Table 3. *Refinement of a thin crystal*

Dimensions in mm. Dimensions (1) are from a single-cycle least-squares refinement varying all allowed parameters. Dimensions (2) are from a single-cycle least-squares refinement omitting ($hk0$) reflexions from data set B'.

	Initial dimensions	Dimensions (1)	Dimensions (2)	Ideal Dimensions
Data set A' (b rotation axis)				
(100)	0·096000	0·089645	0·096000	0·100000
(010)	0·140000	0·192937	0·140000	0·140000
(001)	0·004000	0·001590	0·001588	0·002000
Data set B' (c rotation axis)				
(100)	0·100000	0·098257	0·100000	0·100000
(010)	0·144000	0·140046	0·144000	0·140000
(001)	0·004000	0·001600	0·001590	0·002000

obtained by evaluating the random error implicit in the absorption correction.

Extension of the methods here, differentiating the absorption correction for the additional parameters involved for the case of a crystal in the presence of its mother liquor in a capillary (Wells, 1960) appears quite feasible.

It should be noted that using a four-circle geometry, geometrically different measurements of F_h^2 may be made for a single zone. We could label these observations:

$$F_{hii'}^2 = k_i \frac{A_{0hii'}}{A_{hii'}} F_{0hii'}^2$$

where the i' refers to the i'th observation of F_h^2 in the ith zone.

$$R = \sum_{h,i,j,i',j'} W_{hij'j'}\{\ln F_{hii'}^2 - \ln F_{hjj'}^2\}^2$$

and our simultaneous equations are

$$\frac{\partial R}{\partial u_k} = 0 \text{ as before.}$$

The arguments used are still true if we only have one data zone and

$$R = \sum_{h,i',j'} W_{hi'j'}\{\ln (F_{hi'}^2) - \ln (F_{hi'}^2)\}^2$$

where i' and j' refer to geometrically different measurements in one zone. The one scale constant k_1 is set to unity.

References

Busing, W. R. & Levy, H. A. (1957). *Acta Cryst.* **10**, 180.
Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035.
Rae, A.D. (1965). *Acta Cryst.* **19**, 683.
Wells, M. (1960). *Acta Cryst.* **13**, 722.

X-ray Compton–Raman Scattering

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X-ray Compton–Raman scattering is reviewed from an original point of view. The differential cross section for X-ray inelastic scattering from crystals is derived from first principles to explain the coexisting Compton and Raman scattering in solids. This derivation makes it possible to express the cross section in terms of the current correlation of electrons in a crystal. All the electrons, including the core electrons, are treated on an equal basis in this formulation. The relationship between the X-ray absorption spectrum and the inelastic scattering spectrum is discussed in detail. This formulation provides a theoretical justification to the importance of X-ray inelastic scattering experiments in connection with an experimental determination of the two-particle Green's function. In the Appendices the theoretical formulations are given in detail, which apply not only to the ordinary inelastic scattering process, but also to the processes involving Bragg diffraction.

1. Introduction

Recently, interest in X-ray inelastic scattering from crystals has been renewed for several reasons. From a theoretical point of view, this scattering process may be used to check the validity of the one electron model in solids, and to study the many body effects, if any, among the electrons. From an experimental point of

view, inelastic scattering experiments may give an exciting chance, if possible, to obtain the momentum distribution of valence electrons in a crystal.

The energy spectrum of the X-ray inelastic scattering can reveal its typical shape when sample-crystals consist of atoms of very low atomic number. As Suzuki's experiments on lithium and beryllium (Suzuki, 1967; Suzuki, Kishimoto, Kaji & Suzuki, 1970) have shown clearly this typical shape, several of his results are reproduced here. There are three distinct features in the spectra, as shown in Fig. 1: they are currently called the Rayleigh scattering denoted by λ_0, the Compton scattering denoted by its peak position λ_c, and the X-ray Raman scattering denoted by λ_R. The Rayleigh scattering is the elastic scattering of X-rays. The Compton scattering depends strongly on scattering angle, while the X-ray Raman scattering is almost independent of angle. In crystals of atoms which do not have very low atomic numbers, the spectrum does not show the distinct feature of X-ray Raman scattering. The phenomenon that one can observe in these cases is a superposition of the Compton and the X-ray Raman scattering. Therefore, it should preferably be called X-ray Compton–Raman scattering

When a distinct Raman scattering is observed, its spectrum is closely connected to the absorption spectrum, as seen in Fig. 2. In principle, the underlying mechanism of Compton–Raman scattering is the inelastic scattering of photons, especially X-rays, by the electrons in solids.

In order to understand this phenomenon, it is best to start with the classical description of the Compton scattering. The Compton scattering is well known: the
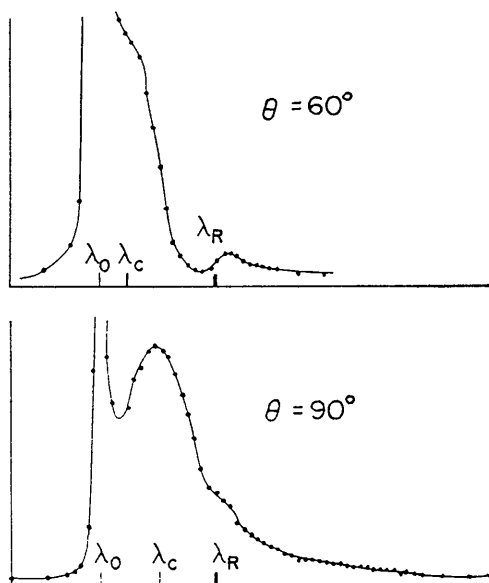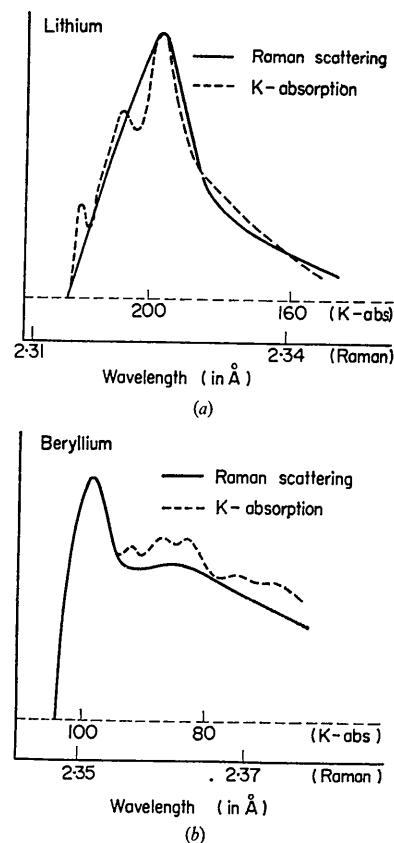

Fig. 2. The relationship between the X-ray Raman spectrum and the X-ray absorption spectrum (Suzuki et al., 1970).

energy loss of a photon in a collision with a free electron. First, this collision will be described classically. Next the collision between a photon and a bound electron will be discussed in a classical model. Then, to make these arguments realistic to some extent, a primitive statistical treatment will be used with the electrons in solids as the scatterers. In this process, one will notice a great difficulty in proceeding via the classical-statistical model, except for the Compton effect of free electrons.

In these classical approaches, the cross section of the scatterers, namely electrons, will not be discussed at all. However, to discuss the intensity distribution of the scattered X-rays as a function of energy, one needs, of course, the scattering cross section. Because of the difficulty in pursuing the classical approach with its inadequacy in describing the cross section in a realistic manner, quantum theory has to be introduced to describe X-ray Compton–Raman scattering. The ordinary quantum mechanical treatment (the first-order Born approximation) will then be commented on briefly. In this paper we will formulate a general expression for the X-ray inelastic scattering from a crystal, using a modern technique where all electrons, including the core electrons, are treated on an equal basis.

Fig. 1. X-ray inelastic scattering spectra from beryllium crystals (Suzuki et al., 1970). The Rayleigh (elastic) scattering is denoted by λ_0. The peak position of the Compton scattering is indicated by λ_c, which depends strongly on scattering angles θ. The X-ray Raman scattering is denoted by λ_R.

The detailed mathematical derivations will be described in the Appendices.

2. A classical model (kinematics)

We consider a free photon having the momentum $\hbar\mathbf{k}_{in}$ and the energy $\hbar\omega_{in}$ colliding with a free electron, whose momentum is given by $\mathbf{p}_{in}$. The diagram for this collision is given by Fig. 3. At the time of collision $(t = t_c)$, we have momentum conservation and energy conservation:

$$\hbar\mathbf{k}_{in} + \mathbf{p}_{in} = \hbar\mathbf{k}_{out} + \mathbf{p}_{out} , \qquad (2\text{-}1)$$

and

$$\hbar\omega_{in} + \frac{(p_{in})^2}{2m} = \hbar\omega_{out} + \frac{(p_{out})^2}{2m} , \qquad (2\text{-}2)$$

where the subscript 'out' stands for the particles after collision. As shown in Fig. 3, we introduce the scattering angle θ for the photon, and the angle Ψ for the incoming electron. Using these experimental variables, and also assuming that the energy loss of the photon is negligibly small, compared with the original energy, we obtain

$$\Delta\lambda_{free} = \lambda_{out} - \lambda_{in} = \frac{2h}{mc} \sin^2 \frac{\theta}{2} + \frac{2}{c}\left(\lambda_{in}\sin\frac{\theta}{2}\right)$$

$$\times \left(\frac{|\mathbf{p}_{in}|}{m}\right)\cos\Psi . \qquad (2\text{-}3)$$

The first term is called the Compton shift, which is independent of the initial velocity of the electron and only depends upon the scattering angle. The second term is the Doppler shift depending upon the velocity of the electron. The first term is usually denoted by $\Delta\lambda_C$:

$$\Delta\lambda_C = 0\cdot024(1 - \cos\theta)\text{ Å} . \qquad (2\text{-}4)$$

Since we have treated this problem classically, we definitely have a photon and an electron coming out in the directions given by the conservation rules. Suppose that one can have an energy-analyzing detector which receives only photons of a specific wavelength, and can set it in the direction given by equation (2-1). Then the detector, when tuned to the wavelength given by equation (2-3), picks up one photon with 100% of probability. Otherwise, it can receive no photons; zero-probability case. This occurs without any uncertainty.

