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Diffuse Scattering of X-Rays by Conduction Electrons

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A theoretical expression is obtained for the scattering of x-rays from a completely degenerate free electron gas. Both the classical and the Compton methods are used. The modifications introduced by the periodic potential of the lattice are examined. The scattering by the conduction electrons is found to decrease with the first power of the scattering angle. It is shown that the diffuse scattering by the core electrons decreases as the second power of the angle of scattering. Hence the scattering by the conduction electrons will dominate all other diffuse scattering at sufficiently small angles.

§1.

THE QUANTUM-MECHANICAL theory of the scattering of x-rays has been thoroughly investigated.[1] In practice, however, we may wish to use classical concepts. Again, for incoherent scattering, we may find it convenient to think in terms of photons being scattered by single electrons, as in the Compton effect. In the first, the classical method, the interference between two electrons arises from the addition of the amplitudes of the scattered x-rays. In the second, the Compton method, the interference between two electrons arises through the operation of Pauli's exclusion principle. Thus an electron cannot jump into a state already occupied by another electron.

The first method gives the correct *total intensity* of scattered x-rays (relativity and resonance effects neglected). The formula developed by Raman for the ratio S of the actual scattering to that which would occur if the intensities of the scattering from each electron were added, is[2]

$$S=1+\text{time average of } N^{-1}\sum_{r\neq s}\cos k(z_r-z_s). \quad (1)$$

Here N is the total number of electrons, and

$$k=(4\pi/\lambda)\sin\phi/2,$$

where λ is the wave-length of the incident x-rays, and ϕ is the angle of scattering. Wave mechanics gives the formula[3] (relativity and resonance effects neglected)

$$S=1+\int\psi N^{-1}\sum_{r\neq s}\cos k(z_r-z_s)\psi^*dv_1\cdots dv_N. \quad (2)$$

These two expressions for S are identical if we identify the classical time average with the average over $\psi\psi^*$.

If the probability that one electron were at a given position did not depend upon the positions of other electrons, ψ could be written as a product of eigenfunctions of single electrons

$$\psi=\prod_s\psi_s(\mathbf{r}_s,\delta_s),$$

where δ_s denotes the spin variable. In this case (2) reduces to

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[1] See A. H. Compton, Phys. Rev. **47**, 367 (1935) for a comprehensive review of the literature.

[2] C. V. Raman, Ind. J. Phys. **3**, 359 (1928), Eq. (3).

[3] I. Waller and D. R. Hartree, Proc. Roy. Soc. **A124**, 124 (1929), Eq. (14).

$$S=1+N^{-1}\sum_{n\neq n'} f_{nn}f_{n'n'}.$$

We shall use the notation

$$f_{nn'}=\int \psi_n \cos kz \psi_{n'}^* dv$$

with the convention that the integral is zero when n and n' refer to states with opposite spins. The second term usually represents constructive interference. Thus two electrons bound to the same atom may move independently of one another, but their mere confinement to the same atom gives constructive interference, at least at small angles.

The probability of one electron being at a definite position is dependent upon the presence of the other electrons by virtue of Pauli's exclusion principle. This principle is taken explicitly into account by writing the wave function in the form

$$\psi=\sum_P (-1)^{\sigma_P} P \prod_s \psi_s(\mathbf{r}_s, \delta_s).$$

Here P is an operator which permutes the coordinates (including the spin coordinate) of the electrons, and σ_P is the order of the permutation. With this wave function (2) becomes[3]

$$S=1+N^{-1}\sum_{n\neq n'} (f_{nn}f_{n'n'}-f^2_{nn'}). \qquad (3)$$

The last term is intrinsically negative. Its interpretation depends upon our picture of the scattering process. According to the Raman viewpoint, Pauli's exclusion principle lessens the constructive interference between electrons of like spin. According to the Compton viewpoint, Pauli's exclusion principle prohibits those collisions between photons and electrons in which the recoil electron would find itself in a state already occupied by another electron of like spin.

The first purpose of this paper is to discuss in detail the scattering of x-rays in a case where both methods may be carried out exactly (§2 and §3). This case is the scattering by a free electron gas. The second purpose is to examine the scattering by the conduction electrons of actual metals (§4). Finally, we investigate the conditions where this scattering may be observed (§5).

§2.

From the classical standpoint the scattering of x-rays from a free electron gas presents the same problem as the scattering from a monatomic liquid. In the first problem we must find the interference between the individual electrons, while in the second we must find the interference between the individual atoms. The following analysis for a free electron gas follows step by step the well-known analysis[4] for a monatomic liquid.

