

Complementarity between X-rays and neutrons

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In the last decades, with the advent of the modern synchrotron radiation facilities, the possibility of using either neutrons or x-ray to study atomic level characteristics of condensed matter became an important aspect of this area of research. The knowledge of the relative merits of these two powerful tools for the analysis of condensed matter is an important step for those wishing to get the best possible information about either structure or dynamics at the atomic level.

Given the extremely widespread of applications of both techniques even in the limited common areas of applications does not allow for a complete description of all the possibilities open by the two techniques. In this lecture a brief basic comparison is given starting from the well known low order scattering processes, trying to give some idea about the range of applications where the two techniques provide similar or complementary information and the situations where one technique is better than the other, focusing on diffraction experiments and inelastic scattering experiment in the meV energy range.

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Basic Theory of Thermal Neutron Scattering.

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1. – Introductory remarks.

The use of neutron scattering in studying condensed-matter phenomena is well established and often this technique is routinely employed. However, the potentiality of this technique in applicative fields is reduced by the fact that small laboratory-scale sources are not useful as in the case of X-ray sources, for instance. Furthermore, due to intrinsic intensity limits of even large-scale sources, the general performance of a neutron diffraction facility does not compare favourably with an X-ray facility. Finally also the problems connected to the very high cost of neutron scattering facilities have a relevant weight.

Although the serious limits mentioned above have a large impact in the use of neutron scattering in applicative fields, the intrinsic advantages of the neutron as a condensed-matter probe make its use extremely appealing, especially when it is used to give a final answer to a well-defined question.

To identify the various advantages of neutron scattering we recall the most important characteristics of the neutron-atom interaction. The neutron interacts with an atom mainly through the so-called strong nuclear interaction with the nucleus and through the magnetic interaction between its intrinsic magnetic dipole (see table I) and the magnetic dipole of the atom, if any.

TABLE I. – *Properties of the neutron.*

neutron mass	$M = 1.673 \cdot 10^{-24} \text{ g}$
neutron magnetic moment	$\gamma e \hbar / 2Mc = -1.913 \cdot 0.509 \cdot 10^{-23} \text{ erg/Oe}$
neutron kinetic energy	$E = \hbar^2 K^2 / 2M, E(\text{meV}) = 2.0721 K^2 (\text{\AA}^{-1}) = 81.803 / \lambda^2 (\text{\AA})$
Larmor frequency	$\nu_L = 2\gamma e \hbar / 2Mc, \nu_L (\text{Hz}) = 92.34 \cdot 10^6 H(\text{T})$

The first interaction is a very-short-range one as it extends only over the nuclear radius, namely a radius of the order of 10^{-12} cm or less. Though the intrinsic nature of the neutron-nucleus interaction is much less known than the electromagnetic interaction between the X-ray and the atom, we shall see that, in practice, the neutron-nucleus interaction is much simpler. The first important point to be considered is the fact that even the strong nuclear interaction, due to the very small range over which it extends, gives rise to a relatively weak interaction, so that the mean free path of a neutron in condensed matter is generally of the order of centimetres. Moreover the coupling of the neutron with the nucleus makes the interaction completely independent of the chemical environment, thus allowing the use of the neutron in studying the structural effects independently of the chemical bonds. Finally we mention that there is no special trend along the periodic table, so that the neutron diffraction can be used to distinguish even contiguous elements. This fact makes the neutron scattering almost unique in studying order-disorder processes, for instance, in alloys.

Because of all the above advantages the use of neutron scattering has become very important in several fields of condensed-matter research to get unique and well-defined answers.

In the following sections the basic features of neutron scattering will be presented, avoiding the use of a quantum-mechanical treatment. This simplified approach is completely equivalent to the quantum-mechanical one, at least to the lowest nonvanishing order.

1.1. *Qualitative behaviour of neutron-nucleus interaction.* – The detailed analysis of the nuclear interaction in condensed matter has been presented in several textbooks [1], however we shall present a simplified description of the interaction, in a form suitable to perform a close comparison with the companion X-ray scattering.