Next we consider the photon colliding with a bound electron from a classical point of view. Again at the time of collision $(t = t_c)$, we have the momentum and energy conservation

$$\hbar\mathbf{k}_{in} + \mathbf{p}_{in}(t_c) = \hbar\mathbf{k}_{out} + \mathbf{p}_{out}(\text{free}) , \qquad (2\text{-}5)$$

and

$$\hbar\omega_{in} + \frac{[p_{in}(t_c)]^2}{2m} = \hbar\omega_{out} + \frac{[p_{out}(\text{free})]^2}{2m} + E(t_c) , \qquad (2\text{-}6)$$

where the momentum of the bound electron is specified at $t = t_c$, and the binding energy, $E(t_c)$, is also at this time. Unlike in the former Compton case, we do not know the specific values of $p_{in}(t_c)$ and $E(t_c)$; they have to be obtained from the equation of motion for the bound electron. However, we assume they have been found in some manner.

Then, we will have the following result:

$$\Delta\lambda_{bound} = \lambda_{out} - \lambda_{in} = \Delta\lambda_{free} + \frac{\lambda_{in}^2}{hc}E(t_c) . \qquad (2\text{-}7)$$

Here we have an additional shift due to the binding energy. If this binding energy corresponds to one of the atomic levels, the energy loss of the photon is greater in this case than in the free electron case. This shift is the classical origin of the X-ray Raman effect. By probability theory, this event is also unambiguous, provided that $p_{in}(t_c)$ is somehow known.

3. Classical statistical model

So far we have treated the case in which the motion of the electron is well established. However, this is not realistic. When one deals with the electrons in solid, the motions of individual electrons are not known *a priori*. Since the Compton shift λ_C does not depend upon the velocity of the electron, this shift is well defined regardless of the state of the electrons. However, the Doppler shift creates indeterminancy concerning the value of $|p_{in}|\cos\Psi$, even if one could treat an ensemble of electrons in a crystal as a free electron gas. More serious is the shift due to the binding energy: in this case, the indeterminancy is more complicated because of the dependence of $E(t_c)$ on $\mathbf{p}_{in}(t_c)$. These uncertainties lead to the broadening of the Compton intensity
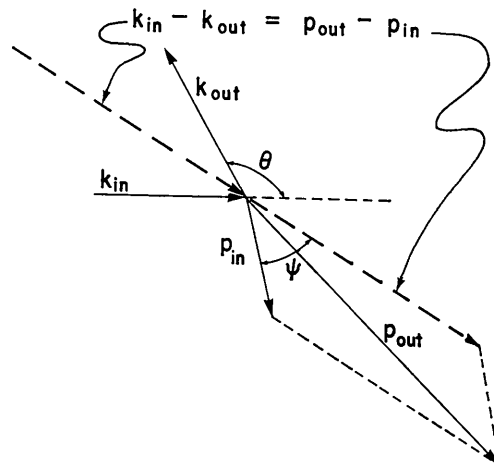

Fig. 3. Diagram of momentum conservation in a collision of a free photon with a free electron. k and $\mathbf{k}_{out}$ are the photon momenta before and after the collision, respectively. The angle θ is the scattering angle of the photon. $\mathbf{p}_{in}$ and $\mathbf{p}_{out}$ are the free electron momenta before and after the collision, respectively. The angle ψ is introduced to give the initial direction of the moving electron.

distribution as a function of the energy or wavelength of the scattered photon:

$$\langle\!\langle \lambda_{\text{out}} \rangle\!\rangle = \lambda_{\text{in}} + \Delta\lambda_c + \frac{2}{c}\left(\lambda_{\text{in}} \sin\frac{\theta}{2}\right)\frac{1}{m}$$

$$\times \langle\!\langle |p_{\text{in}} \cos \Psi| \rangle\!\rangle + \frac{\lambda_{\text{in}}^2}{hc} \langle\!\langle E(t_c) \rangle\!\rangle, \quad (3\text{-}1)$$

where $\langle\!\langle Q \rangle\!\rangle$ indicates that the quantity Q has a distribution. In this case our detector, though tuned to an arbitrary wavelength and set in an arbitrary direction, can receive photons. The number of photons received depends entirely on the distribution of the initial electron momenta, that is, the probability of finding the initial electrons which satisfy the given energy-momentum conservation. In the scattering process, however, a definite energy–momentum conservation rule exists between a photon and an electron.

Let us assume that the density of the electrons in momentum space, that is to say, the momentum distribution, has spherical symmetry and depends only on the magnitude of the momentum. For a bound electron, this assumption implies that the binding force is a central force. Then after some consideration (Appendix I), we will obtain the spectral distribution of the scattered photons to be:

$$J(\lambda_{\text{out}}) \propto \int_{P(\lambda_{\text{out}})}^{\infty} \frac{I(p)}{\dfrac{\partial \lambda_{\text{out}}}{\partial(\cos \Psi)}} \, dp . \quad (3\text{-}2)$$

where $I(p)$ is the momentum distribution.

In the case of conventional Compton scattering where the electrons are considered to be free, this equation reduces to the classical relationship for the Compton spectrum by DuMond (1929), since

$$\frac{\partial \lambda_{\text{out}}}{\partial (\cos \Psi)} = \frac{2}{mc}\left(\lambda_{\text{in}} \sin\frac{\theta}{2}\right) p . \quad (3\text{-}3)$$
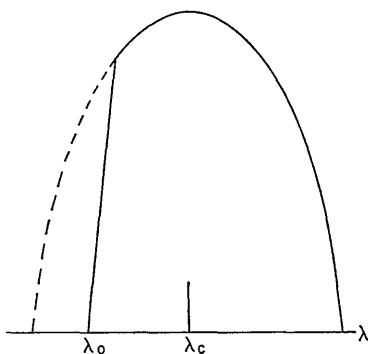
The DuMond expression is

Fig. 4. A spectrum shape of the idealized Compton scattering. The parabolic shape (including dotted curve) is obtained for a non-interacting electron gas when the Pauli exclusion principle is not taken into account. The line shape has a cut-off terminating at λ_0 when the Pauli exclusion principle is considered.

$$J(\lambda_{\text{out}}) \propto (1+\cos{}^2\theta)\,\frac{1}{\sin(\theta/2)} \cdot \int_{P(\lambda_{\text{out}})}^{\infty} \frac{I(p)}{p}\, dp ,$$

$$(3\text{-}4)$$

where $I(p)$ is the momentum distribution of an electron gas, and the polarization factor is taken into account explicitly. Instead of this simple case of free electrons, we have an intractable expression for bound electrons in solids due to the complexity of equation (3-1). The scattering angle dependence, for example, is no longer the straight forward equation (3-4). It is hopeless to pursue this track.

The effect from the initial states of the electrons in a crystal has been accommodated in this classical argument by an introduction of momentum distributions. However, we have not so far considered these electrons as quantum particles. One of the most important quantum conditions for electrons in a crystal is the Pauli exclusion principle. Using an electron gas model, equation (3-2) produces the parabolic profile centered on the value, λ_c, (see Fig. 4) if the Pauli exclusion principle is not applied. However, this principle demands that the recoil electron should be above the Fermi level. This causes the distortion on lower energy transfer side of the spectrum (see Fig. 4). For the bound-electron case, this means that no intensity appears until the energy loss becomes equal to the binding energy, and the spectrum may spread towards the higher energy transfer side (see Fig. 5). The conditions for final states of the scattered electrons cannot be so easily accommodated into the classical arguments as was the case for initial states.

In the ordinary classical development for X-ray Raman scattering, one abandons the momentum conservation rule by saying that overall momentum is conserved including nuclei. This assumption may be a practical way out, because the restriction on possible final states is more severe for Raman scattering than for Compton scattering, and equation (3-2) becomes useless anyway. Then one might say that a photon in X-ray Raman scattering experiences an energy loss of just the same amount as in the optical Raman scattering, since only the energy conservation rule should be taken into account. Strictly speaking, this argument is, of course, a gross approximation. It is, nevertheless, true that one must take into account not only the distribution of the initial states, but the restriction on possible final states in order to predict a reasonable spectrum for the X-ray inelastic scattering.

The question then arises whether, in spite of discarding the above-mentioned *ad hoc* arguments for the final state, we can still obtain a spectrum in a way similar to the one which we have used in dealing with the initial states. It should be remembered that the conditions for the initial states modified the energy–momentum rule from a rigid one, equation (2-3) or (2-7), to a more loose one with indeterminancy for the electron states, equation (3-1). In obtaining the scattered intensity, as the previous discussions of probabi-

lity have shown, we have assessed the probability with which a given momentum–energy conservation rule holds. However, we may take another approach; using a generalized mathematical function, we may write the rigid conservation rule, such as equation (2-7), as

$$\delta(\hbar\mathbf{k}_1 + \mathbf{p}_1 - \hbar\mathbf{k}_2 - \mathbf{p}_2)$$
$$\delta[\hbar\omega_1 + E_1(\mathbf{p}_1) - \hbar\omega_2 - E_2(\mathbf{p}_2)] \quad (3\text{-}5)$$

since in this case this event occurs with 100% assurance if equations (2-1) and (2-3) hold, otherwise there is no chance of occurrence. Here the subscripts 1 and 2 stand for 'in' and 'out' states. We consider the function (3-5) as the possibility of occurrence of the event $(\mathbf{k}_1, \mathbf{p}_1) \to (\mathbf{k}_2, \mathbf{p}_2)$, although the correct power of the delta function (δ^1, δ^2 or higher) has not yet been determined. Just by logical deduction we may obtain a certain function $J(\mathbf{k}_1\mathbf{p}_1 \to \mathbf{k}_2\mathbf{p}_2)$ to describe the loose conservation rule, equations (3-1).

