X-ray Bragg scattering in the Born–Oppenheimer approximation. II.
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Abstract

With the use of van Hove's pair correlation function it is shown that, in the Born–Oppenheimer approximation, X-ray Bragg scattering is elastic and thermal diffuse scattering is inelastic.

It is commonly assumed that X-ray Bragg scattering from crystals is elastic and that thermal diffuse scattering (TDS) is inelastic, but this appears to be proven only in the harmonic approximation of the atomic motions (Laval, 1941; von Laue, 1948). This assumption was recently doubted by Stewart (1977), who discussed vibrational averaging in the adiabatic theory of the electronic wave-functions and found two different expressions for Bragg scattering and for elastic scattering [Stewart (17) and (21)]. Such a result would imply that Bragg scattering is, in principle, not an observable quantity. On the other hand, the separation of the TDS background under the Bragg peak by means of Mössbauer experiments and by calculating the ratio of elastic to inelastic scattering (Bärnighausen, 1975, 1978) is only meaningful if our above assumption is correct. We tried to prove it in a preceding paper (Scheringer, 1979; hereafter SCHE) but did not fully achieve our aim. In this paper we shall give a complete derivation in the Born–Oppenheimer approximation of the electronic wavefunctions. The appropriate means appears to be the particle pair-correlation function introduced by Van Hove (1954, hereafter VH) and Glauber (1955). This function contains the time dependence of the scattering, which plays the decisive role for the transfer of energy from the vibrating lattice to the X-ray, and *vice versa*. In some standard text books (James, 1948; Cochran, 1964; Maradudin, Montroll, Weiss & Ipatova, 1971; Willis & Pryor, 1975) the energy transfer is not fully treated (because of the smallness of the effect) and the presentations are centred on the calculation of the scattered intensity. The pair-correlation function has mainly been applied to the scattering of neutrons and is extensively described in this context (VH; Sjölander, 1964; Marshall & Lovesey, 1971). For X-ray scattering we have to identify the particles with electrons and can then directly apply VH's theory. In our presentation we shall mainly follow VH and Sjölander (1964).

We proceed as follows: first we set up the basic equation for the coherent scattering of X-rays (partial differential cross section) and sort out the elastic contribution. Then we introduce the crystal as a three-dimensionally periodic distribution of electron density and show that the elastic part of the scattering from this density distribution follows Bragg's law. Finally we eliminate the non-Bragg scattering and show that it is inelastic and that its distribution in reciprocal space is essentially diffuse.

We consider a system of M electrons, combine VH's

equations (2), (4) and (6) [VH(2) *etc.*], introduce the Thomson scattering length e^2/mc^2 for the scattering of X-rays by an electron, and obtain, in the first Born approximation, for the coherent partial differential cross section

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right)_{coh} = M\left(\frac{e^2}{mc^2}\right)^2 \frac{q'}{q} \frac{1}{2\pi}$$
$$\times \int_{-\infty}^{+\infty}\!\!\int \exp(i\mathbf{K}.\mathbf{x} - i\omega t) \, G(\mathbf{x}, t) \, d\mathbf{x} \, dt. \quad (1)$$

We have omitted the polarization factor in (1), since it is commonly introduced in the stage of data reduction. q and q' are the absolute values of the wavevectors of the incident and scattered photon respectively, and the conservation laws for energy and quasi-momentum apply (VH; Sjölander, 1964; Cochran & Cowley, 1967). $G(\mathbf{x}, t)$ is the space/time-dependent pair-correlation function for the electrons in the system, and is given by

$$G(\mathbf{x},t) = \frac{1}{M} \int \langle \hat{\rho}(\mathbf{x}', 0) \, \hat{\rho}(\mathbf{x} + \mathbf{x}', t) \rangle \, d\mathbf{x}', \quad (2)$$

where

$$\hat{\rho}(\mathbf{x}, t) = \sum_{J=1}^{M} \delta[\mathbf{x} - \hat{\mathbf{X}}_J(t)] \quad (3)$$