Of course, to allow for the description of diffraction phenomena involving particles, as is the case of the neutron, we have to attribute to the particle an appropriate wavelength (de Broglie wavelength), which is given by (see table I)

$$(1.1) \quad \lambda = \frac{h}{p},$$

where $p = mv$ is the impulse of the particle, m being its mass, v the velocity and h the Planck constant. In this way we can describe the interaction between the neutron and a single nucleus as the interaction between an incoming wave of given wavelength and a properly chosen matter density $\rho_N(\mathbf{r})$ which interacts with the wave. If we consider the wave scattered in a given direction as described in fig. 1, we can assume that its amplitude is proportional to the matter density in each volume element $d\mathbf{r}$. Of course, all the contributions produced by different volume elements must be summed including the various phase differ-

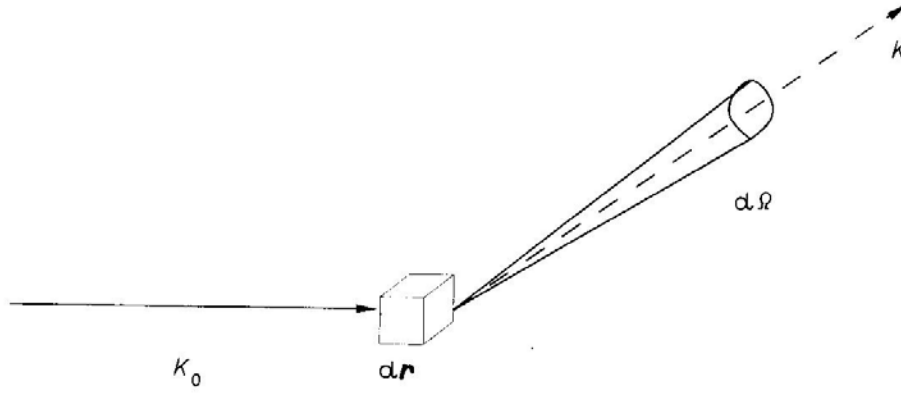


Fig. 1. – Scattering geometry in real space, K_0 incoming-neutron wave vector, K , outgoing-neutron wave vector, $d\Omega$ solid angle, dr volume element.

ences. Then we have

$$(1.2) \quad \psi = A \int \exp [i\mathbf{K}_0 \cdot \mathbf{r}] \exp [-i\mathbf{K} \cdot \mathbf{r}] \rho_N (\mathbf{r} - \mathbf{R}_0) d\mathbf{r},$$

where the integral extends over the volume where $\rho_N (\mathbf{r})$ is nonzero, \mathbf{R}_0 is the position of the nucleus, A is a constant dependent on the nature of the interaction between neutron and nucleus, \mathbf{K}_0 and \mathbf{K} are the wave vectors of the waves corresponding to the incoming and outgoing neutron, respectively. Of course, we have

$$(1.3) \quad K_0 = K = \frac{2\pi}{\lambda},$$

as is the case for elastic scattering. The description we have employed in fact refers to elastic scattering because the nucleus is tacitly assumed to be infinitely massive, *i.e.* it is held in a fixed position. Looking at eq. (1.3) we see that, when we use a wavelength of the order of $1 \text{ \AA} = 10^{-8} \text{ cm}$, which is typical in condensed-matter studies, the typical value of $\mathbf{K} \cdot \mathbf{r}$ is such that

$$(1.4) \quad |\mathbf{K} \cdot \mathbf{r}| \leq Kr \leq 10^{-3}$$

because the nuclear radius is less than 10^{-12} cm . Therefore, with an approximation which is as good to at least 0.1%, we can assume

$$(1.5) \quad \psi = \text{const} \cdot \exp [-i\mathbf{Q} \cdot \mathbf{R}_0],$$

where \mathbf{Q} is the wave vector transfer:

$$(1.6) \quad \mathbf{Q} = \mathbf{K} - \mathbf{K}_0.$$

The constant appearing in eq. (1.5) depends on the nucleus and on the nature of the interaction. The flux of neutrons scattered into the direction defined by the

wave vector \mathbf{K} is proportional to the square modulus of the wave amplitude ψ :

$$(1.7) \quad \psi = B|\psi|^2 = \text{const.}$$

Therefore, the scattering from a single nucleus is completely isotropic and defined by a single constant dependent on the specific nucleus only.

When more than one nucleus is present, the amplitude ψ is the sum of the contributions of the various nuclei at sites \mathbf{R}_l . We get

$$(1.8) \quad \psi = \text{const.} \cdot \sum_l \exp [i\mathbf{Q}\mathbf{R}_l],$$

so that the flux of scattered neutrons is given by

$$(1.9) \quad \phi = B|\psi|^2 = \text{const.} \cdot \sum_l \sum_{l'} A_l A_{l'} \exp [i\mathbf{Q}(\mathbf{R}_l - \mathbf{R}_{l'})],$$

where A_l and $A_{l'}$ are properly chosen constants that describe the scattering process from a single nucleus.