The momentum δ function, for instance, can be expressed by

$$\delta(\hbar\mathbf{k}_1 + \mathbf{p}_1 - \hbar\mathbf{k}_2 - \mathbf{p}_2) = \int d^3r \exp\{-i\mathbf{p}_2\mathbf{r}\} \cdot$$
$$\times \exp\{+i\mathbf{p}_1\mathbf{r}\} \cdot \exp\{i\hbar(\mathbf{k}_1 - \mathbf{k}_2)\mathbf{r}\}$$
$$= \int d^3r \; \Psi_{p2}(r)\Psi_{p1}^{+}(r) \exp\{i\hbar(\mathbf{k}_1 - \mathbf{k}_2)\mathbf{r}\}$$
$$= \langle\mathbf{p}_2|\exp\{i\hbar(\mathbf{k}_1 - \mathbf{k}_2)\mathbf{r}\}|\mathbf{p}_1\rangle, \quad (3\text{-}6)$$

where $\Psi_p(r) = \exp\{i\mathbf{p} \cdot \mathbf{r}\}$. This is the matrix element of $\exp\{i\hbar(\mathbf{k}_1 - \mathbf{k}_2)\mathbf{r}\}$ between the two momentum states $\mathbf{p}_1$ and $\mathbf{p}_2$. If the electron wave function is given by a plane wave, equation (3-6) holds strictly. If the electrons are bound to an atom, for instance, a hydrogen atom, the matrix element represents the conservation of angular momentum; it is the selection rule of spectroscopy, although we cannot write down the left-hand side as it was written in equation (3-6). It is therefore reasonable to assume that the matrix element (3-6), is, indeed, the true momentum conservation with the real possibility of the occurrence of the event, regardless of the form of the electron wave functions. Our desired function $J(k_1 p_1 \to k_2 p_2)$ must be given by the matrix elements (3-6) or better by its modulus squared since probability should be a real quantity:

$$J(k_1 p_1 \to k_2 p_2) \propto |\int d^4x \; \Psi_{p2}^{*}(x)\Psi_{p1}(x)$$
$$\times f_{k2}^{*}(x)f_{k1}(x)|^2. \quad (3\text{-}7)$$

Here we have included energy conservation, and $f_k(x)$ is the photon wave packet which equals $\exp[ik \cdot x]$ in case of plane waves.

We have thus obtained a reasonable expression for the spectrum in which both requirements for the initial and the final states are treated in the same way by extending the concept of momentum–energy conservation and using probability theory.

The derivation of equation (3-7) has been based entirely on a 'physical' argument. Our next task is to derive equation (3-7) or a more rigorous form, from a set

of basic equations. Since equation (3-7) has a form commonly found in quantum mechanics, we will proceed *via* a quantum mechanical formulation of the X-ray inelastic scattering problem.

4. Quantum mechanical formulation

Let us first write down the Hamiltonian for a system in which the photon interacts with many electrons in a crystal:

$$\mathsf{H} = \frac{1}{8\pi}\int d^3r(\mathbf{E}^2 + \mathbf{H}^2) + \int d^3r\,\Psi^{+}\left[\frac{p^2}{2m}\right.$$
$$\left. + V(r) - \mathscr{E}_F\right]\Psi$$
$$- \frac{e}{mc}\int d^3r\,\Psi^{+}\mathbf{A}\cdot\mathbf{p}\Psi + \frac{e^2}{2mc^2}\int d^3r\,\Psi^{+}\Psi A^2, \quad (4\text{-}1)$$

where we used $\nabla \cdot \mathbf{A} = 0$ (the radiation or Coulomb gauge). The first term is the photon field Hamiltonian; the second, the many-electron part; $\mathscr{E}_F$ is the Fermi energy; and the third and fourth terms comprise the interaction Hamiltonian. Generally we can prove that the contribution from the third $(\mathbf{A} \cdot \mathbf{p}\Psi)$ is negligibly small for the interaction between ordinary X-rays and electrons. So we will drop it.* The term $\Psi^{+}\Psi A^2$, which is usually called the A^2 term, is essential not only in the Compton–Raman scattering, but also in X-ray diffraction.

Ordinarily, to calculate the intensity distribution of scattered photons, it is common to use Fermi's 'golden rule', which is the first order Born approximation using the $\Psi^{+}\Psi A^2$ term as an interaction Hamil-

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* In the final result, the $\mathbf{A} \cdot p\psi$ term yields a more complicated polarization factor than the $A^2\psi^{+}\psi$ term; the latter gives the Malus law. To check the effect due to the $\mathbf{A} \cdot p\psi$ term experimentally, it is best to measure the polarizations of scattered photons in comparison with the Malus law, since the intensity change due to that term may be insensitive.
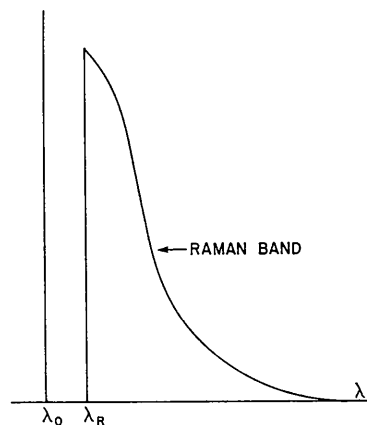

Fig. 5. A possible spectral profile for the idealized Raman scattering. The spectrum starts at the energy loss λ_R which is the same value expected from the optical Raman effect, and forms a band towards the large energy loss side.

tonian. After the intensity distribution is obtained, an additional assumption, which is called an 'impulse' approximation, is often introduced to calculate the relevant matrix elements. The 'impulse' approximation is essentially the quantum counterpart of the classical free electron Compton scattering. The other approximation, which is called an 'adiabatic' approximation, is sometimes introduced to calculate the matrix element in the case of bound electrons. This approximation, as it is currently formulated, replaces the crystal by an ensemble of independent isolated atoms, making it almost impossible to study real solid state effects.

Recently, Kuriyama & Alexandropoulos (1971) formulated a more general expression for the intensity distribution without using the Born approximation. They have used a quantum field theoretic technique to derive the spectral distribution in the Heisenberg representation.

Let us define a physical vacuum, $|\bar{0},0;0\rangle\equiv|0\rangle$, as the state of no photons and all the crystal electrons below the Fermi levels. With this definition, we replace the system of the crystal electrons by an electron-hole picture. When a photon is incident on a crystal in its ground state, we characterize this state as that of one photon k and no electrons and no holes in the crystal, and we denote it by

$$|\bar{0},0;k;\text{in}\rangle. \quad (4\text{-}2)$$

After the incoming photon is scattered inelastically by the crystal, we have a final state in which the outgoing photon has undergone energy loss and momentum transfer and has created one hole and one electron in the crystal. Such a final state is characterized by

$$|\bar{E},E;k';\text{out}\rangle \quad (4\text{-}3)$$

where $\bar{E}$ indicates the hole energy below the Fermi level. The 'in' and 'out' states are Heisenberg states.

The scattering amplitude associated with the transition from state (4-2) to state (4-3) is given by

$$S(E,\bar{E},k,k')\equiv\langle\bar{E},E;k';\text{out}|\bar{0},0;k;\text{in}\rangle. \quad (4\text{-}4)$$

This quantity can be calculated by the LSZ reduction formula (Appendix II):

$$S(E,\bar{E},k,k')=\frac{i}{(2\pi)^2}\frac{e^2}{m}\frac{1}{\sqrt{k,k'}}[\varepsilon(\mathbf{k}'v)\cdot\varepsilon(\mathbf{k}v)]$$
$$\times\int d^4x\exp\{-i(k'-k)x\}u_E^{\ddagger}(x)v_{\bar{E}}(x), \quad (4\text{-}5)$$

where we use the four-vector x, k, etc., and $\hbar=c=1$, and $u_E(x)$ forms a positive energy complete set and $v_{\bar{E}}(x)$ forms a negative energy complete set. u_E and $v_{\bar{E}}$ satisfy the Schrödinger equation. The transition probability is given by $|S(E,\bar{E},k,k')|^2$, and gives the spectrum predicted by equation (3-7). We use here the total transition probability instead of the customary transition probability per unit time (i.e. rate). In the present discussion the choice of either one of them does not make any difference in the results; however, the

former quantity was chosen because it provides a more compact theoretical formulation. The total probability of a photon state k making a transition to state k' (for inelastic scattering) or to state 0 (for absorption) corresponds to a differential cross section, not a total cross section.

Since the incoming photon can create an electron and a hole in any possible combination of their states E and $\bar{E}$, the probability of the incoming photon k making a transition to the state k' should be given by the sum of such all possible crystal states:

$$W^{\text{inel}}(k\to k')=\sum_E^{(+)}\sum_{\bar{E}}^{(-)}|S(E,\bar{E},k,k')|^2. \quad (4\text{-}6)$$

Using equation (4-5), we can write equation (4-6) as

$$W^{\text{inel}}(k\to k')=\frac{1}{(2\pi)^4}\left(\frac{e^2}{m}\right)^2\frac{1}{kk'}[\varepsilon(\mathbf{k}v)\cdot\varepsilon(\mathbf{k}'v)]^2$$
$$\times\int\int d^4x_1 d^4x_2\exp\{-i(k-k')(x_1-x_2)\}$$
$$\times\sum_E\sum_{\bar{E}}v_{\bar{E}}^{\ddagger}(x_1)u_E(x_1)u_E^{\ddagger}(x_2)v_{\bar{E}}(x_2), \quad (4\text{-}7)$$

where the two sums are performed over all the positive E (unoccupied states) and over all the negative $\bar{E}$ (occupied states), respectively. Using the electron field operator, $\Psi(x)$, the sum can be performed and is given by the Fermi vacuum expectation value (Appendix III):

$$\sum_E\sum_{\bar{E}}v_{\bar{E}}^{\ddagger}(x_1)u_E(x_1)u_E^{\ddagger}(x_2)v_{\bar{E}}(x_2)$$
$$=\langle\Psi^+(x_1)\Psi(x_1)\Psi^+(x_2)\Psi(x_2)\rangle$$
$$-\langle\Psi^+(x_1)\Psi(x_1)\rangle\langle\Psi^+(x_2)\Psi(x_2)\rangle. \quad (4\text{-}8)$$

Since $\Psi^+(x)\Psi(x)$ is the electron density operator $\varrho(x)$, equation (4-8) reduces to

$$\langle\{\varrho(x_1)-\langle\varrho(x_1)\rangle\}\{\varrho(x_2)-\langle\varrho(x_2)\rangle\}\rangle$$
$$=\langle\Delta\varrho(x_1)\cdot\Delta\varrho(x_2)\rangle. \quad (4\text{-}9)$$

Finally we obtain

$$W^{\text{inel}}(k\to k')=C(k,k')\{\varepsilon(\mathbf{k}v)\cdot\varepsilon(\mathbf{k}'v)\}^2$$
$$\times\int\int d^4x d^4y\exp\{-i(k-k')(x-y)\}$$
$$\times\langle\Delta\varrho(x)\Delta\varrho(y)\rangle, \quad (4\text{-}10)$$

where

$$C(k,k')=\frac{1}{(2\pi)^4}\left(\frac{e^2}{m}\right)^2\frac{1}{kk'}. \quad (4\text{-}11)$$

Equation (4-10) implies that $W^{\text{inel}}(k\to k')$ is given by the double four-dimensional Fourier transform of the electron charge correlation $\langle\Delta\varrho(x)\Delta\varrho(y)\rangle$. Equation (4-10) is a general expression for the differential cross section in X-ray Compton–Raman scattering.