is the charge density operator and $\hat{\mathbf{X}}_J(t)$ is a Heisenberg operator. For different times these operators do not commute. The angle brackets denote the average over all initial thermal states and thus form the time average. The summation over all final states of the system (which are in agreement with the conservation laws) is already contained in $G(\mathbf{x},t)$. The Born–Oppenheimer approximation is only implicitly contained in $G(\mathbf{x},t)$. The Heisenberg operators $\hat{\mathbf{X}}_J(t)$ of (3) contain the position vectors $\mathbf{x}_J$ of the electrons and the Hamiltonian of the system. The total wavefunction for the Hamiltonian may be separated into an electronic and a nuclear wavefunction according to the Born–Oppenheimer approximation. In contradistinction to VH(10) we have chosen an alternate formulation of $G(\mathbf{x},t)$ in (2), as was given by Sjölander (2.2) and (2.3), which reveals the similarity to the Patterson function in the space variable $\mathbf{x}$. Equation (1) shows that the cross section is essentially given by the four-dimensional space/time Fourier transform of the correlation function $G(\mathbf{x},t)$.

The separation of the cross section according to elastic and inelastic parts, which is our main concern, can be obtained with VH by considering the limit $|t| = \infty$ and so gaining that part of the scattering which does not depend on the time t. With $|t| = \infty$ the $\hat{\rho}$ operators in (2) are statistically independent and, therefore, the average of the product is identical with the product of the averages. In the time average $\langle \hat{\rho}(\mathbf{x} + \mathbf{x}', t) \rangle$ time is no longer relevant and the operators $\hat{\rho}$ become particle densities ρ which now commute.

Hence, from (2) we obtain for the limit $|t| = \infty$

$$G(\mathbf{x},\infty) = \frac{1}{M} \int \langle \rho(\mathbf{x}') \rangle \langle \rho(\mathbf{x} + \mathbf{x}') \rangle \, d\mathbf{x}', \qquad (4)$$

corresponding to VH(20). $G(\mathbf{x},\infty)$ gives rise to elastic scattering only, which is shown as follows. We use the Fourier representation of the δ function

$$\delta(\omega) = \frac{1}{2\pi} \int \exp(-i\omega t) \, dt, \qquad (5)$$

introduce (4) and (5) in (1), and obtain

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)^{\text{elast}}_{\text{coh}} = \left(\frac{e^2}{mc^2} \right)^2 \delta(\omega) \int \exp(i\mathbf{K}.\mathbf{x})$$

$$\times \int \langle \rho(\mathbf{x}) \rangle \langle \rho(\mathbf{x} + \mathbf{x}') \rangle \, d\mathbf{x}' \, d\mathbf{x}. \qquad (6)$$

(6) is consistent only with $\omega = 0$, or with

$$\hbar\omega = \hbar\omega(q) - \hbar\omega(q') = 0,$$

whereby the property of elastic scattering is proven. We further deduce from (6) that coherent elastic scattering arises from the convolution of $\langle \rho(\mathbf{x}) \rangle$ with $\langle \rho(-\mathbf{x}) \rangle$; this convolution product is known as the Patterson function. It is expedient to eliminate the convolution integral in (6), and also the dependence on ω, which is of no further interest. Thus, we integrate over ω, reformulate the double integral and obtain

$$\left(\frac{\partial \sigma}{\partial \Omega} \right)^{\text{elast}}_{\text{coh}} = \left(\frac{e^2}{mc^2} \right)^2 \left| \int \exp(i\mathbf{K}.\mathbf{x}) \langle \rho(\mathbf{x}) \rangle \, d\mathbf{x} \right|^2, \qquad (7)$$

corresponding to the first term of VH(23).