All the above relationships contain multiplicative constants due to the fact that the flux of scattered neutrons depends on the intensity of the incoming beam. Therefore, it is usual to introduce a quantity called scattering cross-section, which depends on the scattering process and is independent of the incoming-beam intensity. We give a general definition of cross-section as follows: given an incoming-beam intensity j_0 (neutron per unit surface and unit time) of neutrons having energy E , the flux $d\phi$ (number of neutrons per unit time) of neutrons scattered within the solid angle $d\Omega$ and having energy $E = E - \varepsilon$ within the energy interval $d\varepsilon$ is proportional to j_0 :

$$(1.10) \quad d\phi = \text{const.} \cdot j_0 d\Omega d\varepsilon;$$

the constant depends on the sample and on the nature of the interaction and is called differential scattering cross-section. Usually it is written in the form

$$(1.10a) \quad d\phi = \frac{d^2\sigma}{d\Omega d\varepsilon} j_0 d\Omega d\varepsilon;$$

when we consider the purely elastic scattering, *i.e.* $E = E_0$, we write

$$(1.10b) \quad d\phi = \frac{d\sigma}{d\Omega} j_0 d\Omega.$$

According to eq. (1.7) the cross-section for the scattering from a single nucleus can be written as follows:

$$(1.7a) \quad \frac{d\sigma}{d\Omega} = \text{const} = |b|^2,$$

where b is a constant called scattering amplitude. When many nuclei are

present, we have

$$(1.9a) \quad \frac{d\sigma}{d\Omega} = \sum_{ll'} b_l b_{l'} \exp[i\mathbf{Q}(\mathbf{R}_l - \mathbf{R}_{l'})].$$

1.2. *Coherent and incoherent scattering.* – It is useful for many purposes to modify eq. (1.9a) to extract the effect of the scattering amplitude fluctuations. In fact the scattering amplitude b_l fluctuates in real samples due to many reasons: b_l depends on the isotope distribution and fluctuates on a given nucleus due to the nuclear spin. Therefore, it is useful to split b_l as follows:

$$(1.11) \quad b_l = b + \Delta_l,$$

where b is the average value of b_l and Δ_l is a fluctuation. If we consider, for instance, a sample containing a single element having many isotopes, we have

$$(1.12) \quad \langle \Delta_l \rangle = 0 \quad \text{and} \quad \langle \Delta_l \Delta_{l'} \rangle = \langle \Delta_l^2 \rangle \delta_{ll'},$$

where $\langle \dots \rangle$ indicates the average over the isotope distribution. The second relation is due to the fact that the occupancy of the site l is completely independent of the occupancy of the site l' . Using eq. (1.12) we can write eq. (1.9a) in the following form:

$$(1.13) \quad \frac{d\sigma}{d\Omega} = |b|^2 \sum_{ll'} \exp[i\mathbf{Q}(\mathbf{R}_l - \mathbf{R}_{l'})] + N \langle \Delta_l^2 \rangle,$$

where the first term depends on the nuclear positions and gives rise through the interference of different waves to diffraction effects, while the second term is constant and depends on the nature of the sample. The first contribution is generally called coherent-scattering cross-section, while the second one is referred to as incoherent-scattering cross-section. Actually the information contained into the incoherent-scattering cross-section is apparently limited, however it is evident that eq. (1.13) relies strongly on eq. (1.12) which is valid only in the case of no correlation between Δ_l and $\Delta_{l'}$ at two different sites. A case where eq. (1.12) is no longer valid is that of a substitutional binary alloy. In this case the alloy sites are occupied more or less randomly by two atoms A and B . Therefore, if b_A and b_B are the scattering amplitudes relative to A and B atoms, we have

$$(1.14) \quad b = xb_A + yb_B,$$

while

$$(1.15) \quad \Delta_l = \begin{cases} y(b_A - b_B) & \text{if } A \text{ is present at the site } \mathbf{R}_l, \\ x(b_B - b_A) & \text{if } B \text{ is present at the site } \mathbf{R}_l, \end{cases}$$

where $x = 1 - y$ is the concentration of the A atom. If no short-range order is

present, we have

$$(1.16) \quad \langle \Delta_l \Delta_{l'} \rangle = xy(b_A - b_B)^2 \delta_{ll'} ,$$

so that eq. (1.13) again holds. On the other hand, if some short-range order is present as is almost always the case, $\langle \Delta_l \Delta_{l'} \rangle$ is a decaying function of $\mathbf{R}_l - \mathbf{R}_{l'}$ and the incoherent scattering is no longer isotropic. Therefore, the study of this contribution can be useful in analysing the short-range correlations in alloys.

2. – Magnetic scattering of neutrons.

2.1. *Magnetic interaction.* – Due to the fact that a neutron brings a magnetic moment $\gamma = -1.913$ nuclear magnetons μ_N ($1\mu_N = e\hbar/2Mc$, M being the unit nuclear mass), there is a dipole-dipole interaction when the neutron impinges a system containing magnetic moments. Actually there is the case of paramagnetic substances as well as systems where a magnetic alignment exists, *e.g.* ferromagnets.