The probability that a particular electron lies within the volume element dv_m at the same time that another particular electron lies within the volume element dv_n is

$$P(dv_m/V)(dv_n/V),$$

where V is the total volume of the electron gas. Since the medium is isotropic, P is a function only of the distance r between the two volume elements, i.e., between the two electrons. Eq. (1) may now be transformed to[5]

$$S=1-n4\pi\int_0^\infty (1-P)\frac{\sin kr}{kr} r^2 dr, \qquad (4)$$

where n is the density of electrons.

If the electrons moved independently of one another, then $P=1$, and the interference would average out to zero. Actually, Pauli's exclusion principle tends to keep electrons of like spin apart. Since the configurations favorable to constructive interference are thereby reduced, the average interference will be destructive, at least for small angle scattering.

The function $1-P$ for a free electron gas is[6]

$$1-P=(9/2)\left(\frac{\sin (r/d)-(r/d)\cos (r/d)}{(r/d)^3}\right)^2. \qquad (5)$$

Here $d=\lambda_0/2\pi$, where λ_0 is the wave-length of the fastest electrons, namely, $2(3n/\pi)^{-1/3}$. $1-P$ has been plotted in Fig. 1a. It has the important property that

$$n4\pi\int_0^\infty (1-P)r^2 dr=1,$$

i.e., the integral of the "electron hole" density is equivalent to one positive electron. Hence scattering in the forward direction will be completely destroyed by interference.

[4] Compton and Ellis, *X-Rays in Theory and in Experiment* (1935), pp. 177–185.
[5] Reference 4, Eq. (3.80).
[6] E. Wigner and F. Seitz, Phys. Rev. **43**, 807 (1933).

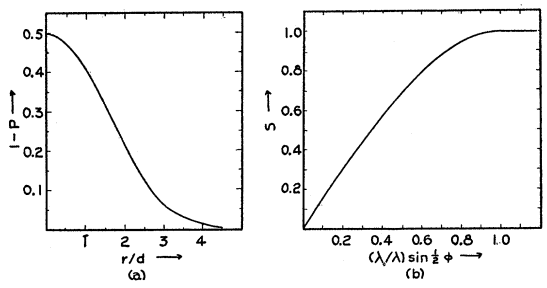

FIG. 1. Classical representation of scattering by free electron gas. The "electron hole" density (a) gives rise by destructive interference to an S value (b) less than unity.

In order to obtain an explicit expression for S, we have merely to substitute (5) into (4). We obtain (see Fig. 1b)

$$S=\begin{cases}(1/2)(3x-x^3), & x<1\\ 1 \qquad\qquad , & x>1,\end{cases} \tag{6}$$

with $x=kd/2=(\lambda_0/\lambda)\sin(\phi/2)$.

The method of performing the integration in (4) will be briefly sketched. We obtain with obvious transformations

$$S=1-\left(\frac{3}{2\pi ix}\right)\int_{-\infty}^{\infty}\left(\frac{\sin z-z\cos z}{z^3}\right)^2 e^{i2xz}zdz.$$

Since the integrand has no poles in the complex plane, we may choose any path for the integration, say the path Γ_1 of Fig. 2. Express the integrand as the sum of three terms, containing the factors exp $2i(x+1)z$, exp $2ixz$, exp $2i(x-1)z$, respectively. The integral of the first two terms vanishes, since no pole lies between the path Γ_1 and an infinite semicircle in the upper half-plane, on which the two terms vanish. If $x>1$, the third term likewise vanishes. Now the integral of the third term along Γ_1 is equal to $-2\pi i$ times its residue at $z=0$, plus its integral taken along the path Γ_2. If $x<1$, this integral along Γ_2 vanishes, since the integrand is zero along an infinite semicircle in the lower half-plane. We are thus left with $-2\pi i$ times the residue of the third term at $z=0$. This leads us directly to (6).

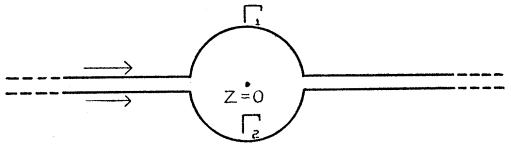

FIG. 2. Paths of integration used in evaluating S.

§3.

In the case of a free electron gas, Eq. (3) reduces to

$$S=1-N^{-1}\sum_{n\neq n'} f_{nn'}{}^2.$$

A simple phenomenological interpretation of this equation is the following.

