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REVIEWS OF MODERN PHYSICS VOLUME 30, NUMBER 1 JANUARY, 1958

X-Ray Scattering by Thermal Agitation of Atoms in a Crystal

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THERMAL agitation of atoms in a crystal produces plane wave trains in the electronic density of a crystal. These wave trains, which exist in great number and are propagated in all directions with different wavelengths, selectively reflect incident x-rays in all directions. The intensity of scattering produced in this way is determined by the frequency, the amplitude, and the shape of the atomic oscillations which form the reflecting waves, and by the electronic density. Conversely, when the intensity of the scattering is known, it is possible to determine the electronic density.

We use the following notation: $\mathbf{m}$, a translation of the crystal lattice; $\mathbf{j}$, the vector which defines the average position of an atom in the unit cell; and $\mathbf{M}$, a translation of the reciprocal lattice. The $\mathbf{M}$ and $\mathbf{m}$ vectors are related by

$$\mathbf{M}\cdot\mathbf{m}=\cdots, -2, -1, 0, 1, 2, \cdots.$$

Also, g is the number of atoms in a unit cell; N, the number of unit cells in the crystal; μ_j, the mass of an atom in the position j, where here j is an index that runs over the values 1 to g; μ, mass and v, volume of the unit cell; m, mass of the crystal; and E, the number of electrons in a unit cell; so that

$$\mu=\sum_j \mu_j \quad\text{and}\quad m=\mu N.$$

Also $\mathbf{S}$, $\mathbf{T}$, $\cdots$ are the fundamental wave vectors of the plane-wave trains of the atomic oscillations. They are vectors inscribed in the first Brillouin zone with their origin at the center and their extremities distributed with uniform density, their number being equal to N. An harmonic oscillation of the atoms that is related to $\mathbf{S}$, forms an infinity of plane wave trains[1] piloted by the vectors, $\mathbf{S}+\mathbf{M}$.

We denote by $\nu_{S\gamma}$, $\nu_{T\delta}\cdots$ the frequencies of atomic oscillations associated with the fundamental wave vectors $\mathbf{S}$, $\mathbf{T}$, $\cdots$ and the $3g$ modes of oscillation of the g atoms of a unit cell, where γ and δ are indexes that

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[1] (a) J. Laval, Bull. soc. franç. minéral. **64**, 1 (1941). (b) J. phys. radium **15**, 545, 657 (1954).

range from 1, 2, ⋯, $3g$ over these modes. Also $\mathbf{U}(\mathbf{m},j,S,\gamma)$ is written for the displacement of the jth atom in cell $\mathbf{m}$, in the mode of oscillation that is specified by $\mathbf{S}$ and γ. It is convenient also to write $U(\mathbf{m},j)$ for the total displacement of the jth atom in cell $\mathbf{m}$. Here S as an index serves to distinguish between the N different values of the vector $\mathbf{S}$ in the first Brillouin zone, while γ serves to label the $3g$ different modes of oscillation of the atoms of a unit cell, so

$$\mathbf{U}(\mathbf{m},j)=\sum_{S,\gamma}\mathbf{U}(\mathbf{m},j,S,\gamma).$$

We write ν for the frequency and λ for the wavelength of the incident radiation and f_j for the structure factor of the atom at site $\mathbf{j}$; and $\mathbf{X}$ for the scattering vector,

$$\mathbf{X}=(\mathbf{u}'-\mathbf{u})/\lambda \quad \text{and} \quad X=(2/\lambda)\sin(\phi/2),$$

where $\mathbf{u}'$ and $\mathbf{u}$ are unit vectors giving the directions of propagation of the scattered and incident radiation respectively, and ϕ is the scattering angle, that is the angle between $\mathbf{u}$ and $\mathbf{u}'$.

Actually[2] each scattered radiation has a scattered wavelength λ' not equal to λ, but the relative difference $|\lambda'-\lambda|/\lambda$ is less than 10^{-6} when $\lambda=1A$.