A detailed treatment of the magnetic interaction is somewhat complex and the readers are referred to the standard textbook of Lovesey[1], for instance.

A simple description can be obtained using the same approach followed in the case of nuclear scattering. As in that case we can introduce a density function $m(\mathbf{r})$ which represents the magnetic-interaction density, so that the neutron wave amplitude ψ is given by

$$(2.1) \quad \psi = A \int \exp [i\mathbf{K}_0 \cdot \mathbf{r}] \exp [-i\mathbf{K} \cdot \mathbf{r}] m(\mathbf{r}) d\mathbf{r} .$$

However, because the magnetic interaction is produced by the electrons present in the matter, eq. (1.4) does not hold and the magnetic scattering is not isotropic. Therefore, the flux of scattered neutrons can be written in the following form:

$$(2.2) \quad \phi = B |f_m(\mathbf{Q})|^2 ,$$

where $f_m(\mathbf{Q})$ is a magnetic form factor which is the Fourier transform of $m(\mathbf{r})$.

The actual shape of $m(\mathbf{r})$ and hence the form factor $f_m(\mathbf{Q})$ can be calculated if the electron states are known and tabulations are available for the most significant atoms and ions.

Due to the vector nature of the neutron-electron interaction the factor B in eq. (2.2) is dependent on the direction of the momentum transfer \mathbf{Q} , while the form factor is in general a vector and depends on the direction of the magnetic-moment distribution which is a vector density and not a scalar density. The

magnetic cross-section can be written in the form

$$(2.3) \quad \frac{d\sigma}{d\Omega} = \left(\frac{r_0 \gamma}{2} \right)^2 |\hat{Q} \times [\hat{Q} \times \mathbf{f}_m(\mathbf{Q})]|^2,$$

where the magnetic form factor is given by

$$(2.4) \quad \mathbf{f}_m(\mathbf{Q}) = \int \mathbf{m}(\mathbf{r}) \exp [i\mathbf{Q}\mathbf{r}] d\mathbf{r}$$

and $r_0 = e^2/mc^2$ is the classical electron radius. Because we have

$$(2.5) \quad \mathbf{f}_{m\perp}(\mathbf{Q}) = \hat{Q} \times [\hat{Q} \times \mathbf{f}_m(\mathbf{Q})] = f_m(\mathbf{Q}) \{ \hat{f}_m(\mathbf{Q}) - [\hat{Q} \cdot \hat{f}_m(\mathbf{Q})] \hat{Q} \},$$

we can state that the quantity determined using the magnetic neutron scattering is the transversal (with respect to the momentum transfer \mathbf{Q}) component of the magnetic-moment distribution. Therefore, for instance, if the neutron scattering is studied in a ferromagnet applying the magnetic field along a direction perpendicular to \mathbf{Q} , we get a magnetic cross-section proportional to $f_m(\mathbf{Q})$, while the cross-section is zero if the magnetic field is parallel to \mathbf{Q} .

The magnetic neutron scattering is particularly interesting if we consider the case of a polarized incoming neutron beam. If \mathbf{p} is a vector describing the polarization, then the total (nuclear and magnetic) cross-section is given by

$$(2.6) \quad \frac{d\sigma}{d\Omega} = \sum_{ll'} \left[b_l b_{l'} + \frac{r_0 \gamma}{2} - 2\mathbf{p} \cdot \mathbf{f}_{m\perp}^{(l)}(\mathbf{Q}) b_{l'} + \right. \\ \left. + \left(\frac{r_0 \gamma}{2} \right)^2 \mathbf{f}_{m\perp}^{(l)}(\mathbf{Q}) \cdot \mathbf{f}_{m\perp}^{(l')}(\mathbf{Q}) \right] \exp [i\mathbf{Q}(\mathbf{R}_l - \mathbf{R}_{l'})],$$

where a new mixed term is present which represents an interference effect between nuclear and magnetic scattering. Such a term is clearly absent when $p = 0$ and can be used to have a safe distinction between nuclear and magnetic contributions.

2.2. Comparison between neutron and X-ray scattering. – The presence of a finite range of the magnetic-moment density makes the behaviour of the magnetic neutron scattering very similar to that of X-ray charge (Thomson) scattering. In fact, as in the case of X-rays the magnetic neutron scattering is not isotropic, however an important qualitative difference is present. In the case of X-rays the form factor is governed by the total electron density, so that it is not strongly affected by the chemical bonds possibly present in various substances. In the case of neutrons, on the other hand, the magnetic density $m(\mathbf{r})$ is generally produced by the valence electrons, the same electrons involved in the bonds, so that the form factor of a given element can change appreciably in changing the chemical environment. This behaviour can be used to extract information on

the chemical bonds as well as on the magnetic properties of various systems, however the magnetic neutron scattering is not generally useful to derive accurate structural data, apart from the utility in identifying the magnetic structures.