We regard the scattering of x-rays as the simple Compton scattering of photons by individual electrons. The intensity of scattering in any direction is given by the Thomson formula (apart from relativity corrections). During the collision the scattering electron suffers a change of momentum which is calculable from the principles of conservation of energy and of momentum. Since the wave properties of the photon are not considered, constructive and destructive interference between two electrons does not occur. However, we must recognize that the electrons obey Pauli's exclusion principle. We thus exclude those collisions for which the final quantum state of the electron is already occupied. In the case of a (completely degenerate) Fermi gas, the final momentum must thus lie outside the Fermi surface in momentum space.

The scattering factor S may thus be calculated as follows. We calculate the momentum $\mathbf{\Delta p}$,

$$|\mathbf{\Delta p}|=(2h\nu/c)\sin(\phi/2),$$

which an electron must absorb to scatter a photon through the angle ϕ. Then $S(\phi)$ is equal to that fraction of the volume inside the Fermi

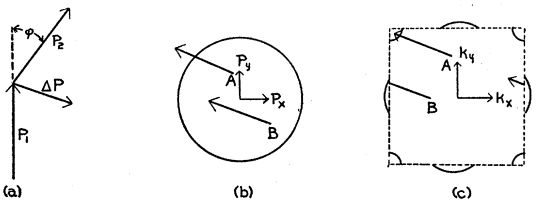

FIG. 3. Compton representation of scattering by a free electron gas. The momentum change of a photon (a) during a collision is accompanied by an opposite change in momentum of the scattering electron (b). Electrons at such positions as A in momentum space are effective, while those in such positions as B are not effective. (c) is a schematic diagram analogous to (b) for the case of conduction electrons. The full lines represent the Fermi surface. The dotted square represents the boundary of the (multiply connected) first zone.

surface for which $\Delta\mathbf{p}+\mathbf{p}$ lies outside the Fermi surface (see Fig. 3). A simple calculation shows that this fraction is given by Eq. (6).

§4.

In an actual metal the conduction electrons are not entirely free. A quantum state may no longer be specified by its momentum. Instead, each quantum state is specified by a vector $\mathbf{k}$ which, however, has many properties analogous to that of momentum.[7] In particular, if a photon changes its momentum by $\Delta\mathbf{p}$ in colliding with an electron, the electron must change its $\mathbf{k}$ vector by an amount $\Delta\mathbf{k}=-\Delta\mathbf{p}$. Thus only those states $\mathbf{k}$ are effective in this particular type of scattering for which the state $\mathbf{k}-\Delta\mathbf{p}$ is unoccupied.

The only difference between conduction and free electrons which we need consider is that in the former the Fermi surface in k space is not necessarily a sphere. In fact, k space is divided into an infinite number of zones, each zone being multiply connected.[8] At small angle scattering only transitions between states in the same zone are important.

As the angle of scattering is decreased it is thus evident that S becomes proportional to the area of the Fermi surface. In divalent metals there are just enough conduction electrons to fill the first zone. Hence as the binding in these metals becomes stronger (case of poor conductors) the area of the Fermi surface, together with S, becomes smaller. For extremely tight binding (case of insulators) the area of this surface vanishes.

[7] An excellent review of the quantum theory of conduction electrons is given by H. Bethe, *Handbuch der Physik* (1933), Vol. 24, No. 2.

[8] For example, see reference 7, Fig. 19.

§5.

It remains to investigate the conditions under which diffuse scattering from conduction electrons may be experimentally observed. It is necessary of course that the scattering due to the conduction electrons be comparable to the scattering due to the core electrons.

The diffuse scattering due to each core is given by[9]

$$I=I_e\{(Z'-f^2/Z')+(1-e^{-2M})f^2\}.$$

Here I_e is the Thomson scattering of a single electron, Z' is the number of electrons per core. The structure factor f is given approximately by

$$(4\pi/k)\int_0^\infty u(r)\sin(kr)rdr,$$

where $u(r)$ is the density of the core electrons, and $k=(4\pi/\lambda)\sin(\phi/2)$. For our present purpose we need only know that the temperature dependent Debye-Waller term M contains k^2 as a factor.

Inspection shows that a Taylor expansion of I starts with k^2. The expansion of the first term starts with k^2 since $f(k)$ is an even function of k, and $f(o)=Z'$. That the expansion of the second term starts with k^2 is evident from the dependence of M upon k.

Hence the diffuse scattering from the core electrons at small angles varies as ϕ^2. From Eq. (6) we see that the diffuse scattering by the conduction electrons varies as ϕ. Hence at sufficiently small angles the latter will become greater than the former. Calculation shows that for the particular case of lithium at room temperature the two types of scattering become equal at scattering angles such that

$$(A/\lambda)\sin(\phi/2)=0.04.$$

[9] G. E. M. Jauncey, Phys. Rev. **37**, 1193 (1931); Y. H. Woo, Phys. Rev. **38**, 6 (1931).