We use orthogonal axes, and write V for the magnitude of each vector $\mathbf{V}$, and V_α for its corresponding components along the coordinate axis ($\alpha=1$, 2, 3). The scattering power, $\bar{\omega}$, of the thermal agitation per electron, is to be expressed in terms of the scattering power σ of a free electron. If I is the intensity of the incident radiation per unit area normal to $\mathbf{u}$, and dI the intensity of the radiation scattered in a solid angle $d\Omega$,

$$\bar{\omega}=(NEI\sigma)^{-1}dI/d\Omega, \tag{1}$$

where $\sigma=(r_0\chi)^2$ with $r_0=e^2/\mathrm{mc}^2=2.8\times10^{-3}$ cm, and χ is the polarization factor. The incident electric vector $\mathbf{E}$ may be resolved into $\mathbf{E}_n$ and $\mathbf{E}_t$, respectively, normal and tangential to the plane of scattering, in which case

$$\chi^2=(\mathbf{E}_n{}^2+\mathbf{E}_t{}^2\cos^2\phi)/\mathbf{E}^2.$$

Extinction of the incident x-rays produced by photoelectric effect and by scattering will be neglected as their effect is well known and easy to calculate.

I. QUANTIZATION OF THERMAL OSCILLATIONS

To each harmonic oscillation piloted by the wave vector $\mathbf{S}$ is associated an harmonic oscillation of the same frequency piloted by $-\mathbf{S}$. The energy of these two oscillations is that of a two-dimensional degenerate harmonic oscillator. Quantization of this energy gives progressive oscillations, the displacements $\mathbf{U}(\mathbf{m},j,S,\gamma)$ of which have as components (matrix elements)[3]

$$2\pi U_\alpha(\mathbf{m},j,S,\gamma)_{n,\,n\pm1}=P_\alpha(j,S,\gamma)(hn^0/2N\mu_j\nu_{S\gamma})^{\frac{1}{2}} \times\exp\mp Q_\alpha(\mathbf{m},j,S,\gamma), \tag{2}$$

where the phase Q is given by

$$Q_\alpha(\mathbf{m},j,S,\gamma)=2\pi i[\nu_{S\gamma}t-\mathbf{S}\cdot(\mathbf{m}+\mathbf{j})+\phi_\alpha(j,S,\gamma)].$$

Here n is the vibrational quantum number for the wave mode in question, n^0 means $(n+\frac{1}{2}\pm\frac{1}{2})$, and the amplitudes P are normalized by the condition

$$\sum_{j,\alpha}P_\alpha(j,S,\gamma)^2=1,$$

the range of j being 1 to g and on α, one to three. The (real) vectors $\mathbf{P}(j,S,\gamma)$ and the phases $\phi_\alpha(j,S,\gamma)$ are given by the Fourier matrix.[4]

II. SPECTRAL ANALYSIS OF THE TOTAL RADIATION SCATTERED BY THERMAL AGITATION

The total scattered radiation (excluding incoherent scattering) from the crystal has a displacement which can be expressed in terms of the radiation scattered by a free electron through the factor,

$$\Big[\sum_{m,j}f_j\exp2\pi i\mathbf{X}\cdot(\mathbf{m}+\mathbf{j})\prod_{S,\gamma}\exp2\pi i\mathbf{X}\cdot\mathbf{U}(\mathbf{m},j,S,\gamma)\Big] \times\exp2\pi i\nu t. \tag{3}$$

It is convenient to introduce amplitudes $K(j,S,\gamma)$ and phases $\phi(j,S,\gamma)$ such that

$$\sum_\alpha X_\alpha P_\alpha(j,S,\gamma)\exp2\pi i\phi_\alpha(j,S,\gamma) =XK(j,S,\gamma)(\mu_j/\mu)^{\frac{1}{2}}\exp2\pi i\phi(j,S,\gamma) \tag{4}$$

and also to write

$$a(j,S,\gamma)=XK(j,S,\gamma)(h/2m\nu_{S\gamma})^{\frac{1}{2}}.$$

These expressions give the following forms for the matrix components:

$$[2\pi\mathbf{X}\cdot\mathbf{U}(\mathbf{m},j,S,\gamma)]_{n,\,n\pm1}=a(j,S,\gamma)(n^0)^{\frac{1}{2}} \times\exp\mp Q(\mathbf{m},j,S,\gamma), \tag{5}$$

in which $Q(\mathbf{m},j,S,\gamma)$ is defined like $Q_\alpha(\mathbf{m},j,S,\gamma)$ with the phase $\phi(j,S,\gamma)$ in place of $\phi_\alpha(j,S,\gamma)$. The exponential factors in (3) which involve these matrix components can be evaluated by using the power series for the exponential factor in the form,

$$\exp2\pi i\mathbf{X}\cdot\mathbf{U}(\mathbf{m},j,S,\gamma)=1+(i/1\,!)Z^{(1)}(n,n_1') +(i^2/2\,!)Z^{(2)}(n,n_2')+\cdots, \tag{6}$$

in which $Z^{(p)}(n,n_p')$ is the sum over n_p' of the (n,n_p') matrix elements of the matrix representing $(2\pi\mathbf{X}\cdot\mathbf{U})^p$.

