrations usually have to be kept small to ensure random distribution and this is one of the reasons for a generally low signal. Neutrons can be used with advantage for such investigations if the incoherent-scattering cross section of the host material is small. The particular properties of slow neutrons make it possible to apply a number of experimental methods to obtain the desired information. Variation of incident energy and resolution in momentum space, the use of different isotopes as defects and—in particular if the experiments have to be done at high temperatures—analysis of the energy of the scattered neutrons may help to compensate for the usually low luminosity of neutron sources as compared, e.g., to X-ray tubes. Careful design of the sample’s environment and appropriate choice of experimental parameters allow measurements on samples with defect concentrations down to 0.1 at. % and at temperatures up to several hundred Centigrade. Experimental facilities of this type have been installed in Jülich and in Grenoble. The results obtained so far on various alloy systems show that considerable success is possible.

I. Introduction

Point defects in a crystal give rise to coherent elastic scattering of X-rays and neutrons into the regions between Bragg reflexions. The scattering far away from Bragg peaks is sensitive to the atomic configuration in the immediate neighbourhood of the defect and therefore allows the investigation of the distribution of the forces exerted by the defect on its close neighbours. Several reviews dealing with the theory of diffuse scattering have been published, e.g., Krivoglaz (1969) and Dederichs (1973). Considerable experimental information has been collected on concentrated alloys. As reviewed by Schmatz (1973), so far only few results have been obtained by scattering experiments on non-magnetic point defects in dilute solution. This is mainly due to considerable difficulties in separating the extremely weak signal from the usually high background. First results, however, seemed very promising (Schmatz, 1970) and the need for more detailed information and more extensive investigations was evident.

In view of the fact that the luminosity of X-ray tubes is several orders of magnitude higher than that of a reactor, it seems at first sight very daring to study small concentrations of point defects with neutrons. However, the drawback of low neutron luminosity is at least partly compensated by the use of bigger samples in cases of small incoherent and absorption cross sections.

Working with neutrons offers several additional possibilities: energy analysis, easy variation of incident energy, use of isotopes and elimination of surface effects lead to clearer and more detailed information in certain cases.

As a basis for the discussion of various experimental questions we start with a short outline of the theoretical framework, which we present in a form suitable for our purpose.

II. Theoretical framework

The double differential scattering cross section for thermal-neutron scattering is given by (e.g., Marshall & Lovesey, 1971)

\[
\frac{d^2\sigma}{d\Omega d\omega} (\mathbf{k}, \omega) = \frac{k_1}{k_0} \left\{ \frac{\sigma_{\text{inc, v}}}{\tau} 4\pi S_{\text{inc, v}} (\mathbf{k}, \omega) 
+ \sum_{\nu} b_\nu b_\nu S_\nu (\mathbf{k}, \omega) \right\}.
\]

\(h\mathbf{k}_0\) and \(h\mathbf{k}_1\) are the momenta of the incoming and outgoing neutrons, \(h\mathbf{k} = h(k_0 - k_1)\) is the momentum transfer and \(h\omega = h^2(k_0^2 - k_1^2)/2m\) is the energy transfer to the lattice. \(m\) is the mass of the neutron. \(b_\nu\) and \(b_\nu\) are the coherent scattering lengths of the elements and \(\sigma_{\text{inc, v}}\) is the incoherent-scattering cross section. The scattering functions \(S_{\text{inc, v}}\) and \(S_\nu\) can be visualized as Fourier transforms in space and time of the self-correlation function and the pair-correlation function of the system under investigation. The static and dynamic properties of the system are contained in these quantities. The summations are extended over the different elements in the sample.

An expansion of the scattering functions with respect to \(\mathbf{k}, \nu(t)\), where \(\nu(t)\) is the time-dependent displacement of the atoms due to thermal motion, gives the contributions arising from the simultaneous excitation or annihilation of different numbers of phonons in the
scattering process. As we are dealing with static properties of the sample, we only keep the first term of this expansion which contains $\delta(q)$ and gives the elastic-scattering cross sections. In this part of the scattering cross section the thermal motions show up through the Debye-Waller factor $\exp(-W)$.

For substitutionally dissolved defects in a binary alloy, the coherent elastic-scattering cross section is then

$$
\frac{d\sigma}{d\Omega}(\mathbf{k}) = \frac{1}{N} |b_H \exp(-W_H)\sum_m N_m \exp[i\mathbf{k} \cdot (\mathbf{r}_m + \mathbf{u}_m)] + \sum_j |b_D \exp(-W_D,j) - b_H \exp(-W_H)\sum_m c'_m \exp[i\mathbf{k} \cdot (\mathbf{r}_m + \mathbf{u}_m)]|^2.
$$

(2)

$N$ is the number of atoms in the sample, $b_H$, $b_D$, $\exp(-W_D,j)$ and $\exp(-W_H)$ are the scattering lengths and the Debye–Waller factors of the host and impurity atoms, respectively. $\mathbf{r}_m$ denotes the equilibrium positions of the regular reference lattice homogeneously expanded owing to the defects, $m$ is the counting index of the atoms. $\mathbf{u}_m$ is the static displacement with respect to the expanded reference lattice of an atom on site $\mathbf{r}_m$ due to the presence of all defects.

By index $j$ we denote the type of defect according to its influence on the surrounding atoms. Thereby we allow for defects which do not have the symmetry of the lattice. The occupation number $c'_m$ is one if site $m$ is occupied by a defect of type $j$ and zero otherwise. We introduce the concentration fluctuations $\Delta c'_m$ by

$$
c'_m = c_j + \Delta c'_m
$$

(3)

where

$$
c_j = \frac{1}{N} \sum_m c'_m
$$

(4)

is the average concentration of defects of type $j$. Using the superposition principle we get for the displacement $\mathbf{u}_m$ at lattice site $m$

$$
\mathbf{u}_m = \sum_j \sum_n N_m \Delta c'_n s_{j,m,n}
$$

(5)

where $s_{j,m,n}$ is the displacement at site $m$ in the ideal lattice caused by a defect of type $j$ at site $n$. Restricting ourselves at first to the large class of point defects where $\mathbf{k} \cdot \mathbf{u}_m \ll 1$ in the range of measurement, it is sufficient to use $\exp(i\mathbf{k} \cdot \mathbf{u}_m) = 1 + i\mathbf{k} \cdot \mathbf{u}_m$.