3. – Diffraction in crystals and disordered systems.

In subsect. 1.1 we described the general behaviour of the neutron cross-section. However, as in the case of X-ray diffraction, the actual intensity pattern obtained in an experiment depends even qualitatively on the nature of the sample being investigated. We can distinguish two general cases, namely crystals and disordered systems like amorphous and liquid materials.

In the case of crystals the nuclear positions belong to a (three-dimensional) translation group, *i.e.* each position vector is the sum of a vector position of a unit cell and a vector position within the unit cell:

$$(3.1) \quad \mathbf{R}_{ls} = \mathbf{R}_l + \mathbf{r}_s ,$$

where l runs over the N cells in the crystal and s runs over the r nuclei present in the unit cell. Of course, \mathbf{R}_l generates a Bravais lattice because it can be written as

$$(3.2) \quad \mathbf{R}_l = n_l \mathbf{a}_1 + m_l \mathbf{a}_2 + k_l \mathbf{a}_3 ,$$

where n_l, m_l and k_l are integers and $\mathbf{a}_1, \mathbf{a}_2$ and \mathbf{a}_3 are three vectors defining the translation group. Therefore, in a crystal it is convenient to define

$$(3.3) \quad \bar{b}_s = \langle b_{ls} \rangle \quad \text{and} \quad \Delta_{ls} = b_{ls} - \bar{b}_s ,$$

where $\langle \dots \rangle$ indicates the average over all the cells in the crystal but holding fixed the site s within the cell. Then, using eq. (1.9a), we get

$$(3.4) \quad \frac{d\sigma}{d\Omega} = \left| \sum_l \sum_s (\bar{b}_s + \Delta_{ls}) \exp [i\mathbf{Q}(\mathbf{R}_l + \mathbf{r}_s)] \right|^2 .$$

Thanks to the fact that $\langle \Delta_{ls} \rangle = 0$, we can split the cross-section into two contributions as in eq. (1.13). We get

$$(3.5) \quad \frac{d\sigma}{d\Omega} = \left| \sum_s \bar{b}_s \exp [i\mathbf{Q}\mathbf{r}_s] \sum_l \exp [i\mathbf{Q}\mathbf{R}_l] \right|^2 + \\ + N \sum_s \sum_{s'} \sum_l \langle \Delta_{0s} \Delta_{ls'} \rangle \exp [i\mathbf{Q}(\mathbf{r}_s - \mathbf{r}_{s'})] \exp [i\mathbf{Q}\mathbf{R}_l] .$$

Because of the lattice periodicity we have

$$(3.6) \quad \sum_l \exp [i\mathbf{Q}\mathbf{R}_l] = \begin{cases} N & \text{if } \mathbf{Q} \text{ is a reciprocal-lattice vector,} \\ 0 & \text{otherwise.} \end{cases}$$

This relationship can be written in a compact form as follows:

$$(3.7) \quad \sum_l \exp[i\mathbf{Q}\mathbf{R}_l] = N \sum_{\mathbf{G}} \delta_{\mathbf{Q}\mathbf{G}} = \frac{(2\pi)^3}{\Omega_0} \sum_{\mathbf{G}} \delta(\mathbf{Q} - \mathbf{G}),$$

where \mathbf{G} is a reciprocal-lattice vector and $\delta_{\mathbf{Q}\mathbf{G}}$ indicates the Kroneker symbol, while $\delta(\mathbf{Q} - \mathbf{G})$ is the Dirac delta-function. As is well known, the reciprocal-lattice vectors have the following property:

$$(3.8) \quad \mathbf{G} \cdot \mathbf{R}_l = 2\pi \cdot (\text{integer})$$

and are given by

$$(3.9) \quad \mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3,$$

where \mathbf{b}_1 , \mathbf{b}_2 and \mathbf{b}_3 define the unitary traslation in the reciprocal lattice. Equation (3.7) is a form of the well-known Bragg law. As a consequence of eqs. (3.5) and (3.7) we can state that the elastic cross-section contains two terms: the first one accounts for the Bragg scattering and is nonzero only for selected values of the momentum transfer, while the second is in general relatively structureless and hence much more isotropic. It is important to note that the differential cross-section of Bragg scattering is of the order of N^2 , while the diffuse term is of the order of N , as is seen in eq. (3.5) considering that $\langle \Delta_{0s} \Delta_{ls'} \rangle$ is a rapidly decaying function of l . Therefore, the Bragg scattering is due to the coherence between the waves scattered by two nuclei, in such a way that, when the Bragg law is verified, all the waves interfere constructively with each other, thus giving rise to a very high cross-section. The diffuse term, on the contrary, is connected to the almost incoherent scattering due to the scattering amplitude fluctuations Δ_{ls} . Therefore, the incoherent scattering, if accurately determined, can allow the study of the local environment in partially disordered systems, *e.g.* random alloys and hydrogen-bonded compounds.