In a similar manner, the differential cross section for photon absorption by a crystal is obtained as follows:

$$W^{abs}(k \to 0) = \sum_E \sum_E |\langle \bar{E}, E; 0; \text{out} |\bar{0}, 0; k; \text{in}\rangle|^2$$

$$= B(k) \iint d^4x d^4y \exp\{-ik(x-y)\}$$

$$\times \langle \Delta j_\varepsilon(x) \Delta j_\varepsilon(y) \rangle, \quad (4\text{-}12)$$

where

$$B(k) = \frac{1}{(2\pi)^2} \cdot \frac{1}{k}, \quad (4\text{-}13)$$

and $j_\varepsilon(x)$ is the component of the electron current operator along the photon polarization direction*

$$\mathbf{j}(x) = -i \frac{e}{2m} [\Psi^+(x)\nabla\Psi(x) - (\nabla\Psi^+(x))\Psi(x)], \quad (4\text{-}14)$$

and $\Delta\mathbf{j} = \mathbf{j} - \langle \mathbf{j} \rangle$. Therefore, W^{abs} is given by the Fourier transform of the electron current correlation.

A continuity equation connects current and charge; in terms of current and charge correlations this is

$$\nabla_x\nabla_y : \langle \Delta\mathbf{j}(x)\Delta\mathbf{j}(y)\rangle = e^2 \frac{\partial}{\partial t_x} \frac{\partial}{\partial t_y} \langle \Delta\varrho(x)\Delta\varrho(y)\rangle. \quad (4\text{-}15)$$

Denoting the Fourier transform of the $\langle \Delta\mathbf{j} \cdot \Delta\mathbf{j} \rangle$ by $J(k_1, k_2)$, equation (4-12) immediately reduces to

$$W^{abs} \propto |k|^{-1}\varepsilon J(k,k)\varepsilon, \quad (4\text{-}16)$$

while, with the use of (4-15), equation (4-10) becomes

$$W^{inel}(k \to k') \propto \left(\frac{|\mathbf{k}-\mathbf{k}'|}{\omega'-\omega}\right)^2 sJ(\kappa,\kappa)s, \quad (4\text{-}17)$$

where s is the unit vector defined by $(\mathbf{k}-\mathbf{k}')/|\mathbf{k}-\mathbf{k}'|$ and κ is the four vector $(|\mathbf{k}-\mathbf{k}'|s, \omega'-\omega)$. Equation (4-17) is quite general and holds for co-existing Compton and Raman scattering.

It appears that we have obtained a relationship between the absorption cross section and the inelastic cross section, since both equations (4-16) and (4-17) contain the common tensor J. However, because of the difference in the variables $k = (\mathbf{k}, -\omega = -|\mathbf{k}|)$ in equation (4-16) and $\kappa = (\mathbf{k}-\mathbf{k}', \omega'-\omega)$ in equation (4-17), the connection is not straightforward for the following reasons. (1) A set of matrix elements given by $\varepsilon J(k,k)\varepsilon$ is independent of the set given by $sJ(\kappa,\kappa)$ s. Hereafter we abbreviate $J(k,k)$ as $J(k)$. (2) Since ε is perpendicular to $\mathbf{k}$, and s is parallel to κ, absorption experiments can only determine the matrix elements such as $J_{xx}(0,0,k_z;\omega)$ and $J_{yy}(0,0,k_z;\omega)$, while an inelastic scattering experiment gives $J_{zz}(0,0,k_z; \omega)$. Therefore neither of the experiments alone can determine the whole set of the matrix elements $J(k)$, unless the system being studied is isotropic or of a high degree of symmetry. This situation merely reflects the fact that the absorption

cross section is a functional of the transverse dielectric function of the electron system, while the inelastic scattering cross section is a functional of the longitudinal dielectric function. (3) In the inelastic scattering one needs to know $J(\kappa, \omega'-\omega)$ where $|\kappa| = |\mathbf{k}-\mathbf{k}'| \neq \omega - \omega'$, while the $J(\mathbf{k},\omega)$ for absorption are obtained for $\omega = |\mathbf{k}|$. One can, however, connect W^{inel} with W^{abs} only when the Fourier transform of the electron current correlation, $J(k)$ or $J(\kappa)$, is, or is nearly, independent of the momentum (or its transfer) $\mathbf{k}$ or κ.

This condition has a significant physical meaning: when the electrons in a crystal are well localized around atoms, that is $|\kappa| \cdot r_i < 1$ where r_i is the effective radius of the ith electron, the Fourier transform of the current correlation becomes almost independent of κ, the momentum transfer, as in the case of the X-ray anomalous dispersion correction. When this condition is satisfied for an isotropic sample, the differential cross section for the inelastic scattering is given* by that for absorption:

$$W^{inel}(k \to k') \propto (\omega-\omega')^{-2} \sin^2(\theta/2)$$
$$(\varepsilon \cdot \varepsilon')^2 \tfrac{1}{3} \operatorname{Tr} J(\kappa,\kappa). \quad (4\text{-}18)$$

This agrees with experimental conditions for observing a distinct Raman scattering. If the above-mentioned condition is not satisfied, that is to say, if the $J(\kappa)$ depends strongly on κ, the differential cross section for the inelastic scattering displays the characteristic Compton scattering usual for a large momentum transfer.

In reality the electrons in a crystal are not in such an idealized condition; see, for instance, the energy spectrum of the X-ray inelastic scattering in a solid made up of elements of large atomic number. Our equation (4-17) still holds for the general case.

5. Conclusion

We have reduced the differential cross section for the X-ray inelastic scattering from a crystal to a form which is essentially governed by the property of the electron charge or current correlation. In this formulation all of the electrons in a crystal have been treated on an equal basis, regardless of whether they are core or valence electrons. The electron charge or current correlation is a very important quantity in almost all fields of solid state physics, since it contains all of the information on the interactions of many electrons inside a solid. The correlation is essentially a two-particle Green's function on which recent theoretical studies are centered. In general it is not easy to calculate the correlation or the two-particle Green's function for an interacting electron system. One of the most important conclusions in this paper is that, by means of X-ray inelastic scattering experiments, the Fourier transforms

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* Equation (4-14) is only part of current defined later in Appendix II.

* This equation was first derived by Mizuno & Ohmura (1967) who used a dipole approximation in the first order Born approximation.

of the correlation or the two-particle Green's function can be obtained in spite of current difficulty in calculating it. X-ray inelastic scattering, therefore, provides a significant opportunity of studying, directly, a general quantity which characterizes the properties of electrons in solids.

As we have mentioned in § 4, the current correlation forms a tensor, the elements of which are connected to the differential cross section of either inelastic scattering or absorption. In principle, two independent experiments, one for absorption and another for inelastic scattering, provide complementary information on the current correlation, that is, the two-particle Green's function. Such results may be compared with, and even complement, the frequency response data (conductivity and susceptibility) of solids, which are connected with the current correlation by the Kubo formula (Kubo, 1959; Ziman, 1969).

An immediate benefit from our expression for the cross section is found in the determination of the momentum distribution of valence electrons in solids containing elements of high atomic number. As we have discussed, the current correlation arising from the core electrons can be obtained from the absorption spectrum. Subtracting this absorption spectrum from the inelastic scattering spectrum, one can obtain a spectrum essentially due to the valence electrons alone. From this new spectrum one can derive the momentum distribution, or the charge correlation for the valence electrons.

Another important aspect is found in the temperature dependence of the correlation. Of special interest may be the behaviour of the correlation near the transition or critical temperature associated with phase transitions of the second kind (such as magnetic and ferroelectric transitions).

Since the current correlation contains many-body effects, collective excitations of electrons in solid, such as plasmons, can also be studied by the inelastic scattering experiments.

APPENDIX I

Derivation of equation (3–2)

The intensity of photons scattered inelastically between the wavelength region λ and $\lambda + d\lambda$ is denoted by $J(\lambda)$ $d\lambda$. This quantity contains contributions from all initial electrons. Since the momentum distribution, $I(p)$, is assumed to be dependent only on the magnitude of

momenta, the intensity which is produced by the initial electrons having the magnitude of momenta between p and $p + dp$ can be written $[\Delta J(\lambda)]_p d\lambda$. For the fixed magnitude of momenta, the electrons which happen to have the same value of $(p \cos \psi)$ contribute scattering between λ and $\lambda + d\lambda$. Since the momentum distribution is assumed to be spherically symmetric, the number of the electrons which satisfy the above condition is given by

$$I(p) \int_0^{2\pi} d\Phi \sin \psi d\psi = 2\pi I(p) \, d(\cos \psi) \, .$$

Since, in this classical picture, each electron definitely scatters a photon, the intensity caused by these electrons is given by

$$[\Delta J(\lambda)]_p d\lambda = 2\pi I(p) \, d(\cos \psi) \, .$$

Since λ is given as a function of ψ by equation (3-1), we can write

$$[\Delta J(\lambda)]_p \left[\frac{\partial \lambda}{\partial(\cos \psi)} \right]_p d(\cos \psi) = 2\pi I(p) \, d(\cos \psi) \, .$$

or

$$[\Delta J(\lambda)]_p = 2\pi \cdot \frac{I(p)}{\left[\dfrac{\partial \lambda}{\partial(\cos \psi)} \right]_p} \cdot$$

$J(\lambda)$ is obtained by summing $[\Delta J(\lambda)]_p$ over all possible magnitudes of p which can produce photons of wavelength λ. Equation (3-2) obtains.