Disregarding all contributions to the Bragg terms we get for the elastic coherent-scattering cross section

$$
\frac{d\sigma}{d\Omega}(\mathbf{k}) = \frac{1}{N} \sum_j \sum_n N_m \Delta c'_n \exp(i\mathbf{q} \cdot \mathbf{r}_n) \times [b_D \exp(-W_D,j) - b_H \exp(-W_H) + i\mathbf{k} \cdot \sum_m s_{j,m,n} \exp[i\mathbf{k} \cdot (\mathbf{r}_m - \mathbf{v}_m)]]^2,
$$

(6)

where $\mathbf{k} = \tau + \mathbf{q}$, $\tau$ is a reciprocal-lattice vector, and $b = c_j b_D \exp(-W_D,j) + (1 - c_j) b_H \exp(-W_H)$. Using the Fourier transforms $\tilde{c}_j$ and $\tilde{s}_j$ of the concentration fluctuation $\Delta c'_n$ and the strain field $s_{j,n}$ defined by

$$
\tilde{c}_j(q) = \frac{1}{N} \sum_n N_m \Delta c'_n \exp(i\mathbf{q} \cdot \mathbf{r}_n)
$$

(7)

$$
\tilde{s}_j(q) = \sum_n N_m s_{j,n} \exp(i\mathbf{q} \cdot \mathbf{r}_n).
$$

(8)

Equation (6) leads to

$$
\frac{d\sigma}{d\Omega}(\mathbf{k}) = N \sum_j |\tilde{c}_j(q)|^2 |b_D \exp(-W_D,j) - b_H \exp(-W_H) + i\mathbf{k} \cdot \tilde{s}_j(q)|^2.
$$

(9)

A further simplification is possible if there is no correlation between the defect types. In this case the concentration fluctuation factors and one obtains for small concentrations, $c_j \ll 1$,

$$
\frac{d\sigma}{d\Omega}(\mathbf{k}) = N \sum_j |\tilde{c}_j(q)|^2 |b_D \exp(-W_D,j) - b_H \exp(-W_H) + i\mathbf{k} \cdot \tilde{s}_j(q)|^2.
$$

(10)

For random distribution of the defects this gives

$$
\frac{d\sigma}{d\Omega}(\mathbf{k}) = \sum_j c_j |b_D \exp(-W_D,j) - b_H \exp(-W_H) + i\mathbf{k} \cdot \tilde{s}_j(q)|^2.
$$

(11)

Cross sections for interstitially dissolved impurities can be obtained in an analogous way. For a random distribution on each of the sublattices and uncorrelated occupation of the sublattices, the result is

$$
\frac{d\sigma}{d\Omega}(\mathbf{k}) = \sum_j c_j |b_D \exp(-W_D,j) - b_H \exp(-W_H) + i\mathbf{k} \cdot \tilde{s}_j(q)|^2.
$$

(12)

$j$ labels the interstitial sites $r_j$ in a unit cell and $\tilde{s}_j(\mathbf{k})$ is defined by

$$
\tilde{s}_j(\mathbf{k}) = \sum_n N_m s_{j,n} \exp[i\mathbf{k} \cdot (\mathbf{r}_m - \mathbf{r}_j)].
$$

(13)

If the condition $\mathbf{k} \cdot \mathbf{u}_m \ll 1$ does not hold in the vicinity of the impurity, higher-order terms of the expansion of $\exp(i\mathbf{k} \cdot \mathbf{u}_m)$ have to be taken into account as discussed, e.g., by Eisenriegler (1971) and Dederichs (1973).

In the framework of lattice statics (Matsubara, 1952; Kanzaki, 1957) it is convenient to express the Fourier transform of the strain field $\tilde{s}_j(\mathbf{k})$ in harmonic approximation by the Fourier transform of the so-called Matsubara–Kanzaki (MK) forces $f_{j,m}$ acting on the neighbouring host-lattice atoms:

$$
\tilde{s}_j(q) = \Phi^{-1}(q) \cdot \tilde{f}_j(q).
$$

(14)
\( \Phi(q) \) is the dynamical matrix of the host-lattice atoms and can be calculated using a Born-von Karman fit to the dispersion curves of the lattice vibrations as measured by inelastic neutron scattering.*

On the basis of the considerations given above, the scattering due to point defects can be calculated for a given model of MK forces.

In order to show the connexions to the scattering close to Bragg peaks (Huang scattering) and to the macroscopic lattice-parameter change, we give the expression for \( \mathbf{f}_j(q) \) in the long-wavelength limit

\[
\mathbf{f}_j(q) = iP_j q
\]

(15)

where \( P_j \) is the dipole force tensor. Trinkaus (1972) has shown how the symmetry and the strength of \( P \) can be deduced from Huang scattering. In addition, the trace of \( P \) is related to the lattice-parameter change per unit concentration \( \Delta a/\Delta c \) by

\[
\text{tr } P = qK \frac{\Delta a}{\Delta c} \cdot V_c
\]

(16)

where \( K \) is the compressibility and \( V_c \) is the volume of the unit cell.

III. Basic experimental questions

For the discussion of whether a particular problem can be investigated by diffuse neutron scattering, we distinguish between questions connected with the choice of the sample and others related to technical problems. Of course, there will be numerous points of interconnexion.