When we consider the scattering in systems where no periodic arrangement of the nuclei is present, the situation changes, because the constructive interference between the waves scattered by two different nuclei cannot take place in general. When this is the case and if the system contains more than one element, it is useful to write the scattering amplitude at the l -th site in the form

$$(3.10) \quad b_l = b_\alpha + \Delta_l,$$

where b_α is the average scattering amplitude of the α -th element, which has been assumed to occupy the l -th site. The fluctuation Δ_l accounts for the change of b_α from site to site due to various effects as nuclear spin and isotope distribution. Therefore, the cross-section can be written as follows:

$$(3.11) \quad \frac{d\sigma}{d\Omega} = \sum_{\alpha\beta} b_\alpha b_\beta \sum_{ll'} \langle \exp[i\mathbf{Q}\mathbf{R}_l] \exp[-i\mathbf{Q}\mathbf{R}_{l'}] \rangle_{l(\alpha)l'(\beta)} + \\ + \sum_{ll'} \langle \Delta_l \Delta_{l'} \exp[i\mathbf{Q}\mathbf{R}_l] \exp[-i\mathbf{Q}\mathbf{R}_{l'}] \rangle,$$

where $\langle \dots \rangle_{l(\alpha)l'(\beta)}$ indicates that the average has to be taken over all the system configurations that contain an atom α at the site l and an atom β at the site l' . Due to its nature the second term in eq. (3.11) is purely incoherent and it is nonzero only when $l=l'$, so that its contribution is isotropic. The first term in eq. (3.11) contains the partially constructive interference connected to the local correlations between different atoms. Then eq. (3.11) is usually written in the form

$$(3.12) \quad \frac{d\sigma}{d\Omega} = \sum_{\alpha\beta} b_{\alpha} b_{\beta} S_{\alpha\beta}(\mathbf{Q}) + N \langle \Delta_l^2 \rangle,$$

where $S_{\alpha\beta}(\mathbf{Q})$ is called partial structure factor. The determination of $S_{\alpha\beta}(\mathbf{Q})$ is particularly useful because its Fourier transform is given by

$$(3.13) \quad G_{\alpha\beta}(\mathbf{r}) = \frac{1}{(2\pi)^3} \int \exp[i\mathbf{Q}\mathbf{r}] S_{\alpha\beta}(\mathbf{Q}) d\mathbf{Q} = \sum_{l'} \langle \delta(\mathbf{r} - \mathbf{R}_{l'} + \mathbf{R}_l) \rangle_{l(\alpha)l'(\beta)}.$$

Therefore, $G_{\alpha\beta}(\mathbf{r})$ contains the distribution of the relative distances between atoms α and β . Looking at eq. (3.12) it is evident that an actual experiment provides $d\sigma/d\Omega$, so that only properly weighted combinations of the various $S_{\alpha\beta}(\mathbf{Q})$ can be obtained. In general even this combination can be useful, but often one can take great advantage from a combined neutron and X-ray diffraction experiment.

The main difference between neutron and X-ray scattering is due to the fact that the neutron scattering amplitudes should be replaced by the X-ray scattering factors which are dependent on the momentum transfer and have a smooth dependence on the atomic number. Therefore, for instance, an X-ray scattering experiment is of little help in studying order-disorder transitions in systems containing elements of similar atomic numbers, while this is not the case in neutron scattering.

4. - Introduction to inelastic scattering.

4.1. *Generalities.* - In deriving eq. (1.9a) we neglected all inelastic-scattering contributions, by assuming fixed nuclei. However, even in the case of the heaviest elements at very low temperature the nuclei cannot be considered as fixed. Furthermore the typical vibrational frequency ν can be as high as 10^{13} Hz, so that the corresponding quantized energy is $h\nu = 40$ meV. Because the energy of a neutron having a wavelength of 1 Å is about 81 meV (see table I), we see that the vibrational frequency of the nuclei in a system is nonnegligible with respect to the neutron energy.