Introducing this development (6) into (3), we obtain the displacement of the total scattered radiation in the form of a series, each term of which defines a monochromatic scattered radiation.

The radiation that is unaltered in frequency by the scattering process is that for which the Bragg condition, $\mathbf{S}=\mathbf{M}$, is satisfied. The frequencies of the other radiations scattered by the thermal agitation of the atoms

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[2] Compare reference 1(b), p. 546.

[3] L. Brillouin, J. phys. radium **6**, 185 (1935). Also see reference 1(b), p. 550.

[4] Compare reference 1(b), p. 549.

are $\nu \pm p\nu_{S\gamma} \pm q\nu_{T\delta} \pm \cdots$, where the integers p, q, $\cdots$ run over all positive values.

We define the order of the scattering n as the sum of the integers p, $q \cdots$. Thus scattered radiation of order n consists of photons which have acquired or lost n quanta of thermal energy, $h\nu_{S\gamma}$, $h\nu_{T\delta} \cdots$.

However, photons which exchange several quanta with a single harmonic oscillation of the atoms are extremely rare in the total scattered radiation. It has been shown[5] that one can simplify the calculation of scattering power without introducing appreciable error by substituting for each radiation which has the frequency of the form written in the foregoing, when each p, q, etc., is greater than unity, another radiation of the same frequency but which has exchanged single quanta with p, q, etc., incoherent harmonic oscillations of the same frequency, $\nu_{S\gamma}$, ν_{TS}, $\cdots$. In this way the frequency of every scattered radiation may be expressed as $\nu \pm \nu_{S\gamma} \pm \nu_{T\delta} \pm \cdots$, where the terms other than the first may repeat several times.

The radiations of order 1 are the ones which at low and medium temperatures constitute the greatest part of the total radiation scattered by thermal agitation. These are scattered by a single harmonic oscillation of the atoms. There are altogether $3Ng$ of these of increased frequency $\nu + \nu_{S\gamma}$, for which the scattering amplitude or displacement is

$$iF_1(S,\gamma,\mathbf{X}) \exp 2\pi i(\nu+\nu_{S\gamma})t \cdot \Big[\sum_m \exp 2\pi i(\mathbf{X}-\mathbf{S})\cdot\mathbf{m}\Big], \quad (7)$$

where

$$F_1(S\cdot\gamma,\mathbf{X}) = \sum_j f_j(H_j/A(j,S,\gamma))B(j,S,\gamma) \times \exp 2\pi i[(\mathbf{X}-\mathbf{S})\cdot\mathbf{j}+\phi(j,S,\gamma]$$

and

$$B(j,S,\gamma) = a(j,S,\gamma)(n)^{\frac{1}{2}}[1-na^2/1\,!\,2\,! + (n^2+\tfrac{1}{2})a^4/2\,!\,3\,! - \cdots],$$

the a's in the series being $a(j,S,\gamma)$. H_j is the Debye-Waller factor

$$H_j = \prod_{S\gamma} A(j,S,\gamma), \quad (8)$$

and

$$A(j,S,\gamma) = 1-(n+\tfrac{1}{2})a^2/(1\,!)^2 + [(n+\tfrac{1}{2})^2+\tfrac{1}{4}]a^4/(2\,!)^2 - \cdots.$$

Similarly there are altogether other $3Ng$ scattered radiations of order unity of decreased frequency, $\nu - \nu_{S\gamma}$ for which the scattering amplitudes are given by analogous expressions,

$$iF_1(-S,\gamma,\mathbf{X}) \exp 2\pi i(\nu-\nu_{S\gamma})t \times \Big[\sum_m \exp 2\pi i(\mathbf{X}+\mathbf{S})\cdot\mathbf{m}\Big], \quad (9)$$

where

$$F_1(-S,\gamma,X) = \sum_j f_j(H_j/A(j,S,\gamma))C(j,S,\gamma) \times \exp 2\pi i[(\mathbf{X}+\mathbf{S})\cdot\mathbf{j}-\phi(j,S,\gamma)],$$

and

$$C(j,S,\gamma) = a(j,S,\gamma)(n+1)^{\frac{1}{2}}[1-(n+1)a^2/1\,!\,2\,! + ((n+1)^2+\tfrac{1}{2})a^4/2\,!\,3\,! - \cdots].$$