Hitherto our consideration was a general one. To derive Bragg intensities we have to introduce the condition that the system of electrons represents a crystal, *i.e.* that the electron distribution is periodic on average. Thus, our condition is

$$\langle \rho(\mathbf{x}) \rangle = \langle \rho(\mathbf{x} + \mathbf{l}) \rangle, \qquad (8)$$

where $\mathbf{l}$ is a lattice vector. If we introduce (8) into (7), we obtain the Bragg intensity and structure factor as follows. For a crystal with N cells, the integral in (7) assumes the form

$$\sum_{l=1}^{N} \exp(i\mathbf{K}.\mathbf{l}) \int_{\text{cell}} \langle \rho(\mathbf{x}) \rangle \exp(i\mathbf{K}.\mathbf{x}) \, d\mathbf{x}. \qquad (9)$$

With (9) introduced into (7), we obtain for a sufficiently large N

$$\left(\frac{\partial \sigma}{\partial \Omega} \right)^{\text{elast}}_{\text{coh}} = \left(\frac{e^2}{mc^2} \right)^2 N^2 \delta(\mathbf{K} - \mathbf{H}) |F(\mathbf{K})|^2, \qquad (10)$$

where $\mathbf{H}$ is a vector in the reciprocal lattice, and

$$F(\mathbf{K}) = \int_{\text{cell}} \langle \rho(\mathbf{x}) \rangle \exp(i\mathbf{K}.\mathbf{x}) \, d\mathbf{x}. \qquad (11)$$

The δ function in (10) shows that, for a (sufficiently large) crystal, elastic scattering follows Bragg's law. The term $|F(\mathbf{K})|^2$ in (10) shows $F(\mathbf{K})$ to be the structure factor, and with (11) we see that the structure factor is the Fourier transform of the average density in the unit cell. Hence, (10) corresponds to our earlier result SCHE(11a), and (11) to SCHE(11b).

In order to obtain the non-Bragg scattering we subtract the Bragg scattering from the total scattering and thus define with VH(22)

$$G'(\mathbf{x},t) = G(\mathbf{x},t) - G(\mathbf{x},\infty). \qquad (12)$$

To show that this part gives rise to inelastic scattering, we have to introduce $G'(\mathbf{x},t)$ instead of $G(\mathbf{x},t)$ in (1). Since $G'(\mathbf{x},t)$ depends on time we shall never obtain a δ function of ω in (1), like the one in (6). Hence, we shall never obtain $\omega = 0$ for a finite part of the non-Bragg scattering, and thus this scattering is inelastic, and $q' \neq q$. To complete our proof we have to show that inelastic scattering is essentially diffuse in reciprocal space, and does not show sharp maxima like the Bragg peaks. The spatial distribution of the inelastic scattering can conveniently be discussed by considering the corresponding density distribution and then its Fourier transform. We shall do this in the static approximation, $t = 0$, which we also used in SCHE. With SCHE(5) we divide the density according to $\rho = \langle \rho \rangle + \Delta\rho$ and, with SCHE(6), obtain only two parts of $G(\mathbf{x})$. The first part gives rise to the Bragg scattering, the second to the non-Bragg, *i.e.* inelastic scattering. This second part is (in the static approximation)

$$G(\mathbf{x})^{\text{inel}}_{\text{coh}} = \frac{1}{M} \int \langle \Delta\rho(\mathbf{x}') \, \Delta\rho(\mathbf{x} + \mathbf{x}') \rangle \, d\mathbf{x}'. \qquad (13)$$

Apart from the factor $1/M$, (13) represents the inverse Fourier transform of the second term in SCHE(10). (13) also has the form of a Patterson function, but here it refers to the non-periodic part of the density distribution in the crystal, $\Delta\rho$. For $\mathbf{x} = 0$ $G(\mathbf{x})^{\text{inel}}_{\text{coh}}$ has a high peak, and for increasing $|\mathbf{x}|$ $G(\mathbf{x})^{\text{inel}}_{\text{coh}}$ flattens out but retains a certain structure with positive and negative regions. This remaining structure corresponds to the coupling of the thermal motions of the atoms in the crystal. For $|\mathbf{x}| \to \infty$ $G(\mathbf{x})^{\text{inel}}_{\text{coh}}$ becomes zero because $\Delta\rho(\mathbf{x}')$ and $\Delta\rho(\mathbf{x} + \mathbf{x}')$ in (13) are no longer correlated and the thermal average becomes $\langle \Delta\rho(\mathbf{x}') \rangle \langle \Delta\rho(\mathbf{x} + \mathbf{x}') \rangle$, which is zero by virtue of the definition of $\Delta\rho$, *cf.* SCHE(6). Hence, the Fourier transform of (13) is essentially flat, *i.e.* the thermal coherent inelastic scattering is diffuse (TDS). There are certain singularities in the TDS spectrum (critical points) which are due to a possible slow convergence of $G(\mathbf{x})^{\text{inel}}_{\text{coh}}$ (for $|\mathbf{x}| \to \infty$) and to the periodic structure of the crystal (Van Hove, 1953, 1954; Maradudin, Montroll, Weiss & Ipatova, 1971, pp. 150–166).