III(a) Samples

A major nuisance may be the incoherent elastic scattering of the sample, which cannot be separated from the coherent elastic scattering. Normally, because of the small concentrations, incoherent scattering from the defects, with the exception of hydrogen, plays a minor role.† The incoherent scattering cross sections vary in a very irregular way with atomic number as shown in the lower part of Fig. 1. Elements like Be, C, Al, Nb, Pb and Bi are particularly favourable. For these elements the absorption cross sections are also small. Most of the values of \( \sigma_{inc} \) are obtained as the difference between the total scattering cross section and the coherent-scattering cross section. Therefore, the accuracy is normally poor. Some values of \( \sigma_{inc} \) are determined by direct scattering.

For a discussion of the coherent scattering, we take it as a basis equation (11). The scattering amplitude \( ib_n \cdot \mathbf{k} \cdot \mathbf{S}(q) \) due to the distortions adds coherently to the Laue amplitude \( b_n - b_n \). Values for \( b_{coh} \) are shown in the upper part of Fig. 1. It is evident that systems with neighbouring elements may show considerable Laue scattering in contrast to the situation with X-rays. Also, there may be large differences in the scattering length for isotopes of a given element, which may become particularly important in the case of ternary alloys. For binary alloys in some cases (e.g., Al-Ti) the use of isotopes allows a change of sign of the interference term \( (b_n - b_n)b_{coh}/2k \cdot \mathbf{S}(q) \).

When discussing a particular project, neutron absorption must also be taken into account. In favourable cases sample diameters of several centimetres can be used. Surface effects are thus much less important than for X-rays.

To get full information on the \( \mathbf{k} \) dependence of the scattering cross section, it is highly desirable to work with single crystals. The orientational averaging in polycrystalline samples smears structural details severely.

III(b) Experimental conditions

Comparison of a sample with defects against a standard of the pure host material would in principle allow an extraction of the scattering due to the defects. Such a technique has been applied successfully at low temperatures (Simson, 1968; Schumacher, 1969; Haubold, 1974), where thermal diffuse scattering is greatly

![Fig. 1. Nuclear coherent scattering lengths and incoherent scattering cross sections for some elements and isotopes (with mass numbers given in parentheses). Data are taken from Bacon (1962) and Shull (1972), and are supplemented by some values given by Schmatz (1973).](image-url)
reduced. However, at high temperatures a tremendous statistical accuracy and extremely close correspondence of sample and standard with respect to the crystal orientation and quality would be required. On the other hand, working at high temperatures may become necessary because in many alloys there is a reasonable solubility of defects only close to the melting point. In these cases, the particular properties of slow neutrons offer a chance to discriminate against inelastically scattered neutrons by energy analysis. This results in a drastic reduction of intensity and its necessity has to be determined from case to case. Fig. 2 allows an estimation of the extent to which phonon scattering will be important in a planned experiment.

Using the relations

\[ h\omega = E_0 + E_1, \quad h\kappa = h(k_0^2 + k_1^2 - 2k_0k_1 \cos 2\theta)^{1/2} \]

and the dispersion of the neutron energies

\[ E = \frac{\hbar^2 k^2}{2m}, \]

one immediately obtains

\[ \kappa = \frac{\sqrt{2m}}{h} \left( E_0 + E_1 - 2\sqrt{E_0E_1 \cos 2\theta} \right)^{1/2} \quad (17) \]

where \( m \) is the neutron mass. Taking the scattering angle \( 2\theta \) as a parameter and keeping the incident energy of the neutrons fixed, (17) gives the loci for the allowed combinations of energy and momentum transfer to the neutrons. In Fig. 2 these relations are shown for \( E_0 = 4.4 \text{ meV} \). The maximum energy a neutron can lose is equal to its initial energy, independent of the scattering angle. In this case \( h\omega = E_0 \) and \( |k| = |k_0| \). Therefore the dashed parabola originating at \( k = 0, \omega = 0 \) is the dispersion of the incoming neutrons. If the value of \( E_0 \) is changed, a set of curves similar to the one shown for \( E_0 = 4.4 \text{ meV} \) is obtained, but starting from a different point on the dashed parabola.

The measured scattering intensity for a given point in \( \kappa-\omega \) space is determined by the value of the scattering functions of the sample at this particular point. For single-phonon processes scattering occurs only along the dispersion curves. For the cases where \( \kappa \) is parallel to the [110] and [111] directions, the longitudinal branches of the phonon dispersion laws in Al and Pb are shown. Whenever there is a point of intersection of the two sets of curves, one-phonon inelastic scattering will be observed at the corresponding angle \( \theta \). Similar considerations have to be applied to the other branches of the dispersion law. It should be emphasized that one has to be careful when trying to make quantitative use of this diagram because usually \( \kappa \) and \( q \) (quasimomentum of the phonon) are not on one line and the direction of \( \kappa \) is not fixed in Fig. 2.

It is seen from the upper part of the picture that with this particular choice of \( E_0 = 4.4 \text{ meV} \) practically no scattering with energy loss will occur in the case of Al. The situation is quite different with the low-lying energies in Pb. To avoid scattering with energy loss here, an incident neutron energy of 1.3 meV has to be chosen. This, however, results in a drastic reduction of the accessible \( \kappa \) range.

From the population factors \( n^\pm \) for phonons

\[ n^- = \frac{1}{\exp(-\hbar\omega/k_B T) - 1} \quad \text{for } \hbar\omega < 0 \]

and

\[ n^+ = \frac{1}{\exp(\hbar\omega/k_B T) - 1} + 1 \quad \text{for } \hbar\omega > 0 \]

it is evident that only scattering with energy gain (where one always obtains points of intersection) can...
be suppressed by sufficiently low temperatures. By plotting the phonon-dispersion laws of the sample onto diagrams like Fig. 2, one can therefore decide at what values of the incident neutron energy inelastic scattering will occur even at low temperatures. Measuring without energy analysis will therefore normally restrict the range in $\kappa$ space.