In general a radiation of order n, scattered by n harmonic oscillations, $S\gamma$, $T\delta$, $\cdots$ has the scattering amplitude,

$$i^n F_n(\pm S\gamma \pm T\delta \pm \cdots, \mathbf{X}) \exp 2\pi i(\nu \pm \nu_{S\gamma} \pm \nu_{T\delta} \pm \cdots)t \times \Big[\sum_m \exp 2\pi i(\mathbf{X} \mp \mathbf{S} \mp \mathbf{T} \cdots)\cdot\mathbf{m}\Big] \quad (10)$$

where

$$\begin{aligned} F_n = \sum_j f_j&[H_j/A(j,S\gamma)A(j,T)\cdots] \\ &\times[B(j,S\gamma)B(j,T)\cdots] \\ &\times \exp 2\pi i[(\mathbf{X} \mp \mathbf{S} \mp \mathbf{T}\cdots).\mathbf{j} \pm \phi(j,S\gamma) \\ &\pm \phi(j,T\delta \pm \cdots], \end{aligned} \quad (11)$$

in which it is to be understood that a C replaces a B when the corresponding sign of $\nu_{S\gamma}$, $\nu_{T\gamma}$, $\cdots$ is $-$ as in the contrasting expressions (7) and (9).

III. INTENSITY OF RADIATION SCATTERED BY THERMAL AGITATION

The various harmonic oscillations represented by (2) are incoherent, consequently the scattered radiations given by (7), (9), and (11) can have no phase relations between themselves. Therefore their intensities add. The radiation (10) of order n that is scattered by the whole crystal is the resultant (summation over $\mathbf{m}$) of the individual waves scattered from each unit cell of the crystal. If

$$\mathbf{X} = \mathbf{M} \pm \mathbf{S} \pm \mathbf{T} \pm \cdots, \quad (12)$$

all of these individual waves are in phase. In this case this radiation scattered by the whole crystal has a maximum intensity, which referred to the intensity of the radiation scattered by a single free electron is, $|F_n(\cdots,\mathbf{X})|^2N^2$, in which $F_n(\cdots,\mathbf{X})$ is written for the factor defined in (11) when $\mathbf{X}$ has the value indicated in (12).

Because the energy of each harmonic oscillation mode of the atoms fluctuates with time, the scattered radiations show corresponding fluctuations in intensity, and only the average intensity is measurable. This requires the use of the average values for the quantum numbers n, n^2, and so on, that appear in the preceding expressions, relative to the intensity of the scattered radiations. Define $b(S\gamma)$ by $b(S\gamma)-\frac{1}{2} = [\exp h\nu_{S\gamma}/k\theta - 1]^{-1}$, in which θ is absolute temperature and k is

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[5] Reference 1(b), p. 554.

Boltzmann's constant. Also write

$$W(S\gamma)^{\pm}=[b(S\gamma)\pm\tfrac{1}{2}]h\nu_{S\gamma} \quad \text{and} \quad W(S\gamma)=b(S\gamma)h\nu_{S\gamma}, \tag{13}$$

and

$$\epsilon(S\gamma)^{\pm}=(2\pi\nu_{S\gamma})^{-1}[2W(S\gamma)^{\pm}/m]^{\frac{1}{2}} \quad \text{and} \quad \epsilon(S\gamma)=(2\pi\nu_{S\gamma})^{-1}.\ (2W(S\gamma)/m)^{\frac{1}{2}}. \tag{14}$$

Making some minor approximations involving error usually less than 10^{-3}, we obtain with $\mathbf{X}$ given by (12),

$$F_n(\mathbf{X})=(\pi X)^n\sum_j f_j'K(j,S\gamma)K(j,T\delta)\cdots\epsilon(s_\gamma)^{\mp} \cdot\epsilon(T\delta)^{\mp}\cdots\exp[\mathbf{M}\cdot\mathbf{j}\pm\phi(j,S\gamma)\pm\cdots]. \tag{15}$$