We have shown that coherent elastic X-ray scattering from crystals is Bragg scattering and that thermal coherent inelastic scattering is diffuse. Since, in our consideration, there are no other types of scattering, we can also state the reverse, namely, that Bragg scattering is elastic and TDS is inelastic.

What then is the solution of the discrepancy of Stewart's (1977) equations, where (17) stands for Bragg scattering and (21) for elastic scattering? Firstly, Stewart generalizes the concept of Bragg scattering so that it can be applied to systems which no longer represent a crystal (for a crystallographer a very unorthodox generalization) and defines Bragg scattering to be the scattering from the thermodynamic

average, $\langle\rho(\mathbf{x})\rangle$. Stewart (1979) found that, for systems with a small number of particles, his (1977) equations (17) and (21) indeed lead to different intensities. Thus for small systems other configurations than the thermodynamic average can also contribute to elastic scattering. Hence, for small systems, Bragg scattering may thus not be an observable quantity. VH also refers to the case of small systems: the asymptotic convergence for $|t| \to \infty$, our equation (4), may then hold only in the mean. In the meantime Stewart (1979) has been able to convince himself that, for large systems, his (1977) equations (17) and (21) lead to the same intensity. Thus, for a crystal where the number of particles is very large, Bragg scattering and elastic scattering always coincide.

References

BÄRNIGHAUSEN, E. (1975). *J. Appl. Cryst.* **8**, 477–487.
BÄRNIGHAUSEN, E. (1978). *J. Appl. Cryst.* **11**, 221–228.
COCHRAN, W. (1964). *Phonons and Phonon Interactions*, pp. 102–118. New York: Benjamin.

COCHRAN, W. & COWLEY, R. A. (1967). *Handbuch der Physik*, **25**, 2a, pp. 59–156. Berlin, Heidelberg, New York: Springer.
GLAUBER, R. J. (1955). *Phys. Rev.* **98**, 1692–1698.
JAMES, R. W. (1948). *The Optical Principles of the Diffraction of X-Rays*. London: Bell.
LAUE, M. VON (1948). *Röntgenstrahlinterferenzen*. Leipzig: Akad. Verlagsgesellschaft.
LAVAL, J. (1941). *Bull. Soc. Fr. Minéral.* **64**, 1–138.
MARADUDIN, A. A., MONTROLL, E. W., WEISS, G. H. & IPATOVA, I. P. (1971). *Theory of Lattice Dynamics in the Harmonic Approximation. Solid State Phys. Suppl.* 3. New York and London: Academic Press.
MARSHALL, W. & LOVESEY, S. W. (1971). *Theory of Thermal Neutron Scattering*. Oxford: Clarendon Press.
SCHERINGER, C. (1979). *Acta Cryst.* A**35**, 340–342.
SJÖLANDER, A. (1964). *Phonons and Phonon Interactions*, pp. 76–101. New York: Benjamin.
STEWART, R. F. (1977). *Isr. J. Chem.* **16**, 137–143.
STEWART, R. F. (1979). Private communication.
VAN HOVE, L. (1953). *Phys. Rev.* **89**, 1189–1193.
VAN HOVE, L. (1954). *Phys. Rev.* **95**, 249–262.
WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.

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Any laboratory interested in participating in the project should contact: Dr D. C. Creagh, Chairman, IUCr X-ray Attenuation Project, Physics Department, Royal Military College, Duntroon, ACT 2600, Australia.

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