APPENDIX II

The scattering amplitude for X-ray inelastic scattering from a crystal

(A) Equations for the photon and the electron Green's functions

The Hamiltonian density for a system of electrons interacting with photons can be written

$$\mathcal{H}(x) = \frac{1}{8\pi} \left[\left(\frac{\partial \mathbf{A}(x)}{\partial t} \right)^2 + \{\nabla \times \mathbf{A}(x)\}^2 \right]$$

$$+ \frac{1}{2m} [\{\nabla + ie\mathbf{A}(x)\}\psi^+(x) \cdot \{\nabla - ie\mathbf{A}(x)\}\psi(x)]$$

$$+ V(x)\psi^+(x)\psi(x) - \mathscr{E}_F\psi^+(x)\psi(x) \, , \qquad \text{(II}A\text{-1)}$$

where $\mathbf{A}$ is the photon field operator; ψ and ψ^+ are the electron field operators; e and m are the charge and mass of the electrons, respectively; the variable x implies the four vector $(\mathbf{r}, t)$; and both Planck's constant $\hbar$ and the velocity of light are set equal to 1. In equation (IIA-1) the energy counter term, $-\mathscr{E}_F\psi^+\psi$, has been introduced to redetermine the total energy of the system with respect to the Fermi energy level of electrons in a crystal. The quantum conditions for field variables state the equal time commutation or anti-commutation rules:

$$\left[\mathbf{A}_i(\mathbf{r}), \frac{\partial A_j(\mathbf{r}')}{\partial t}\right]_- = 4\pi i \delta(\mathbf{r}-\mathbf{r}')\delta_{ij} \qquad (\text{II}A\text{-}2a)$$

$$[A_i(\mathbf{r}),\ A_j(\mathbf{r}')]_- = \left[\frac{\partial A_i(\mathbf{r})}{\partial t}, \frac{\partial A_j(\mathbf{r})}{\partial t}\right]_- = 0 \quad (\text{II}A\text{-}2b)$$

$$[\psi(\mathbf{r}), \psi^+(\mathbf{r}')]_+ = \delta(\mathbf{r}-\mathbf{r}') \qquad (\text{II}A\text{-}2c)$$

$$[\psi(\mathbf{r}), \psi(\mathbf{r}')]_+ = [\psi^+(\mathbf{r}),\ \psi^+(\mathbf{r}')]_+ = 0, \qquad (\text{II}A\text{-}2d)$$

where $[\ ]_-$ and $[\ ]_+$ indicate the commutator and the anti-commutator, respectively.

Since we deal with the electrons in a crystal, they interact not only with ions at lattice points, but also among themselves. Throughout this paper we have been treating all electrons, including the core electrons, on an equal basis in order to discuss both Compton scattering and Raman scattering from a unified point of view (see § 4). Therefore, the expression $V\psi^+\psi$ should be considered as a mere abbreviation of the correct expression:

$$V\psi^+\psi = V_{\text{ion}}(x)\psi^+(x)\psi(x)$$

$$+ \tfrac{1}{2}\int d\bar{x}\,\psi^+(x)\psi^+(\bar{x})v(x,\bar{x})\psi(\bar{x})\psi(x), \quad (\text{II}A\text{-}3)$$

where V_{ion} is the bare crystal potential due to the ions at the lattice points, and $v(x,\bar{x})$ is the instantaneous bare Coulomb potential. We use the radiation (or Coulomb) gauge where the photon field $\mathbf{A}$ is transverse ($\nabla \cdot \mathbf{A} = 0$).

The Hamiltonian (see §4) is given by $H(t) = \int d^3r\,\mathscr{H}(x)$. Using the quantum equation of motion for an operator,* we obtain

$$i\,\frac{\partial\psi(x)}{\partial t} = -\frac{1}{2m}\{\nabla - ieA(x)\}^2\psi(x)$$

$$+ \{V(x) - \mathscr{E}_F\}\,\psi(x) \qquad (\text{II}A\text{-}4)$$

$$\Box\,\mathbf{A}(x) = 4\pi \mathbf{j}(x), \qquad (\text{II}A\text{-}5)$$

where

$$\Box = \frac{\partial^2}{\partial t^2} - \nabla^2.$$

The 'current operator' $\mathbf{j}(x)$ is defined by

$$\mathbf{j}(x) = \mathbf{j}^{(0)}(x) + \mathbf{j}^{(1)}(x), \qquad (\text{II}A\text{-}6)$$

where†

$$\mathbf{j}^{(0)}(x) = -\frac{ie}{2m}[\psi^+(x)\nabla\psi(x) - \{\nabla\psi^+(x)\}\psi(x)]$$

$$(\text{II}A\text{-}7)$$

and

$$\mathbf{j}^{(1)}(x) = -\frac{e^2}{m}\psi^+(x)\psi(x)\mathbf{A}(x). \qquad (\text{II}A\text{-}8)$$

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* The equation of motion for a operator Q is given by $t\,\dfrac{\partial Q}{\partial t} = [Q,\mathrm{H}]$.

† Part of the current operator $\mathbf{j}^{(0)}$ is the electron current which was used in § 4 without the superscript (0).

To proceed, we define the electron Green's function and the photon Green's function:

$$G(x_1,x_2) = (-i)\langle 0|\varepsilon(t_1,t_2)T[\psi(x_1)\psi^+(x_2)]|0\rangle \quad (\text{II}A\text{-}9)$$

and

$$D_{ij}(x_1,x_2) = i\langle 0|T[A_i(x_1)A_j(x_2)]|0\rangle, \qquad (\text{II}A\text{-}10)$$

respectively, where

$$\varepsilon(t_1,t_2) = \begin{cases} +1 & \text{for} \quad t_1 > t_2 \\ -1 & \text{for} \quad t_1 > t_2, \end{cases}$$

and $|0\rangle$ is the Heisenberg state vector describing the ground state of the system represented by the total Hamiltonian (IIA-1) which may be called the physical vacuum or simply the vacuum state. The vacuum state* is the one which does not contain any photons, quasi-particles (electrons excited above the Fermi level) or quasi-antiparticles (holes left behind below the Fermi level). Hereafter we abbreviate $\langle 0|Q|0\rangle$ by $\langle Q\rangle$. The symbol $T[\ldots]$ implies the Dyson chronological (time-ordering) operation which orders the enclosed field operator from right to left in the order of increasing time coordinates.†

The photon Green's function and the electron Green's function satisfy the following equations which follow from the field equations (IIA-4), (IIA-5) and the commutation relations (IIA-2a,b) and (IIA-2c):

$$i\,\frac{\partial G(1,2)}{\partial t_1} = \left(-\frac{\nabla_1^2}{2m}\right)G(1,2) + \langle T[V(1)\psi(1)\psi^+(2)]\rangle$$

$$+ \frac{e}{2m}\langle T[\mathbf{A}(1)\nabla_1\psi(1)\psi^+(2)]\rangle$$

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* At finite temperatures, the system will be statistically distributed over all of its excited levels. This means that the ground state average, $\langle 0|\cdots|0\rangle$, which is used to calculate the $T=0$ propagator, must be replaced by an average over a grand canonical ensemble.

† For two time dependent operators $A(t_1)$ and $B(t_1)$,

$$T[A(t_1)B(t_2)] =$$
$$\theta(t_1-t_2)A(t_1)B(t_2) + \theta(t_2-t_1)B(t_2)A(t_1) \quad (\text{II}A\text{-}11)$$

$$\varepsilon(t_1,t_2)T[A(t_1)B(t_2)] =$$
$$\theta(t_1-t_2)A(t_1)B(t_2) - \theta(t_2-t_1)B(t_2)A(t_1), \quad (\text{II}A\text{-}12)$$

where

$$\theta(t) = \begin{cases} +1 & \text{for } t > 0 \\ 0 & \text{for } t < 0. \end{cases}$$

Since $[d\theta(t)/dt] = -[d\theta(-t)/dt] = \delta(t)$, we obtain

$$\frac{\partial}{\partial t_1}\langle \varepsilon(t_1,t_2)T[A(t_1)B(t_2)]\rangle = \left\langle \varepsilon(t_1,t_2)T\left[\frac{\partial A(t_1)}{\partial t_1}B(t_2)\right]\right\rangle$$
$$+ \delta(t_1-t_2)\langle[A(t_1),B(t_2)]_+\rangle$$

$$(\text{II}A\text{-}13)$$

$$\frac{\partial}{\partial t_1}\langle T[A(t_1)B(t_2)]\rangle = \left\langle T\left[\frac{\partial A(t_1)}{\partial t_1}\cdot B(t_2)\right]\right\rangle$$
$$+ \delta(t_1-t_2)\langle[A(t_1),B(t_2)]_-\rangle \quad (\text{II}A\text{-}14)$$

Applying equation (IIA-13) to equation (IIA-9), we will obtain the equation for the electron Green's function (IIA-15) in the text. To obtain the equation for the photon Green's function, we have to perform differentiation on (IIA-14) once more with respect to t_1.

$$+ \frac{e}{2m} \nabla_1 \langle T[\mathbf{A}(1)\psi(1)\psi^+(2)] \rangle$$

$$- \frac{ie^2}{2m} \langle T[\mathbf{A}^2(1)\psi(1)\psi^+(2)] \rangle + \delta(1-2) ,$$

(IIA-15)

and

$$\Box D_{i,j}(1,2)$$
$$= 4\pi i \langle T[j_i(1)A_j(2)] \rangle + 4\pi \delta_{i,j}\delta(1-2) , \quad (\text{II}A\text{-16})$$

where the variable, say 1, is short for $x_1 = (\mathbf{r}_1, t_1)$. These equations contain the vacuum expectation values of time ordered products of the field operators, such as $\langle T[\mathbf{A}(1)\psi(1)\psi^+(2)] \rangle$ etc.