Here f_j' is the reduced structure factor,

$$f_j'=f_jH_j, \tag{16}$$

obtained by multiplying by the Debye-Waller factor, which on the average is, from (8), given by

$$H_j=\exp[-\pi^2X^2\sum_{S\gamma}K(j,S\gamma)^2\epsilon(S\gamma)^2]. \tag{17}$$

IV. X-RAY SCATTERING CONSIDERED AS SELECTIVE REFLECTION BY WAVES OF ELECTRONIC DENSITY FORMED BY THERMAL AGITATION

On analyzing the electron density of a crystal by means of a Fourier integral one finds the harmonic components developed by thermal agitation. A component of order n, produced by n harmonic oscillations of the atoms, has at the point $\mathbf{x}$ the displacement,

$$i^nF_n(\mathbf{X})v^{-1}\exp 2\pi i[st-(\mathbf{M}\pm\mathbf{S}\pm\mathbf{T}\pm\cdots)\cdot\mathbf{x}] \tag{18}$$

in which $\mathbf{X}$ is given by (12) and

$$s=\pm\nu_{S\gamma}\pm\nu_{T\delta}\pm\cdots. \tag{19}$$

These waves of electronic density are piloted by $\mathbf{R}=\mathbf{M}\pm\mathbf{S}\pm\mathbf{T}\pm\cdots$, or by $-\mathbf{R}$ according as the quantity s is positive or negative. These are precisely the waves of electronic density (18) which scatter the radiation (10). They reflect the radiation selectively when the condition (12) is satisfied, that is when $\mathbf{X}$ equals their wave vector $\mathbf{R}$, if s is positive, or $-\mathbf{R}$, if s is negative. In the first case the reflected radiation is of increased frequency $\nu+s$, in the second case it is of diminished frequency $\nu-|s|$. Thus, by Doppler effect interaction, we find again the alteration of frequency resulting from quantization of thermal energy.

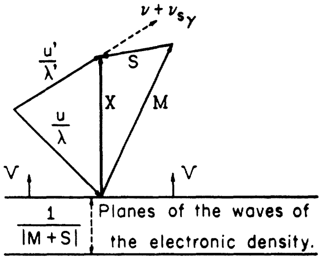
V. SCATTERING POWER OF THERMAL AGITATION

The scattering power of thermal agitation does not depend sensitively either on the volume or the shape of the crystal. To simplify the calculation, we suppose that the crystal is a parallelopiped with edges parallel to those of a unit cell and containing N_1, N_2, N_3 lattice units in these directions, so $N=N_1N_2N_3$. Assuming the Born cyclic conditions,[6] the waves of electronic density are piloted by wave vectors equal to the translations $\mathbf{G}$ of the Gibbs lattice, so

$$\mathbf{G}=\sum_\alpha G_\alpha(\mathbf{L}_\alpha/N_\alpha),$$

where $\mathbf{L}_\alpha$ are the basis vectors of the reciprocal lattice and the G_α run over all positive and negative integers and nought.

FIG. 1.



We take the same origin for reciprocal lattice, Gibbs lattice, and $\mathbf{X}$. The end point of $\mathbf{X}$ we call the scattering pole. If the scattering pole falls on a point $\mathbf{G}$ of the Gibbs lattice, that is if $\mathbf{X}=\mathbf{G}$, all the radiations scattered by the waves (18) of electronic density such that

$$\mathbf{M}\pm\mathbf{S}\pm\mathbf{T}\pm\cdots=\mathbf{G}$$

are selectively reflected (12); and all other radiations scattered by thermal agitation are completely extinguished by interference.

When the scattering pole is not on a point $\mathbf{G}$ of the Gibbs lattice, we find, on adding up the intensities of all the scattered radiations that the total intensity is sensibly that which we would obtain if a point of the Gibbs lattice coincided with the scattering pole, that is, if waves of electronic density (18) existed in the crystal such that (12) might be satisfied.[7] Thus the calculation of scattering power always reduces to the calculation of intensities of selectively reflected radiations.