At higher temperature also inelastic scattering by energy gain may exceed the elastic diffuse scattering due to point defects by orders of magnitude (see e.g. Fig. 9). To discriminate between elastically and inelastically scattered neutrons, crystal analysers or time-of-flight (TOF) techniques can be used. Both methods have been extensively discussed in the literature with respect to their application to high-resolution experiments. The question of which of them is preferable depends on the problem under consideration. Usually, if there is only a limited range of energy transfer which is of interest, crystal analysers are superior to high-resolution TOF because of better time efficiency. However, in a TOF spectrometer many detectors may be operated simultaneously at different scattering angles. Generally speaking, a TOF method will usually give an overall picture in a shorter time and will allow one to trace unexpected phenomena on the basis of the recorded data more easily. It is important to note that the path in $\kappa-\omega$ space along which an individual TOF spectrum is taken is not a straight line but is rather given by the particular curve of Fig. 2 which corresponds to the scattering angle under consideration. In the case of purely elastic scattering, this will not affect the results but careful analysis is necessary if the scattering is quasi-elastically broadened by diffusion, and if the measured width has to be corrected. The TOF-method is very flexible with respect to resolution which can be reduced in favour of a higher intensity of scattered neutrons.

**IV. Spectrometers for elastic diffuse scattering**

IV. (a) *Mechanical set-up*

The principal components of a neutron spectrometer with energy analysis are (Fig. 3): the monochromator $M$, which serves to select a limited band of wavelengths from the white spectrum coming from the reactor $R$, and the analyser $A$, which allows a determination of the energy of the neutrons scattered by the sample $S$. In a TOF spectrometer the analyzer consists of a chopper which releases bursts of neutrons and a flight path in connexion with appropriate electronic equipment to record the scattered neutrons as a function of their flight time between chopper and detector.

In designing a neutron spectrometer to be used for diffuse elastic scattering from dilute alloys, six aspects are of major importance because of the extremely weak signal that has to be detected:

1. In view of the fact that the variation of the cross-section with $\kappa$ is usually rather smooth, $\kappa$ resolution should be reduced in favour of a higher rate of scattered neutrons (broader band of incident energies).
2. The overall background has to be kept as low as possible.

![Fig. 3. Principal arrangement of a spectrometer with energy analysis: R reactor, M monochromator, S sample and A analyser; $\theta$ is the scattering angle.](image)

**Fig. 4.** Horizontal cross-cuts of the spectrometer for diffuse neutron scattering in Jülich (a) and the D7 instrument at Grenoble (b).
3. Any scattered neutrons not coming directly from the sample should be prevented from being recorded in the detectors.
4. As many detectors as possible should be used simultaneously to reduce the measuring time.
5. As it is only elastic scattering that is of interest, all neutrons which have undergone inelastic scattering should be discriminated against.
6. Quick handling and processing of data is essential to monitor the experiment’s progress.

It was with particular attention to these requirements that the two spectrometers have been designed which are now in operation at the Forschungsreaktor DIDO (FRJ2) in the Kernforschungsanlage Jülich and at the High Flux Reactor at the Institut Laue-Langevin in Grenoble. Horizontal cross cuts in the scattering plane of the two spectrometers are shown in Fig. 4. Both facilities are connected to cold-neutron sources via neutron guide tubes. The purpose of the cold source is to increase the fraction of slow neutrons in the spectrum coming from the reactor. The fact that the spectrometers are installed at neutron guide tubes actually means an offence against point 2 of the above requirements because the divergence of the incident beam is limited to the angle of total reflection of the neutron guides. This is typically of the order of half a degree whereas 2° or 3° could be accepted for reasons of resolution. On the other hand, the spectrometer is in this way far from the reactor core and this gives a considerable reduction in the overall background.

The monochromating device used in Jülich is a mechanical velocity selector. This is essentially a cylinder of neutron absorbing material with helical slots in it (Fig. 5). It is rotated around an axis parallel to the neutron beam. The advantage of such a device is its relatively high transmission, of the order of 80% and the fact that the transmitted wavelength may be altered by just changing the speed of rotation (without shifting the position of the sample). The resolution is approximately constant for all wavelengths and can be influenced by tilting the rotor axis with respect to the neutron beam (variation of the angle \( \psi \)). The minimum mean wavelength obtainable is restricted to about 3.5 Å for mechanical reasons. A Fermi chopper can be installed if energy analysis is necessary.

The Grenoble instrument is equipped with a pyrolytic graphite monochromating crystal of 5 × 9 cm. The resolution obtained in this way is much better, of the order of 2 to 3%. Fig. 6 shows the momentum-space diagram for the 002 and 004 reflexions of the
crystal. The distribution of the neutrons as a function of momenta in the neutron guide H15 is indicated on a logarithmic scale. It is evident that the relative intensities due to first and second-order reflexions depend on the reflecting angle \( \psi \). ‘Contamination’ from higher-order reflexions can be removed by a cooled filter of polycrystalline Be with a cut-off wavelength of 4 Å. On the long-wavelength side the range of incident wavelengths is limited by the lattice parameter of graphite and the maximum possible deflection angle to about 6 Å. From the relation

\[ \Delta \lambda = \Delta \theta \tan \theta + \Delta \tau \]

it follows that the resolution changes with deflection angle and therefore with wavelength.

The chopping device used in Grenoble is a flat disc of absorbing material with appropriate open sections. Its axis of rotation is parallel to the direction of the neutron beam. Such a device has the advantage of being relatively flexible with respect to width and number of open sections. However with large beam cross sections the duration of the pulses becomes long. In this case, if full use is to be made of the 3 cm wide beam, the elastic peak actually obtained in the TOF spectrum is broadened by a factor of five as compared to what follows from the 2% wavelength resolution even if the maximum chopper speed (9000 cycles/min) is used. On the other hand Fermi choppers as used in Jülich have the disadvantage of an inhomogeneous beam profile.