At this stage it is convenient to introduce the variational derivatives defined by Schwinger's action principle. Schwinger (1951 a, b) added an 'external c-number source' to the Hamiltonian density. The Hamiltonian density due to the external source, $\mathbf{J}(x)$, is given by

$$\mathcal{H}_s(x) = -\mathbf{J}(x)\mathbf{A}(x) . \quad (\text{II}A\text{-17})$$

After the necessary equations are generated, the external source function $\mathbf{J}$ will be set equal to zero at the end. With the $\mathcal{H}_s$ in the Hamiltonian, the action principle gives

$$\langle T[Q(1)A_i(2)] \rangle = \langle Q(1) \rangle \langle A_i(2) \rangle - i \frac{\delta \langle Q(1) \rangle}{\delta J_i(2)} ,$$

(IIA-18)

where $Q(x)$ is an operator in the Heisenberg representation. From this relation we can immediately notice that the photon Green's function (IIA-10) could have been defined by

$$D_{i,j}(12) = \lim_{\mathbf{J} \to 0} \frac{\delta \langle A_j(1) \rangle}{\delta J_j(2)} , \quad (\text{II}A\text{-19})$$

because, in the limit of $\mathbf{J} \to 0$, the vacuum expectation value of the photon field operator, $\langle \mathbf{A} \rangle$, vanishes.*

The expectation values of the time ordered products which have appeared in (IIA-15) and (IIA-16) can thus be reduced further by use of equation (IIA-18). It is customary to write the final expressions for the Green's function equations in a certain formal way, one which

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* In a classical sense, one may think of the expectation value of the radiation field intensity $E(x)$ or $\frac{\partial}{\partial t} A(x)$ as an observable quantity. However, the expectation value $\langle |E(x)| \rangle$ or $\left\langle \left| \frac{\partial A(x)}{\partial t} \right| \right\rangle$ at any possible state $|\rangle$ always vanishes in the case of photons which do not have an absolute coherence. Therefore, the Maxwell equations for the expectation values of radiation field E, which gives the fundamental equations for the dynamical theory of X-ray diffraction, do not exist. This implies, to be exact, that the radiation field inside the crystal cannot be described by the classical field vector E. Of course, this statement does not necessarily mean that there are no radiation wave fields inside the crystal, but that the classical wave-field concept is not sufficient to describe the behavior of photons inside the crystal.

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defines inverse Green's functions:

$$\int d\bar{1} G^{-1}(1\bar{1})G(\bar{1}2) = \delta(1-2) \quad (\text{II}A\text{-20})$$

and

$$\sum_k \int d\bar{1} D_{ik}^{-1}(1\bar{1})D_{kj}(\bar{1}2) = 4\pi\delta_{ij}\delta(1-2) . \quad (\text{II}A\text{-21})$$

The inverse Green's functions are obtained from equations (IIA-15), (IIA-16) and (IIA-18)

$$G^{-1}(12) = K(12) - \Sigma_a(12) - \Sigma_b(12) \quad (\text{II}A\text{-22})$$

and

$$D_{ij}^{-1}(12) = \delta_{ij}\Box(1)\delta(1-2) - \Pi_{ij}(12) , \quad (\text{II}A\text{-23})$$

where

$$K(12) = \left[i \frac{\partial}{\partial t_1} + \frac{\nabla^2(1)}{2m} \right] \delta(1-2) - \Sigma_c(12) \quad (\text{II}A\text{-24})$$

$$\Sigma_a(12) = \left[\frac{ie}{2m} \{ \nabla(1)\langle A(1) \rangle + \langle A(1) \rangle \nabla(1) \} \right.$$
$$\left. + \frac{e^2}{2m} \{ \langle A(1) \rangle^2 \} \right] \delta(1-2) \quad (\text{II}A\text{-25})$$

and

$$\Pi_{ij}(12) = \lim_{\mathbf{J} \to 0} 4\pi \frac{\delta \langle j_i(1) \rangle}{\delta \langle A_j(2) \rangle} . \quad (\text{II}A\text{-26})$$

The symbols $\Box(1)$ and $\nabla(1)$ imply $\frac{\partial^2}{\partial t_1^2} - \nabla^2(1)$ and $\frac{\partial}{\partial \mathbf{r}_1}$, respectively. $\Sigma_b(12)$ contains higher order variational derivatives. To obtain (IIA-26) we have made use of the chain rule. Equation (IIA-21) could have been obtained in a straightforward by use of the definition (IIA-19).* Equation (IIA-26) can be connected to the electron Green's function $G(12)$ since the expectation value of the current $\langle j_i(x) \rangle$ can be written [from (IIA-7), (IIA-8), (IIA-9) and (IIA-18)]

$$\langle j_i(1) \rangle = \lim_{2 \to 1+} \left[-\frac{e}{2m}(\nabla_1 - \nabla_2)_i + i \frac{e^2}{m} \{ \langle A_i(1) \rangle \right.$$

---

* Using the definition (IIA-19) of the photon Green's function which is equivalent to (IIA-10), we can easily derive the equation for the photon Green's function. First it should be remembered that in Schwinger's formulation there is an additional current $\mathbf{J}$ due to $\mathcal{H}_s$. Therefore the current $\mathbf{j}$ in the field equation (IIA-5) should be replaced by $\mathbf{j} + \mathbf{J}$. Then let us take a derivative of the modified field equation with respect to $J_j(2)$:

$$\Box \frac{\delta \langle A_i(1) \rangle}{\delta J_j(2)} = 4\pi \frac{\delta \langle j_i(1) \rangle}{\delta J_j(2)} + 4\pi \frac{\delta \langle J_i(1) \rangle}{\delta J_j(2)} . \quad (\text{II}A\text{-27})$$

The last term on the right hand side is equal to $4\pi\delta_{ij}\delta(1-2)$. The chain rule states

$$\frac{\delta \langle j_i(1) \rangle}{\delta J_j(2)} = \sum_k \int d\bar{1} \frac{\delta \langle j_i(1) \rangle}{\delta \langle A_k(\bar{1}) \rangle} \frac{\delta \langle A_k(\bar{1}) \rangle}{\delta J_j(2)} . \quad (\text{II}A\text{-28})$$

In the limit $\mathbf{J} \to 0$, equation (IIA-27) reduces by use of the definition (IIA-19) to

$$\Box D_{ij}(12) = \sum_k \int d\bar{1} \Pi_{ik}(1\bar{1})D_{kj}(\bar{1}2) + 4\pi\delta_{ij}\delta(1-2) . \quad (\text{II}A\text{-29})$$

$$-i\frac{\delta}{\delta J_i(1)}\Big]\Big]G(12),\qquad\text{(II}A\text{-30)}$$

where $1_+ =(r_1,t_1+\varepsilon)$ with infinitesimally small positive quantity ε. The quantity Π_{ij} is called the generalized polarizability.* The mass operator $\sum_e(12)$ comes from the decoupling of the time ordered product $\langle T[U(1)\psi(1)\psi^+(2)]\rangle$, because of both the electron–electron interactions and the lattice vibrations.† If these effects can be neglected, then $\sum_e(12)$ reduces to $V_{ion}(1)\delta(1-2)$ from equation (IIA-3).†

It should be noted that the equation for the electron Green's function has been derived with the non-vanishing $\mathbf{J}$, while that for the photon has been derived in the limit of $\mathbf{J}=0$.

In the Green's function equations, (IIA-20) and (IIA-21), there are some terms, such as $\sum_b G$ and Π, which still contain the variational derivatives. It is customary to reduce these terms to more compact forms in terms of a vertex function. A vertex function which we need at the present time is the one for the radiation part. We denote it by $\Gamma^R_i(12;3)$, the definition of which is

$$\Gamma^R_i(12;3)=\lim_{\mathbf{J}\to 0}\frac{\delta G^{-1}(12)}{\delta\langle A_i(3)\rangle},\qquad\text{(II}A\text{-31)}$$

where G^{-1} is given by equation (IIA-22). From equation (IIA-20) and its adjoint form, we find‡

$$\frac{\delta G(12)}{\delta\langle A(_k3)\rangle}=-\int\!\!\int d\bar1 d\bar2\,G(1\bar1)\Gamma^R_k(\bar1\bar2;3)G(\bar22)\,.$$
$$\text{(II}A\text{-32)}$$

The variational derivatives appearing in equations (IIA-20) and (IIA-21) have the form $\dfrac{\delta G}{\delta J}$. By use of the chain rule and the definition of the photon Green's function (IIA-19) in the limit of $\mathbf{J}=0$, we can write

$$\lim_{\mathbf{J}\to 0}\frac{\delta G(12)}{\delta J_i(3)}=\sum_{\bar k}\int d\bar1\,\frac{\delta G(12)}{\delta\langle A_{\bar k}(\bar1)\rangle}\cdot D_{\bar k i}(\bar13)$$

$$=(-1)\sum_{\bar k}\int d\bar1 d\bar2 d\bar3\,G(1\bar1)\Gamma_{\bar k}^R(\bar1\bar2;\bar3)$$

$$\times G(\bar22)D_{\bar k i}(\bar33)\,.\qquad\text{(II}A\text{-33)}$$

Hereafter in this paper we will omit the summation and the integral signs in equations such as (IIA-33): the bar on the top of variables indicates integration over those variables, and the bar on subscripts indicates summation over those subscripts.

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* This quantity Π_{ij} is denoted by Γ_{ij} in a previous paper (Ashkin & Kuriyama, 1966).

† To decouple this term, we need other source terms in the Hamiltonian such as $U\psi^+\psi$, etc.

‡ Equation (IIA-20) can be written in a symbolic (matrix) form as $G^{-1}G=I$. Performing a functional derivative operation, δ_A, on this, we obtain $\delta_A G^{-1}\cdot G+G^{-1}\delta_A G=0$. Operating G from left, and applying the adjoint form of equation (IIA-20), $G\cdot G^{-1}=I$, we find $\delta_A G=-G\cdot\delta_A G^{-1}\cdot G$, which is the equation (IIA-32).

In the lowest order of approximation, in which $\sum_b$ and $\dfrac{\delta\sum}{\delta\langle A\rangle}$ can be neglected, the vertex function, (IIA-31), is given by

$$\Gamma^R_i(12;3)=-\frac{ie}{2m}\,[\nabla_i(1)\{\delta(1\text{-}3)\delta(1\text{-}2)\}$$
$$+\delta(1\text{-}3)\nabla_i(1)\delta(1\text{-}2)]\,,\qquad\text{(II}A\text{-34)}$$

by substituting (IIA-25) into (IIA-31). Another quantity that we need later is the functional derivative of the vertex function:

$$\frac{\delta\Gamma^R_i(12;3)}{\delta\langle A_j(4)\rangle}=-\frac{e^2}{m}\,\delta_{ij}\delta(1\text{-}2)\delta(1\text{-}3)\delta(1\text{-}4)\,.\quad\text{(II}A\text{-35)}$$

In the same order of approximation the equation for the electron Green's function is written finally in the limit of $\mathbf{J}=0$,

$$G^{-1}(1\bar1)G(\bar12)=\delta(12)\,,\qquad\text{(II}A\text{-36)}$$
where

$$G^{-1}(12)=K(12)\,,\qquad\text{(II}A\text{-37)}$$

because $\sum_a(12)$ vanishes in the limit of $\mathbf{J}=0$. The photon Green's function satisfies the equation (IIA-21), in which $\Pi(12)$ is approximated by dropping the last term $\dfrac{\delta G}{\delta J}$ in equation (IIA-30).