The scattering power, $\bar{\omega}$, of thermal agitation may be developed into a series,

$$\bar{\omega}=\bar{\omega}_1+\bar{\omega}_2+\cdots, \tag{20}$$

the nth term representing the contribution of scattering of order n. Let us suppose that the scattering pole is in a first zone M, on a point G of the Gibbs lattice. One single fundamental wave vector $\mathbf{S}$ satisfies the equality $\mathbf{X}=\mathbf{M}+\mathbf{S}$, another $\mathbf{S}'$, satisfies $\mathbf{X}=\mathbf{M}-\mathbf{S}'$, and $\mathbf{S}'=-\mathbf{S}$. Each of the two wave vectors, $\mathbf{M}+\mathbf{S}$ and $-(\mathbf{M}-\mathbf{S}')$ which are respectively equal to $\mathbf{X}$ and $-\mathbf{X}$, pilots $3g$ harmonic oscillations of the atoms. Those piloted by $\mathbf{M}+\mathbf{S}$ form $3g$ wave trains of electronic density (Fig. 1)

$$iv^{-1}F_1(\mathbf{M}+\mathbf{S})\exp 2\pi i[\nu_{S\gamma}t-(\mathbf{M}+\mathbf{S})\cdot\mathbf{x}]. \tag{21}$$

Likewise those piloted by $-(\mathbf{M}-\mathbf{S}')$ produce $3g$ wave

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[6] I. Waller, thesis (Upsala, 1925); M. Born and M. Goppert-Mayer, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24, pp. 2, 645. Repts. Progr. in Phys. **9**, 294 (1942–1943).

[7] Compare reference 1(a), p. 55.

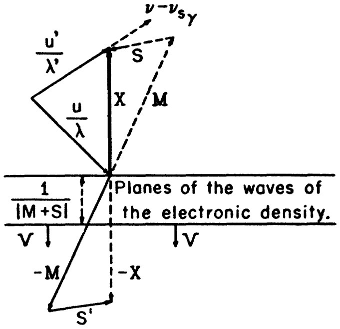

FIG. 2.

trains of electronic density (Fig. 2),

$$iv^{-1}F_1(\mathbf{M}-\mathbf{S}')\exp-2\pi i[\nu_{S\gamma}t+(\mathbf{M}-\mathbf{S}')\cdot\mathbf{x}]. \quad (22)$$

Consequently there are $6g$ selectively reflected radiations of order 1. Of these, $3g$, reflected by the waves (21), are of increased frequency, $\nu+\nu_{S\gamma}$, and have an intensity relative to the scattering by a free electron of

$$(NX^2/2\mu)\sum_{\gamma=1}^{3g}\frac{W_{S\gamma}^-}{\nu_{S\gamma}^2}|\Phi_1(S\gamma)|^2,$$

in which

$$\Phi_1(S\gamma)=\sum_j f_j'K(j,S\gamma)\exp 2\pi i[\mathbf{M}\cdot\mathbf{j}+\phi(j,S\gamma)]. \quad (23)$$

Similarly the $3g$ radiations reflected by the waves (22) have diminished frequencies, $\nu-\nu_{S\gamma}$ whose total intensity is given by a similar expression having W^+ in place of W^-, S' in place of S in ϕ_1, and $-\phi(j,S'\gamma)$ in place of $+\phi(j,S\gamma)$. Since the atomic oscillations which give rise to (21) and (22) are piloted by two equal and opposite wave vectors, it follows that they have the same frequency in pairs, so $\nu_{S'\gamma}=\nu_{S\gamma}$, and $K(j,S'\gamma)=K(j,S\gamma)$, also $\phi(j,S'\gamma)=-\phi(j,S\gamma)$, so $\Phi_1(S'\gamma)=\Phi_1(S\gamma)$, and the crystalline structure factors $\Phi_1(S\gamma)$ and $\Phi_1(S'\gamma)$ are equal in pairs. Thus altogether the $6g$ selectively reflected radiations of order 1, have a total intensity

$$(NX^2/\mu)\sum_{\gamma=1}^{3g}(W_{S\gamma}/\nu_{S\gamma}^2)|\Phi_1(S\gamma)|^2. \quad (24)$$

$(\mathbf{X}=\mathbf{M}+\mathbf{S})$; and the scattering power, of order 1, per crystal electron, relative to that of a free electron, $\bar{\omega}_1$, is the same expression divided by NE.

In similar fashion we may evaluate the higher order scattering powers by adding the intensities of the radiations that are selectively reflected by the electronic density waves produced by more harmonic oscillations of atoms.[8] The number of selective reflections which contribute to the nth-order scattering power is $N^{n-1}(6g)^n/n!$. As n increases their number increases, but each of them weakens still more rapidly.