In Jülich the scattered neutrons are detected in 30 BF3 counting tubes, 5 cm in diameter, which are mounted fixed on one side of the sample and three blocks of three detectors each attached to movable arms on the other side. The sample-detector distance is 80 cm. Four movable arms with eight 3He counters each are installed at the Grenoble instrument. The distance between sample and detectors may be varied from 40 to 130 cm with fittings for 97 and 130 cm at present available. There is essentially no collimation in front of the detectors in either instrument. The angle of acceptance is determined by the diameters of the sample and of the detectors. Screens of neutron-absorbing material serve to prevent neutrons scattered from the windows of the sample vacuum chamber from being recorded. To do this effectively, the sample container is given a large diameter. Keeping the sample in vacuum is essential even if measurements are done at room temperature in order to avoid air scattering.

**IV. (b) Electronic equipment**

The spectrometers are connected to computers for data acquisition and control of the experiments. At Jülich a small computer, PDP 8/I, is used for data collection and to control experimental parameters such as sample and detector positions, temperature, selector frequency, etc. via CAMAC modules. On-line connections exist to a computer of medium size (Siemens 306) and to the KFA computing center (IBM 370/168 and 370/158). During the course of an experimental run data related to different values of experimental parameters are stored on the disc of the S306. Standard software routines in the S306 for first evaluation and reduction of data are automatically activated from the control tape read by the PDP 8/I. Results can be displayed on a Tektronix 4010 graphic terminal close to the experiment. For the final evaluation, data are transferred to the IBM computer. In case the background computers are not available the PDP 8/I alone can control the course of the experiment with only a few restrictions. Data are then punched on paper tape and processing is done off-line.

The Grenoble instrument (D7) is directly connected to a medium-size computer (Telefunken TR 86) which is shared by several experimental facilities. 4K of storage area is assigned to the data acquisition of the spectrometer D7. Again CAMAC standard is used to computer-control the adjustment of experimental parameters. Basic software routines and a graphical display are available for first data manipulations and inspection. Further evaluation of data is done off-line. To keep electronic noise low in the counting system, in both instruments the pulses recorded by the detectors are converted to low-impedance digital signals by amplifiers mounted directly on the counting tubes.

Whenever a burst of neutrons is released from the chopper a sequence of periodic pulses is triggered which is counted in the time-channel counter. Each time a neutron pulse is sensed on any of the input channels assigned to the various detectors, the current content of the time-channel counter is read into a 12-bit register and is combined with the number of the input channel to give the address of the memory location in the computer, the content of which is to be incremented by one.

Special precautions are taken against errors in encoding which might occur if, e.g., two input channels happen to sense a signal at the same time. As in some cases the statistical rate on the detectors may be rather high (Bragg reflexions) a statistical-in-sequential-out buffer is used to derandomize the data transfer to the computer at the Grenoble instrument.

**IV. (c) Resolution and range in momentum space**

For very mobile defects such as H in metals or ions in superionic conductors, the time-of-flight resolution at the elastic position is of interest because line broadening due to the diffusive motion may become observable (see e.g., Springer, 1972). With a normalized resolution function \( R_\epsilon(t) \) the measured intensity will be given by

\[ I(t) = \int_{-\infty}^{\infty} I_0(t+\tau)R_\epsilon(\tau)d\tau \]

where \( I_0(t) \) is the intensity distribution for infinitely good resolution. The various components of the instruments and experimental parameters contribute in
different ways to the total resolution function. For the Jülich instrument, we give the following example: 64 time channels of 40 $\mu$s width, mean wavelength of incident neutrons 4.4 Å, 185 chopper periods per second. In this case, with the fixed geometry of the spectrometer, the width of a pulse of monochromatic neutrons would be 100 $\mu$s, which agrees with the measured width of Bragg peaks. With the wavelength distribution of the incident beam taken into account (FWHM = 17% if $\lambda = 4.4$ Å), the width is 250 $\mu$s or 6.2 time channels.

Assuming that the width of the measured line can be determined with an accuracy of 10%, line broadening by quasi-elastic scattering would be observable if the mean energy transfer exceeds 0.7 meV.

To give corresponding figures for the Grenoble instrument we select the following set of experimental parameters: $\lambda = 4.4$ Å, FWHM = 3%, $v_{\text{chopper}} = 117$ cycles/s, channel width 32 $\mu$s. This gives a calculated width of the elastic peak of 230 $\mu$s or 7.2 time channels which agrees well with experimental observation and is mainly determined by the opening time of the chopper. Here Bragg peaks have the same width and cannot be distinguished easily from the line width. The energy resolution is found to be almost equal to that of the Jülich instrument. Improvement is possible however by choosing a narrower chopper slit, not making use of the full width of the beam.

The range in momentum space is determined by the minimum wavelength obtainable. The maximum $\kappa$ values that can be arrived at are 4.1 Å$^{-1}$ in Grenoble and 2.9 Å$^{-1}$ in Jülich.

In Fig. 7(a) we show the distribution of experimental points in the scattering plane which results when on the Jülich spectrometer a sample is rotated through an angular range of 180° in steps of 10°. The Ewald circles corresponding to the different angular settings are shown together with the circles which give the magnitude of $\kappa$ for the individual positions of the fixed detectors. Each point of intersection of the two sets of curves indicates a position in the reciprocal plane where a TOF spectrum is taken. For reference, the boundaries of the first Brillouin zone in the {110} plane of Al are indicated.

For the 0° position of Fig. 7(a) the half maximum contours of the resolution volumes are shown for every fifth detector in Fig. 7(b). For detector No. 20 the whole area contributing to the scattering is indicated. This is important for the discussion of intensities measured near Bragg peaks. Generally the resolution is quite sufficient for most problems in diffuse elastic scattering, but if sharp peaks or narrow minima occur, corrections may become necessary, as will be shown in § V. Because of the much narrower band of incident wavelengths at the Grenoble instrument, $\kappa$ resolution is good enough to trace the scattering even fairly close to Bragg peaks.