Therefore, to derive the cross-section as defined in eq. (1.10a) we have to

consider the Fourier transform of the time-dependent wave amplitude, that is:

$$(4.1) \quad \tilde{\psi}(\omega) = \int \exp[-i\omega t] \psi(t) dt,$$

where the time-dependent amplitude is the generalization of that given in eq. (1.2) taking into account the time dependence of the nuclear position:

$$(4.2) \quad \psi(t) = \int \exp[i\mathbf{K}_0 \cdot \mathbf{r}] \exp[-i\mathbf{K} \cdot \mathbf{r}] \rho_N[\mathbf{r} - \mathbf{R}_0(t)] d\mathbf{r}.$$

Because in eq. (1.7) the particle flux is proportional to the square modulus of the amplitude, we have that the energy-dependent flux (through the relationship $\hbar\omega = E$) is given by

$$(4.3) \quad \phi(\varepsilon) = B \int \exp[-i\omega t] \langle \exp[i\mathbf{Q}\mathbf{R}_0(0)] \exp[-i\mathbf{Q}\mathbf{R}_0(t)] \rangle dt,$$

where the average has to be taken over all possible vibrations. Actually a detailed calculation of this average implies a quantum-mechanical treatment of the nuclear vibrations, but many results can be obtained avoiding such an approach. The generalization of eq. (4.3) to the case of many moving nuclei is easily obtained, so that the following form for the cross-section is derived, according to eq. (1.10a):

$$(4.4) \quad \frac{d^2\sigma}{d\Omega d\varepsilon} = \frac{1}{2\pi} \sum_{ll'} b_l b_{l'} \int \exp[-i\omega t] \langle \exp[i\mathbf{Q}\mathbf{R}_l(0)] \exp[-i\mathbf{Q}\mathbf{R}_{l'}(t)] \rangle dt.$$

Using this equation we shall derive the cross-section appropriate to some simple case, namely the elastic Bragg scattering in the case of the moving nuclei and the inelastic scattering from a high-frequency sound wave (phonon).

4.2. *Bragg scattering and Debye-Waller factor.* – To derive the purely elastic scattering in a crystal using eq. (4.4), we observe that in this case there exists a set of equilibrium positions $\mathbf{R}_l^{(0)}$ of the nuclei, while the time-dependent positions can be obtained adding a time-dependent (small) fluctuation $u_l(t)$. The fluctuation $u_l(t)$ is not a completely random function of the site and of the time, however $\mathbf{u}_l(0)$ and $\mathbf{u}_{l'}(t)$ become uncorrelated when t becomes larger and larger. Therefore, we have

$$(4.5) \quad \lim_{t \rightarrow \infty} \langle \exp[i\mathbf{Q}\mathbf{R}_l(0)] \exp[-i\mathbf{Q}\mathbf{R}_{l'}(t)] \rangle = \langle \exp[i\mathbf{Q}\mathbf{R}_l] \rangle \langle \exp[-i\mathbf{Q}\mathbf{R}_{l'}] \rangle.$$

To evaluate the average of the exponentials appearing in the right-hand side of eq. (4.5), we observe that it is reasonable to assume a Gaussian distribution for

each Cartesian component of the fluctuations \mathbf{u}_l , then we have

$$(4.6) \quad \langle \exp[i\mathbf{Q}(\mathbf{R}_l^{(0)} + \mathbf{u}_l)] \rangle = \exp[i\mathbf{Q}\mathbf{R}_l^{(0)}] \prod_{\alpha=1}^3 \int_{-\infty}^{+\infty} du_{l\alpha} \cdot \\ \cdot P_{\alpha}(u_{l\alpha}) \exp[iQ_{\alpha} u_{l\alpha}] = \exp[i\mathbf{Q}\mathbf{R}_l^{(0)}] \exp[-W_l],$$

where the Debye-Waller factor $\exp[-W_l]$ is given by

$$(4.7) \quad \exp[-W_l] = \prod_{\alpha=1}^3 \exp[-Q_{\alpha}^2 \langle u_{l\alpha}^2 \rangle].$$

In eqs. (4.6) and (4.7) the index α runs over the three Cartesian coordinates x , y and z . In view of eq. (4.5) it is useful to split the integrand of eq. (4.4) in the following way:

$$(4.8) \quad \langle \exp[i\mathbf{Q}\mathbf{R}_l(0)] \exp[-i\mathbf{Q}\mathbf{R}_l(t)] \rangle = \\ = F_{l'}(t) + \exp[i\mathbf{Q}(\mathbf{R}_l^{(0)} - \mathbf{R}_l^{(0)})] \exp[-W_l - W_{l'}],$$

where $F_{l'}(t)$ contributes to the purely inelastic scattering only, while, using the second term, eq. (3.5) is regained by properly inserting the Debye-Waller factor. We have

$$(4.9) \quad \frac{d^2\sigma}{d\Omega d\varepsilon} = \frac{1}{2\pi} \sum_{l'} \int \exp[-i\omega t] F_{l'}(t) dt + \\ + \vartheta(\omega) \left\{ \left| N \sum_s \bar{b}_s \exp[-W_s] \exp[i\mathbf{Q}\mathbf{r}_s] \sum_G \delta_{\mathbf{Q}G} \right|^2 + \right. \\ \left. + N \sum_{ss'} \sum_l \langle \Delta_{0s} \Delta_{ls'} \rangle \exp[i\mathbf{Q}(\mathbf{r}_s - \mathbf{r}_{s'})] \exp[-W_s - W_{s'}] \exp[i\mathbf{Q}\mathbf{R}_l] \right\}.$$

Because $\exp[-W]$ is a decreasing function of the momentum transfer, its presence produces only a decrease of the intensity of the elastic-scattering contribution at high momentum transfer.