The harmonic components of thermal agitation have frequencies distributed according to a density $D(\nu)$ which increases with ν, roughly like ν^2, passing through secondary maxima up to a principal maximum ν_M, slightly below the upper boundary of the spectrum. Thus the atomic oscillations of highest frequency are most numerous. Among scattered radiations of order n, those which are scattered by oscillations of high frequency form a numerical ratio which increases with n. Consequently for large n, the scattering power, $\bar{\omega}_n$, is almost entirely caused by the oscillations whose frequencies are only slightly less than ν_M, and

$$\bar{\omega}_n\simeq(|\Phi_n|^2/E)\left[\frac{3gX^2W(\nu_M)}{\mu\nu^2_M}\right]^n\cdot(n!)^{-1}.$$

Here $W(\nu_M)$ is the average energy (13) of the oscillations of frequency ν_M. The factor Φ_n is determined by the structure factors of the atoms, by their positions in the unit cell, by the amplitudes $K(j,s\gamma)$, and phases $\phi(j,S\gamma)$. As n increases the ratio $|\Phi_n|^2/|\Phi_{n-1}|^2$ fluctuates, but only slightly when n is large, and as a whole remains near $\frac{1}{3}$, giving on the average, $\bar{\omega}_n/\bar{\omega}_{n-1}\leq C/n$ with $C=gX^2W(\nu_M)/\mu\nu^2_M$.

For all crystals the frequency ν_M is near to 5×10^{12} sec^{-1}. Besides when the product $X^2W(\nu_M)$ increases the reduced structure factors, f_j' vanish, because f_j and H_j are rapidly decreasing functions of X, and moreover H_j decreases when $W(\nu_M)$ increases. The scattering power of thermal agitation becomes infinitesimal and ceases to be measurable as soon as $3X^2W(\nu_M)/\mu$ exceeds about 10^{25} cgs, that is, as soon as C reaches the value unity. As long as the x-rays scattered by thermal agitation have appreciable intensity, the series (20) converges rapidly, roughly like that for e^x when x is less than 1. And by an averaging effect, every scattering power $\bar{\omega}_n$, of high order n, varies only slightly for a large change in direction of the scattering vector, the more slightly as n is larger.

However, these conclusions are valid only for large n. If n is small the scattering power usually varies strongly when the scattering vector changes its direction, above all, if the scattering pole is moving near to a point of the reciprocal lattice on a ray of a first zone. And for one given angle described by the scattering vector, the scattering power $\bar{\omega}_1$ undergoes the largest variation because it is only due to $6g$ atomic oscillations which in pairs have the same frequency and parallel displacements. At medium temperature and if $\mathbf{X}$ is large (greater than 2×10^8 cm^{-1}), the scattering power $\bar{\omega}_1$ may be less than the scattering power $\bar{\omega}_2$. When the temperature approaches the melting point of the crystal, the scattering power $\bar{\omega}_3$ usually ought to be taken into account. The first term which seems negligible is $\bar{\omega}_4$ or $\bar{\omega}_5$. Therefore retention simply of $\bar{\omega}_1$ gives too small a value for the scattering power of thermal agitation. Such a result may be applied at most to

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[8] Compare reference 1(a), pp. 68–80. Also P. Olmer, Bull. Soc. franç. minéral. 71, 144 (1948); H. Curien, *ibid.* 75, 197 and 343 (1952). Also see reference 1(b), pp. 659–665.

the case of low temperature, or in which X remains less than 10^8 cm^{-1}.

The intensity of the selectively reflected radiations increases like $\epsilon_{S\gamma}{}^2$ with the average amplitude $\epsilon_{S\gamma}$ (14) of atomic oscillations. At the same time the selective reflections by electronic waves are weakened by thermal agitation, like Bragg reflections, each atomic structure factor, f_j, is reduced by the Debye-Waller factor. Therefore as the temperature rises from absolute zero, the scattering power of thermal agitation first increases, passes through a maximum, and then diminishes. The ratio $\bar{\omega}_n/\bar{\omega}_{n-1}$ increases with X and with the temperature.