(B) The scattering amplitudes

In § 4, the scattering probability amplitude is defined entirely in terms of Heisenberg 'in' and 'out' states. The scattering amplitude associated with a transition between two well-defined states is a matrix element of what Heisenberg (1942) called the S matrix. S matrix elements can be expressed entirely in terms of the vacuum expectation values of products of the field operators involved. These vacuum expectation values, in turn, can be expressed by simpler vacuum expectation values, such as the electron Green's function and the photon Green's function. The technique, which extracts information from Heisenberg states and displays it in products of Heisenberg field operators sandwiched between the vacuum states, is called the Lehman, Symanzik & Zimmermann (1955, 1957) reduction formula (Low, 1955). We will use this formula to calculate the scattering amplitudes in §4 without being involved in the details.*

If one can define, in a broad sense,† single particle states for particles, anti-particles and photons, then the wave packets of those particles in their single particle states satisfy the following equations:

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* The details of the LSZ reduction formula can be found in references Barton (1963), Schweber (1962), and Bjorken & Drell (1965).

† The energy eigenvalues of the interacting 'electron–hole' system can be complex numbers, since lifetimes of such one-particle states become finite (Hedin, 1965). For photons, such one-particle states exist, because photons are free before they interact with the 'electron–hole' system of a crystal.

$$\left[i\frac{\partial}{\partial t} + \frac{\nabla^2}{2m} - \mathscr{E}_F \right] u_E(x) - \int d\bar{x} \sum_e (x,\bar{x}) u_E(\bar{x}) = 0 \tag{IIB-1}$$

$$\left[i\frac{\partial}{\partial t} + \frac{\nabla^2}{2m} - \mathscr{E}_F \right] v_{\bar{E}}(x) - \int d\bar{x} \sum_e (x,\bar{x}) v_{\bar{E}}(\bar{x}) = 0 , \tag{IIB-2}$$

$$\square \, \mathbf{f}_k(x) = 0 \tag{IIB-3}$$

where u_E, $v_{\bar{E}}$ and $\mathbf{f}_k$ form a complete orthonormal set of one-particle wave packets. The set of u_E's is constructed only from the positive energy wave functions of 'electrons' which are excited above the Fermi level; the set of $v_{\bar{E}}$'s is constructed only from the negative energy wave functions of 'holes' which are created below the Fermi level; and that of $\mathbf{f}_k$ is constructed only from the positive frequency photon wave functions.

When we apply the LSZ reduction formula to the present problems, we must remember our situation that the 'electrons' and 'holes' are confined to a limited space, namely a crystal, while photons are not restricted to any finite space. This situation does not appear in the scattering problems of elementary particles, for which the LSZ reduction formula has been used. We, therefore, make a few modifications in the application of the reduction formula, so that the final expression of the S matrix elements holds for the scattering from a crystal of finite spatial size (Ashkin & Kuriyama, 1966).

The scattering amplitude for the X-ray inelastic scattering from a crystal is then given by

$$S(E,\bar{E},k,k') \equiv \langle \bar{E},E; k'; \text{out} \, |0,0; k; \text{in} \rangle$$

$$= (-1)i^4 \sum_{i,j} \int_\Omega d(\overline{123456}) u_E^+(\bar{1}) v_E(\bar{2})$$

$$\times \{\mathbf{f}_{k'}^*(\bar{3})\}_i \{\mathbf{f}_k(\bar{4})\}_j$$

$$\times K(\overline{15}) K^+(\overline{62}) \square(\bar{3}) \square(\bar{4}) \, \{\langle T[\psi(\bar{5})$$

$$\times \psi^+(\bar{6}) A_i(\bar{3}) A_j(\bar{4})] \rangle\}_{J=0} , \tag{IIB-4}$$

where Ω indicates the integral ranges only inside the crystal; i and j indicate spatial components of a vector; the symbol $+$ implies adjoint operation and $K(12)$ is given previously by equation (IIA-24). Making use of the variational derivative equation (IIA-18) repeatedly, we obtain

$$\lim_{J=0} \langle T[\psi(1)\psi^+(2) A_i(3) A_j(4)] \rangle$$

$$= G(12) D_{ij}(34) - iG(1\bar{1}) G(\bar{2}2)$$

$$\times D_{\overline{mi}}(\bar{3}3) D_{\bar{i}j}(\bar{4}4) \gamma_{\overline{mi}}(\overline{12}; \overline{34}) , \tag{IIB-5}$$

where

$$\gamma_{ij}(12; 34) = -\frac{\delta \Gamma_i^R(12; 3)}{\delta \langle A_j(4) \rangle} + \Gamma_i^R(1\bar{1}; 3)$$

$$G(\overline{12}) \Gamma_j^R(\overline{22}; 4) + \Gamma_j^R(1\bar{1}; 4) G(\overline{12}) \Gamma_i^R(\overline{22}; 3) . \tag{IIB-6}$$

Here the convention for integrations and summations applies to the repeated variables and subscripts with a bar. The vertex function Γ^R has been derived previously. When equation (IIB-5) is substituted into (IIB-4), the contribution from the first term vanishes. The contribution from the second term can be simplified by the use of the electron Green's function equation (IIA-36):

$$K(1\bar{1}) G(\bar{1}2) = G(1\bar{1}) K^+(\bar{1}2) = \delta(1-2) .$$

Finally we obtain

$$S(E,\bar{E},k,k') = i \sum_{i,j,m,l} \int_\Omega d(\overline{123456})$$

$$\times u_E^+(\bar{1}) v_{\bar{E}}(\bar{2}) \{\mathbf{f}_{k'}^*(\bar{3})\}_i \{\mathbf{f}_k(\bar{4})\}_j$$

$$\square(\bar{3}) D_{mi}(\overline{53}) \square(\bar{4}) D_{lj}(\overline{64}) \gamma_{ml}(\overline{12}; \overline{56}) . \tag{IIB-7}$$

This scattering amplitude thus obtained holds for a general X-ray inelastic scattering in which a photon wave packet is coming into the crystal, and interacts with the electrons in the crystal, and may be Bragg-diffracted as well as scattered inelastically. When the incoming X-rays or the outgoing X-rays nearly satisfy Bragg conditions, the photon Green's function must be solved dynamically from the equation (IIA-21) as has been done in dynamical diffraction (elastic scattering) of X-rays by crystals (Ashkin & Kuriyama, 1966; Kuriyama, 1967, 1968, 1970).

Next we confine ourselves to the ordinary inelastic scattering problems in which no Bragg diffraction takes place and the refractive index correction is not significant.* In that case, the photon Green's function satisfies a simpler equation:

$$\square(1) D_{ij}(12) = 4\pi \delta_{ij} \delta(1-2) . \tag{IIB-8}$$

A plane wave can be considered as an incoming wave packet without loss of generality, since any wave packets can be expanded into a set of plane waves (Ashkin & Kuriyama, 1966). The incoming wave packet polarized linearly is then given by

$$\mathbf{f}_k(x) = [(2\pi)^3 2k \cdot 4\pi]^{-1/2} \varepsilon(\mathbf{k}) \exp\{ik \cdot x\} , \tag{IIB-9}$$

where k is a four vector representing $(\mathbf{k}, -\omega)$ and ε is the polarization direction. Then equation (IIB-7) reduces to a simpler form:

$$S(E,\bar{E},k,k') = \frac{i}{(2\pi)^2} \frac{1}{\sqrt{kk'}} \sum_{i,j} \varepsilon_i(k') \varepsilon_j(k)$$

$$\times \int d(\overline{1234}) u_E^+(\bar{1}) v_{\bar{E}}(\bar{2}) \gamma_{ij}(\overline{12}; \overline{34})$$

$$\times \exp\{-ik'\bar{x}_3\} \exp\{+ik\bar{x}_4\} . \tag{IIB-10}$$

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* In the present formulation, the refractive index correction can be easily taken care of, because this is a matter of renormalization in a quantum field theoretic terminology, and our scattering amplitude is formulated for a crystal of finite size.

The function γ_{ij} has been given previously by equation (IIB-6), in which the dominant term can be found to be the first term by use of equation (IIA-34) and (IIA-35). This situation merely reflects the fact that, for ordinary X-rays, the interaction through the term $\mathbf{p} \cdot \mathbf{A}$ between photons and electrons plays a secondary role. It is a familiar one in X-ray diffraction, where the Kramers–Heisenberg dispersion term* also plays a minor rôle. The γ_{ij} can then be approximated by its leading term:

$$\gamma_{ij}(12;34) = + \frac{e^2}{m} \delta_{ij} \delta(1-2)\delta(1-3)\delta(1-4) \qquad (IIB\text{-}11)$$

by use of equation (IIA-35). Substituting it into equation (IIB-10), we obtain equation (4–5) in the text.