4.3. *Inelastic phonon scattering.* – In an ideal harmonic crystal there exist $3N$ sinusoidal waves (phonons) such that the nuclear (small) fluctuations from the equilibrium positions are given by

$$(4.10) \quad \mathbf{u}_l(t) = \mathbf{e}_{\mathbf{q}j} \exp[i\mathbf{q}\mathbf{R}_l^{(0)}] \exp[i\omega_{\mathbf{q}j} t],$$

where \mathbf{q} and $\omega_{\mathbf{q}j}/2\pi$ are the wave vector and the frequency of the wave, $\mathbf{e}_{\mathbf{q}j}$ is the

polarization vector and j is a branch index. Equation (4.4) can be written as follows:

$$(4.11) \quad \left(\frac{d^2 \sigma}{d\Omega d\varepsilon} \right)_{\text{in}} = \frac{1}{2\pi} \sum_{l'l''} b_l b_{l''} \exp [i\mathbf{Q}(\mathbf{R}_{l'}^{(0)} - \mathbf{R}_{l''}^{(0)})] \cdot \int \exp [-i\omega t] \langle \exp [i\mathbf{Q}\mathbf{u}_l(0)] \exp [-i\mathbf{Q}\mathbf{u}_{l''}(t)] \rangle dt.$$

Then, assuming $u(t)$ small enough, we can develop the exponentials in the right-hand side of eq. (4.11) to the lowest nonvanishing (the second) order, so that the cross-section becomes

$$(4.12) \quad \left(\frac{d^2 \sigma}{d\Omega d\varepsilon} \right)_{\text{in}} = \frac{1}{2\pi} \sum_{l'l''} b_l b_{l''} \exp [i\mathbf{Q}(\mathbf{R}_{l'}^{(0)} - \mathbf{R}_{l''}^{(0)})] \cdot \int \exp [-i\omega t] \langle [\mathbf{Q} \cdot \mathbf{u}_l(0)] [\mathbf{Q} \cdot \mathbf{u}_{l''}(t)] \rangle dt,$$

where the subscript in means that only inelastic-scattering contributions have been retained. Substituting eq. (4.10) we get

$$(4.13) \quad \left(\frac{d^2 \sigma}{d\Omega d\varepsilon} \right)_{\text{in}} = N^2 b^2 |\mathbf{Q} \cdot \mathbf{e}_{qj}|^2 \sum_G \delta_{\mathbf{Q}-\mathbf{G},\mathbf{q}} \delta(\omega - \omega_{qj}),$$

where we assumed for simplicity that all the nuclei in the crystal have the same scattering amplitude b . Looking at eq. (4.13) we see that it is possible to measure simultaneously the wave vector \mathbf{q} , the frequency $\omega_{qj}/2\pi$ and the polarization vector \mathbf{e}_{qj} , by performing an inelastic-neutron-scattering experiment. It should be mentioned that the classical approach we employed resulted in a partially incorrect cross-section, because to derive eq. (4.13) we have tacitly assumed that one wave only is present. Actually this is not the case because many waves are thermally excited. Moreover, we have not used a condition necessary to have real fluctuations $\mathbf{u}_l(t)$. Nevertheless eq. (4.13) contains the most relevant physics. The correct form of the inelastic phonon cross-section as obtained from a full calculation is

$$(4.14) \quad \left(\frac{d^2 \sigma}{d\Omega d\varepsilon} \right)_{\text{in}} = N^2 b^2 \frac{K}{K_0} \frac{1}{2M} \sum_G |\mathbf{Q} \cdot \mathbf{e}_{qj}|^2 \frac{1}{\omega_{qj}} \cdot [n(\omega_{qj}) \delta(\omega + \omega_{qj}) \delta_{\mathbf{Q}+\mathbf{q},\mathbf{G}} + (n(\omega_{qj}) + 1) \delta(\omega - \omega_{qj}) \delta_{\mathbf{Q}-\mathbf{q},\mathbf{G}}],$$

where

$$(4.15) \quad n(\omega) = \left[\exp \left[\frac{\hbar\omega}{K_B T} \right] - 1 \right]^{-1},$$

K_B being the Boltzmann constant and T the absolute temperature.