VI. EVALUATION OF THE ELECTRONIC DENSITY

Let us assume that the scattering pole D (extremity of the vector X) is near a point M of the reciprocal lattice, and that the Bragg selective reflection M is strong. The six acoustic oscillations which contribute to $\bar{\omega}_1$ are piloted by $\mathbf{S}$ and $-\mathbf{S}$ where $\mathbf{S}$ is the vector from M to D, which is very small compared with all the rays in the first zone. These oscillations have low frequencies in the ultrasonic range. They produce an intense scattering of x-rays, so the scattering power, $\bar{\omega}_1$, is strong and almost entirely the result of them whereas the other $6g-6$ atomic oscillations which contribute to $\bar{\omega}_1$ are in the 10^{12} to 10^{13} sec^{-1} frequency range. Also the scattering power of the Compton effect is small in comparison with $\bar{\omega}_1$, so the total value of $\bar{\omega}_1$ scarcely exceeds that of the 6 ultrasonic oscillations. These six oscillations take place in pairs along three orthogonal directions $\mathbf{u}_1$, $\mathbf{u}_2$, $\mathbf{u}_3$; and two oscillations of a same pair have the same frequency; so there are only three distinct frequencies, ν_1, ν_2, and ν_3. Thus in this case the total scattering power is given by

$$\bar{\omega}=(X^2/E\mu)\sum_\alpha \frac{W_\alpha}{\nu_\alpha{}^2}\cos^2(\mathbf{X},\mathbf{u}_\alpha)\,|\Phi_{M,X}|^2+\epsilon, \qquad (25)$$

where ϵ is small compared with the term written. Here W_α is the average energy (13) of the two ultrasonic oscillations of the same frequency ν_α and

$$\Phi_{M,X}=\sum_j f_j'(\mathbf{X})\exp 2\pi i\mathbf{M}\cdot\mathbf{j} \quad\text{and}\quad \mathbf{X}=\mathbf{M}+\mathbf{S}.$$

The quantity $\Phi_{M,X}$ is not exactly equal to the crystalline structure factor, F_M, that is related to the Bragg selective reflection $\mathbf{M}$, because f_j' refers to the scattering vector $\mathbf{M}+\mathbf{S}$ and not to $\mathbf{M}$. But as $\mathbf{S}$ is small compared to $\mathbf{M}$, the relative difference is very small.

It is always possible, by a suitable choice of the fundamental vector $\mathbf{S}$ to make $\mathbf{X}$ parallel to the displacement of two ultrasonic oscillations among the 6 ones, for example to $\mathbf{u}_1$, in which case the total scattering power is almost entirely the result of the two ultrasonic oscillations which take place along the direction of $\mathbf{u}_1$, so only this one term occurs in the sum over α in (25) ($\cos\mathbf{X}\mathbf{u}_2=\cos\mathbf{X}\mathbf{u}_3=0$).

One may estimate the small correction ϵ caused by the other atomic oscillations and by the Compton effect. If the crystal structure is known, $\Phi_{M,X}$ is known too; so it is possible to infer the frequency ν of the two ultrasonic oscillations, and their propagation velocity V, and from V for different directions in the crystal to infer the elasticity coefficients of the crystal.[9]

On the other hand if V is known by mechanical means the measured scattering power permits a determination of the factor $\Phi_{M,X}$.

For a crystal all of the atoms of which are alike one can find the reduced atomic structure factor $f'(\mathbf{X})$ from $\Phi_{M,X}$. Photometry of the x-rays scattered by thermal agitation gives frequency and form of the atomic oscillations,[10] and also the possibility of calculating the Debye-Waller factor, $H(\mathbf{X})$ of (17), and from this the true atomic structure factor, $f=f'/H$. These atomic structure factors so determined apply to the scattering vectors $\mathbf{M}+\mathbf{S}$ (not to $\mathbf{M}$) but from these, owing to the smallness of $\mathbf{S}$ by interpolation, we can find the atomic structure factors $f(\mathbf{M})$ without appreciable error, and finally obtain the electronic density,

$$\rho(\mathbf{x})=v^{-1}\sum_M F_M\exp 2\pi i\mathbf{M}\cdot\mathbf{x}.$$

I thank Professor B. E. Warren for having so willingly read over this study.

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[9] Compare reference 1(a), pp. 110–125. Also G. N. Ramachandran and W. A. Wooster, Acta Cryst. 4, 335 and 431 (1951).

[10] P. Olmer, Bull soc. franç. minéral. 71, 145 (1948); H. Curien, *ibid.* 75, 197 and 343 (1952).