V. Experimental procedure and data evaluation

To work out the scattering arising from the presence of defects it is desirable to measure the same sample with and without defects. This can be most easily done in the case of radiation-induced Frenkel defects where annealing is possible, or with hydrogen in 4d transition metals where it is relatively easy to outgas the sample. In other cases, however, in particular if substitutionally dissolved defects are to be investigated, a standard of the pure host material has to be used for comparison. Such a standard should be similar to the sample where
crystal orientation and quality and also geometry are concerned. The intensities of the phonon peaks observed at corresponding angular settings can be compared to judge whether or not this condition is reasonably well fulfilled.

In both cases the sample and a standard will be interchanged in the beam position at short time intervals to be free of - or at least able to correct for - long-time variations in the efficiency of the counting system. A beam monitor will be used in front of the sample to eliminate variations in the intensity of the primary beam. It is very convenient to have behind the sample a second beam monitor which, like the detectors, is connected to the time-of-flight unit. This not only enables one to correct for varying transmission and for enhanced beam attenuation which may occur if Bragg reflexions are excited but also allows a check on the reliability of the time-channel assignment. It should be emphasized that apart from the considerations given in § IV, there are several additional arguments which favour the use of the TOF analysis.

From the observed line shape it may be judged whether the low-intensity tails of the incident spectrum give rise to Bragg scattering. Higher-order contamination may also become a serious handicap if the second order is Bragg-scattered and the region of a forbidden first-order reflexion is investigated. To demonstrate the importance of this effect we give in Table 1 some intensity ratios $I_{\text{1st order}} / I_{\text{2nd order}} = I_{\text{110}} / I_{\text{220}}$ measured with a Pb$_{0.98}$Bi$_{0.02}$ crystal in the vicinity of $\lambda = 1.04$ at 15 K at the Grenoble instrument with and without a Be filter.

<table>
<thead>
<tr>
<th>$\kappa_{el}/\tau_{110}$</th>
<th>$I_{110}/I_{220}$ with Be</th>
<th>$I_{110}/I_{220}$ without Be</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>5.10^{-3}</td>
<td>1.6.10^{-4}</td>
</tr>
<tr>
<td>1.04</td>
<td>2.5</td>
<td>2.5.10^{-2}</td>
</tr>
<tr>
<td>1.08</td>
<td>3.0</td>
<td>6.0.10^{-2}</td>
</tr>
</tbody>
</table>

This shows convincingly the importance of the use of the Be filter and also makes evident that even with the filter the errors may become tremendous without TOF analysis. The TOF spectra of Fig. 8 for the case $\kappa_{el}/\tau_{110} = 1.04$ show $I_{110}$ and $I_{220}$ separated. Bragg reflexions when fully excited are of the order of 10$^4$ more intense than the elastic diffuse scattering of most samples. They may therefore give rise to trouble even if the scattered neutrons do not directly strike the detectors. An example is given in Fig. 9. The extra intensity close to the elastic position $E$ found in curve $b$ as compared to curve $a$ is due to a Bragg reflexion pointing away from the detector. On striking the polycrystalline walls of the furnace, the Bragg scattered neutrons gave rise to Debye-Scherrer rings with large scattering angle which were finally recorded in the detector. After absorbing material had been put on the side of the sample curve $a$ was obtained. In general it is not possible to correct for such effects by subtracting the intensity obtained from a standard of the pure host, even if there is a close correspondence between the crystal orientations. This also shows that whenever it is possible no can for the sample should be used. If a can is necessary, one made from a single crystal would be highly desirable.

By referring to the incoherent scattering from a vanadium standard cross sections can be given in absolute units. Careful calibration of the instrument before the experiment is started is therefore essential. It would be very advantageous to have a standard of the same dimensions and comparable incoherent scattering power as the sample. This is not possible.

![Fig. 8. Time-of-flight spectra taken at 15 K from a Pb$_{0.98}$Bi$_{0.02}$ crystal at $\kappa_{el}/\tau_{110} = 1.04$. The peaks centred round positions $E_1$, $E_2$, and $P$ correspond to first and second-order elastic and phonon scattering respectively. The width of the time channels is 15 $\mu$s with the time zero suppressed.](image)

![Fig. 9. Time-of-flight spectra from an Al crystal with (curve $a$) and without (curve $b$) absorbing material at the side of the sample away from the detectors. From its width of 2.5 channels the extra peak close to $E$ in curve $b$ can be identified as Bragg-scattered neutrons which were scattered back to the detectors after striking the furnace. Owing to its extra flight path the peak is shifted from channel 32 to channel 35.](image)
proved successful, whereby a thin wire of vanadium is rotated in the beam position on different radii. Without the usual handicaps of absorption and multiple scattering it is thus possible to simulate the geometry of cylindrical samples.

With calibration spectra and a quick data-handling system at hand it is possible to control the experiment's progress by continuous comparison of measured data to pre-calculated models and by improving counting statistics in those regions which are interesting. Moreover, the reproducibility of effects can be checked at once if data measured at earlier times stay easily accessible. Often advantage can be taken of the easily changeable incident wavelength to reinvestigate certain values of \( \kappa \) and to make sure that no double scattering processes have influenced the result. In most cases the first evaluation will rely on simple summation over the contents of the time channels at the elastic positions. It is helpful to make this summation over different windows to make sure that there are no contributions from inelastic scattering left in the difference between the intensities obtained from the sample and from the pure host.

In the final evaluation of data, a fitting procedure to the measured spectra and application of spline approximations to recorded elastic intensities may be of great help. On one hand this allows the extraction of the scattering cross sections at values of \( \kappa \) intermediate to the experimental ones; on the other hand, the reliability of each individual point is enhanced by being related to its neighbours. Finally the smoothed set of data obtained in this way allows one to draw a contour map showing the cross section in the whole region of interest. As an illustration we show three different stages of data smoothing in Fig. 10(a) to (c). In Fig. 10(a) the computer plot as obtained from the measured cross sections is given. The statistical variations lead to a rather irregular pattern. The diamond-like structure at \( A \) indicates the failure of a particular detector at a particular measurement. This point was disregarded when the measured data were reduced into one quarter of the lattice symmetry and spline functions applied for constant magnitudes of \( \kappa \). The intermediate result is shown in Fig. 10(b). A second application of spline functions for constant directions of \( \kappa \) leads to Fig. 10(c). The region close to the 111 Bragg reflection has been left out and is indicated by cross-hatching.