In a similar fashion to the above problem, the scattering amplitude for absorption is given by

$$S(E,\bar{E},k,0) \equiv \langle \bar{E}, E; 0; | \text{ out } |\bar{0},0; k; \text{in} \rangle$$

$$= i^3 \sum_i \int_\Omega d(\overline{12345}) u_E^{\ddagger}(\overline{1}) v_{\bar{E}}(\overline{2})[\mathbf{f}_k(\overline{3})]_i$$

$$\times K(\overline{14})K^+(\overline{52})\Box(\overline{3})$$

$$\times \{\langle T[\psi(\overline{4})\psi^+(\overline{5})A_i(\overline{3})]\rangle\}_{\mathbf{J}=0} \ . \qquad (IIB\text{-}12)$$

The application of the variational derivative to the vacuum expectation value in (IIB-12) yields

$$\lim_{J=0} \langle T[\psi(1)\psi^+(2)A_i(3)]\rangle = \frac{\delta G(12)}{\delta J_i(3)}$$

$$= -G(1\overline{1})\Gamma_k^R(\overline{12};\overline{3})G(\overline{2}2)D_{\bar{k}i}(\overline{3}3) \ . \qquad (IIB13)$$

Again using $K(1\overline{1})G(\overline{1}2) = G(1\overline{1})K^+(\overline{1}2) = \delta(1-2)$, $\Box(1)D_{ij}(12) = 4\pi\delta_{ij}\delta(1-2)$ (neglecting Bragg diffraction) and equation (IIA-34) for Γ, we obtain

$$S(E,\bar{E},k',0) = \frac{i}{2\pi} \frac{1}{\sqrt{k}} \frac{ie}{2m} \int_\Omega d\overline{1}\{\varepsilon(k) \cdot [\nabla(1)$$

$$- \nabla(1')]\} \ u_E^{\ddagger}(1)v_{\bar{E}}(1\cdot) \exp\{ikx_1\} \qquad (IIB\text{-}14)$$

where the variable $1'$ is set equal to 1 after the ∇-operation is performed, and we used the transversality condition $\nabla \cdot \mathbf{f}_k = 0$.

APPENDIX III

Derivation of equation (4-8)

When we calculated the transition probabilities for the inelastic scattering process and for the absorption process, we encountered the following quantities:

$$\sum_E \sum_{\bar{E}} v_{\bar{E}}^{\ddagger}(1)u_E(1)u_E^{\ddagger}(2)v_{\bar{E}}(2) \equiv iS(12) \qquad (III\text{-}1)$$

and

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* Among X-ray diffractionists, this term is called the Hönl dispersion correction.

$$J_{ij}(12) = [\nabla(1) - \nabla(1')]_i [\nabla(2) - \nabla(2')]_j$$

$$\times \sum_E \sum_{\bar{E}} v_{\bar{E}}^{\ddagger}(1')u_E(1)u_E^{\ddagger}(2)v_{\bar{E}}(2') \ , \qquad (III\text{-}2)$$

where the variables $1'$ and $2'$ are set equal to 1 and 2, respectively, after ∇-operations are performed. The functions u_E and $v_{\bar{E}}$ are the 'electron' wave function and the 'hole' wave function for their one-particle states, as defined by equations (IIB-1) and (IIB-2). Essentially, these equations are the Schrödinger equations for the 'electrons' and the 'holes' in a crystal which is completely free from any influence due to photons. In these Schrödinger equations we have included the term due to electron–electron interaction in addition to the interaction with the ions. Therefore, the solutions of these equations must be the exact solutions for the 'electrons' and the 'holes' in a real crystal, whether one can solve them in practice, or not. In other words, the quantities defined by equations (III-1) and (III-2) must follow from the properties of the crystal electrons only, and not from the photon field. From this point on, our problem thus reduces to one of the many body problems dealing with the electrons in a crystal. Although the same notation, ψ and ψ^+, are used to represent the electron field operators in this section, they are no longer influenced by the photon field at all.

In general, the electron field operators, $\psi(x)$ and $\psi^+(x)$, can be expanded in terms of the complete sets, u_E and $v_{\bar{E}}$:

$$\psi(x) = \sum_E b_E u_E(x) + \sum_{\bar{E}} d_{\bar{E}}^{\ddagger} v_{\bar{E}}(x) \qquad (III\text{-}3)$$

and

$$\psi^+(x) = \sum_E b_E^{\ddagger} u_E^{\ddagger}(x) + \sum_{\bar{E}} d_{\bar{E}} v_{\bar{E}}^{\ddagger}(x) \ , \qquad (III\text{-}4)$$

where the summation range of E is limited only to positive energies, and that of $\bar{E}$, to negative energies. The quantities b_E and d_E are the anihilation operators for an 'electron' and a 'hole' respectively. The $b_E^{\ddagger}$ and $d_E^{\ddagger}$ are the creation operators for an 'electron' and a 'hole', respectively. The following vacuum expectation values can be calculated with the aid of the creation annihilation operators (note the order of the field operators!):

$$\langle \psi^+(1)\psi(2) \rangle = \sum_{\bar{E}} v_{\bar{E}}^{\ddagger}(1)v_{\bar{E}}(2) \qquad (III\text{-}5)$$

and

$$\langle \psi^+(1)\psi(2)\psi^+(3)\psi(4) \rangle$$

$$= \sum_E \sum_{\bar{E}} v_{\bar{E}}^{\ddagger}(1)u_E(2)u_E^{\ddagger}(3)v_{\bar{E}}(4)$$

$$+ \sum_{\bar{E}} \sum_F v_{\bar{E}}^{\ddagger}(1)v_{\bar{E}}(2)v_{\bar{F}}^{\ddagger}(3)v_{\bar{F}}(4) \ . \qquad (III\text{-}6)$$

Therefore we obtain

$$iS(12) = \langle \psi^+(1)\psi(1)\psi^+(2)\psi(2) \rangle - \langle \psi^+(1)\psi(1) \rangle$$

$$\times \langle \psi^+(2)\psi(2) \rangle = \langle \varrho(1)\varrho(2) \rangle - \langle \varrho(1)\rangle\langle\varrho(2) \rangle \qquad (III\text{-}7)$$

and

$$J_{i,j}(12) = (\nabla_1 - \nabla)_i (\nabla_2 - \nabla_2')_j [\langle \psi^+(1')\psi(1)$$

$$\times \psi^+(2)\psi(2')\rangle - \langle \psi^+(1')\psi(1)\rangle$$

$$\times \langle \psi^+(2)\psi(2')\rangle]$$

$$= (-1)\left(\frac{2m}{ie}\right)^2 [\langle j_i^{(0)}(1)j_j^{(0)}(2)\rangle$$

$$- \langle j_i^{(0)}(1)\rangle\langle j_j^{(0)}(2)\rangle], \qquad \text{(III-8)}$$

where we introduced the density operator $\varrho(1) = \psi^+(1)\psi(1)$ and the current operator $j^{(0)}$ defined by equation (IIA-7). From equation (III-7), it is obvious that $iS(12)$ is related to the generalized dielectic function (including the core electrons).

References

ASHKIN, M. & KURIYAMA, M. (1966). *J. Phys. Soc. Japan*, **21**, 1549.

BARTON, G. (1963). *Introduction to Advanced Field Theory*, Ch. 4. New York: Interscience.

BJORKEN, J. D. & DRELL, S. D. (1965). *Relativistic Quantum Fields*, Ch. 16. New York: McGraw-Hill.

DuMOND, J. W. M. (1929). *Phys. Rev.* **33**, 643.

HEDIN, L. (1965). *Phys. Rev.* **139**, A796.

HEISENBERG, W. (1942). *Z. Phys.* **120**, 513, 678.

KUBO, R. (1959). *Lectures in Theoretical Physics*, Vol. 1, p. 120. Edited by W. BRITTIN, New York: Interscience.

KURIYAMA, M. (1967). *J. Phys. Soc. Japan*, **23**, 1369.

KURIYAMA, M. (1968). *J. Phys. Soc. Japan*, **25**, 846.

KURIYAMA, M. (1970). *Acta Cryst.* A**26**, 56.

KURIYAMA, M. & ALEXANDROPOULOS, N. G. (1971). *J. Phys. Soc. Japan*, **31**, .

MIZUNO, Y. & OHMURA, Y. (1967). *J. Phys. Soc. Japan*, **22**, 445.

LEHMAN, H., SYMANZIK, K. & ZIMMERMANN, W. (1955). *Nuovo Cim.* **1**, 1425.

LEHMAN, H., SYMANZIK, K. & ZIMMERMAN, W. (1957). *Nuovo Cim.* **6**, 319.

LOW, F. (1955). *Phys. Rev.* **97**, 1392.

SCHWEBER, S. S. (1962). *An Introduction to Relativistic Quantum Field Theory*, Chs. 17d and 18d. New York: Harper & Row.

SCHWINGER, J. (1951a). *Proc. Nat. Acad. Sci. U.S.A.* **37**, 452.

SCHWINGER, J. (1951b). *Proc. Nat .Acad. Sci. U.S.A.* **37**, 455.

SUZUKI, T. (1967). *J. Phys. Soc. Japan.* **22**, 1139.

SUZUKI, T., KISHIMOTO, T., KAJI, T. & SUZUKI, T. (1970). *J. Phys. Soc. Japan*, **29**, 730.

ZIMAN, J. M. (1969). *Elements of Advanced Quantum Theory*, Ch. 4.4. Cambridge Univ. Press.

The One-Dimensional Anti-Phase Domain Structures. I. A Classification of Structure and the Patterson Method Applied to the Layer Sequence Determination

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The one-dimensional anti-phase domain structures with an out-of-step vector $\mathbf{u} = (\mathbf{a} + \mathbf{b})/2$ are classified into the following three kinds: (1) The complex out-of-step structure, (2) the complex *APD* (antiphase domain) structure, (3) the simple *APD* structure. These structures are characterized by the use of the similar symbols to the Zhdanov symbol. Intensity formulae are derived for some typical cases. The application of the Patterson method gives some useful relations between the symbol adopted and a quantity which is obtained by Fourier cosine transformation of the unitary intensities. Since this quantity is any one of a set of integers of the form $(P^2 - 4qP)$ (P:period, q:integer), the correct layer sequence may be obtained even if the observed intensities are not so accurate. Applications for some ideal and real cases are shown.

1. The unitary intensity

An example of the one-dimensional anti-phase domain structures of A_3B-type with an out-of-step vector,

$$\mathbf{u} = \frac{(\mathbf{a} + \mathbf{b})}{2}, \qquad (1)$$

is shown in Fig. 1, where the out-of-steps occur along the **c** direction at every four unit cells, and the structure consists of two kinds of unit cells as shown in Fig. 2. The structure factor of the unit cell shown in Fig. 2(a), which is denoted by V_0, is expressed as

$$V_0 = f_B + f_A[\exp\{\pi i(\xi + \eta)\} + \exp\{\pi i(\eta + \zeta)\} + \exp\{\pi i(\zeta + \xi)\}]$$

where f_A and f_B are the atomic scattering factors of A and B atoms, respectively, and ξ, η and ζ are the par-

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