VI. Special investigations

To illustrate the progress of experimental work in the field of diffuse elastic neutron scattering from point defects we summarize briefly recent studies on non-magnetic defects performed in Jülich and Grenoble.*

The \( \text{Pb-Bi} \) system

The system \( \text{Pb-Bi} \) was the first to be treated in an early stage of instrument development in Jülich, when no TOF unit was available, by Schumacher (1969). Single crystals of Pb with 2 at. % and 4 at. % of Bi were used. To avoid inelastic scattering a wavelength of 7 Å \( (1.7 \text{ meV}) \) was used and the samples were cooled to 9 K. The \( \kappa \) range covered in this experiment was \( 0.3 \text{ Å}^{-1} \leq \kappa \leq 1.8 \text{ Å}^{-1} \). In Fig. 11(a) lines of constant scattering cross section in the \{110\} plane, obtained from \( \text{Pb}_{0.96} \text{Bi}_{0.04} \) are shown. For comparison in Fig. 11(b) the results of calculations using radially symmetrical MK forces acting on nearest neighbours are given. There is a qualitative agreement except for the intense peak around the point 110. The absence of a similar peak at 001 requires a strain field of the defect with a lower symmetry than that of the host lattice. With a trigonal symmetry assumed for the strain field a model called the 'tripod' model was formulated. This model, in addition to repulsive MK forces acting on all of the twelve nearest neighbors, includes attractive forces acting on three neighbours in one of four equivalent \{111\} planes, as illustrated in the inset of Fig. 11. Such a symmetry recalls the tendency of Bi to form three covalent bonds. The calculated contour lines as given by Schumacher, Schmatz & Seitz (1973) are shown in Fig. 11(c). This model yields a peak at 110 which however is narrower in width and different.*

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* Most of the results are as yet unpublished and will be presented in more detail elsewhere.
in intensity distribution as compared to the measured one. Along the [110] direction the width of the peak is largely determined by the width of the dip in the L [110] phonon dispersion curve shown in Fig. 2, whereas the experimental one is broadened by insufficient resolution. To check the model calculations with improved resolution and in an extended $\kappa$ range the measurements were repeated with the same samples in Grenoble (Seitz, Schmatz, Bauer & Just, 1975). Inelastic scattering contributions now unavoidable for the higher incident energy were separated by TOF. In Fig. 12 the new results are compared with the older ones for the [110] direction. Calibrated independently, the two measurements gave fairly good agreement within the common $\kappa$ range, both in structure and in absolute magnitude. The shape of the peak at 110 can now be seen more clearly. Its width is smaller than one would predict from the phonon spectrum. An estimate of the range in real space of what contributes coherently to this peak gives a minimum value of 50 Å. That means that refined models are required which take into account, e.g., orientational correlations among the 'tripod' forces. Such calculations are in progress.

**Al-base alloys**

Al-base alloys are favourites for elastic diffuse neutron scattering for several reasons: The simple electronic structure of Al makes a number of these alloys accessible to calculations from first principles, as shown by Baratoff & Seitz (1975). Also, Al is a suitable host material for neutron scattering. In addition, much research work has been done in these systems because of their technical importance. As shown in Fig. 13, the lattice parameter change goes from large positive to large negative values and this makes possible a number of comparative studies. With Cu and Mn taken as impurities, the lattice-parameter changes produced are comparable, but the electronic structure of the solute ions is completely different. From the discussion of the PbBi system, we know that a solute atom may have some memory of its own crystal structure. Since Al and Cu are both f.c.c., we expected simple models to be adequate for the description of lattice distortions for the AlCu alloy (Bauer & Seitz, 1975). The contour map in the \{T10\} plane obtained from an AlCu_{0.008} single crystal at 800 K where a homogeneous solution exists has already

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**Fig. 11.** Elastic diffuse neutron scattering from Pb_{0.96}Bi_{0.04} at $T=9$ K. Cross-sections are given in mbarn/sterad-defect atom. (a) Experimental results for the \{T10\} plane. (b) Calculated values for a model with radially symmetrical MK forces on nearest neighbours. (c) Calculated values for the 'tripod' MK force model. The force distribution in this case is shown in the inset.

**Fig. 12.** Comparison of results for Pb_{0.96}Bi_{0.04} in the [110] direction. Circles: Measured by Schumacher (1969) with $\lambda_0=7$ Å FWHM 20%. Crosses: Measured by Seitz et al. (1975) with $\lambda_0=4.5$ Å FWHM = 2%.

**Fig. 13.** Lattice spacing of some Al alloys as a function of concentration [from Pearson (1964)].
Fig. 14. Plot of calculated scattering cross sections in the \(\{110\}\) plane of AlCu for a model with radially symmetrical nearest-neighbour MK forces.

Fig. 15. Scattering pattern obtained from the AlCu_{0.008} crystal at room temperature, indicating the formation of platelet-like precipitations in the \(\{100\}\) planes.

been shown in Fig. 10. Corresponding results of a calculation using central forces of equal magnitude on nearest neighbours only are shown in Fig. 14. The overall agreement is very good. It turns out best in the directions of lattice symmetry and is somewhat less satisfactory in the intermediate region. A possible explanation for these discrepancies can be the uncertainty in the dynamical matrix away from the symmetry directions (see footnote * on p. 164). From the comparison of the experimental values obtained in symmetry directions to calculated cross sections for various models, it could be concluded that the model which seems to be best suited to describe the experimental results is one with central forces \(F_1\) and \(F_2\) on nearest and next-nearest neighbours, the ratio \(F_2/F_1\) being \(-0.2\pm0.1\). This is in qualitative agreement with

lattice fringe measurements in the vicinity of G.P. zones reported by Phillips (1973). At room temperature the AlCu_{0.008} sample showed the scattering characteristic for platelet-like precipitations in the \(\{100\}\) planes as can be seen from the elongated structure along the \([001]\) direction in Fig. 15.

The scattering obtained from an AlMn_{0.003} alloy at 800 K in symmetry directions is shown in Fig. 16 together with the result of model calculations for the case of central forces on nearest neighbours. Clearly significant differences exist, and no model based on forces with inversion symmetry with respect to the defect has proved successful. Different force distributions will have to be tried and a detailed discussion of the problem will be given elsewhere. The fact that it has been possible to obtain reproducible data from an alloy with as little as 0.13 at.% of substitutionally dissolved defects at a temperature as high as 800 K shows the power of the experimental methods described.

Fig. 16. Elastic diffuse-scattering cross section of AlMn_{0.003} in directions of lattice symmetry. The lines give the results of calculations for nearest-neighbour central forces of constant magnitude.
Hydrogen in metals

Hydrogen in metals which is soluted on interstitial sites has been a subject of considerable interest for several years. Numerous studies using neutron and X-ray scattering have been performed. Most of this work was dedicated to determining the structure of the various phases in this alloy and to the investigation of the diffusive behaviour of the protons. For the case of Nb a lattice-parameter change of \( \Delta a/a \cdot e = 0.047 \) at \( T = 165^\circ \text{C} \) seems to be the most accurate value (Pick, 1973) for the \( \alpha \) phase. It has also been shown by diffuse neutron scattering by Conrad, Bauer, Alefeld, Springer & Schmatz (1973) that owing to the coherency strains set up by short-wavelength density fluctuations, the effective interaction energy is lower than for density fluctuations of macroscopic scale. It was therefore of interest whether the lattice distortions caused by the protons could be observed by diffuse scattering. Evidently deuterium had to be used in this case because the incoherent-scattering cross section of hydrogen which is 80 barns dominates all kinds of minor effects.

Niobium being a very weak incoherent scatterer, the standard was loaded with a small concentration of H. This was also considered favourable for the peculiar behaviour of the integrated quasielastic intensity as a function of \( \kappa \), which was shown by Gissler, Jay, Rubin & Vinhas (1973) and which was recently discussed by Wakabayashi, Alefeld, Kehr & Springer (1974).

In Fig. 17 we show the measured ratio of the quasielastic scattering cross sections of D and H in Nb (Bauer, Seitz, Horner & Schmatz, 1974), for the case where \( \kappa \) is parallel to [100], [110] and [111] together with calculated data. Comparing the experimental results with the calculated ones, the following statements can be made:

1. The existence of lattice distortions in the neighbourhood of the defects is established.
2. With the hydrogen atoms on tetrahedral interstitial sites cubic symmetry of the strain field, as made possible by interaction with nearest and next-nearest neighbours, is more suited to describe the experimental results than a tetragonal one which results from nearest-neighbour interactions only.
3. Discrepancies remaining between the measured data and the models so far applied are a modulation of the measured cross section in the region of \( 1 \text{ Å}^{-1} \leq \kappa \leq 2 \text{ Å}^{-1} \) and experimental values for \( q \leq -\pi/4 \) which are much lower than would be expected from the calculations.

It is mainly due to the initiative of Professor W. Schmatz that the spectrometers described here have been set up. His continuing interest in the progress of the work and numerous valuable and clarifying discussions with him and with other colleagues have been indispensable to the final success.

References


Fig. 17. Measured and calculated ratios of the scattering cross sections of D and H in Nb. For the calculations a Debye-Waller exponent of the form \( \kappa^2 u^2 x^2 \) has been used with \( u_h = 0.035 \text{ Å}^{-2} \) and \( u_l = 0.05 \text{ Å}^{-2} \) and \( x \) depending on the type of interstitial site. The full lines represent a model with cubic symmetry of the distortion field, and the broken ones a model with tetragonal symmetry. Tetrahedral interstitial sites are assumed.
Measurement of Diffuse X-ray Scattering between Reciprocal-Lattice Points as a New Experimental Method in Determining Interstitial Structures

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For interstitials the scattering cross section between the Bragg reflexions is very sensitive to the position of the defect atom and the displacements of the neighbouring lattice atoms. In contrast to this the scattering near the Bragg reflexions (Huang scattering) is mainly governed by the displacement field at large distances from the defect and gives information about defect symmetry and strength [Trinkaus, H. (1972). Phys. Stat. Sol. (b) 51, 307-319]. For determining structures of point defects a measurement of scattering far from reciprocal-lattice points is therefore the best suited and most direct method. X-ray measurements of point-defect scattering in this region far from reciprocal-lattice points are difficult. With conventional X-ray set-ups it is not possible to separate the defect scattering from the thermal diffuse and Compton background scattering which is up to two orders of magnitude larger in the case of typical defect concentrations of some $10^{-4}$. Such measurements, however, become possible if large X-ray sources of high luminous density are used in connexion with multidetector arrangements. As an example an experimental arrangement [Haubold, H.-G. & Schilling, W. (1975). To be published; Haubold, H.-G. (1974). Rep. Kernforschungsanlage Jülich, JÜL-1000-FF] is reviewed, in which the scattering cross-section of self-interstitials in aluminum was measured in samples containing an atomic density of interstitials up to $5 \times 10^{-4}$.

1. Introduction

Single interstitials are of great interest: self-interstitials are produced in all radiation-damage processes whereas impurity interstitials are important for mechanical properties of the b.c.c. metals. In many cases their structural positions as well as the magnitude and direction of the lattice displacements around them are unknown. As an example, self interstitials in a f.c.c. lattice are shown in Fig. 1. From symmetry considerations all the six configurations in Fig. 1 are possible. The stable form must be determined experimentally and cannot be calculated from atomic potentials, since these are not known with sufficient accuracy.

Detailed information about interstitial positions and lattice displacements can be obtained from analyses of the diffuse scattering of X-rays or neutrons.

Several successful scattering experiments on single