X-Ray Scattering by a Crystal in an Electric Field*

By A. D. Buckingham†

University of Wisconsin, Theoretical Chemistry Institute, Madison, Wisconsin, U.S.A.

The effects of a strong electric field E on atomic scattering factors f are evaluated to the first order in E, and the precise relationship $f = f^{(0)} - 4\pi i E\alpha \sin \theta / \lambda e$ derived for small angles of scatter 2θ, for X-rays of wave length λ, where $f^{(0)}$ is the unperturbed scattering factor, α the polarizability of the atom and e the protonic charge. An accurate expression is also obtained for scattering by a hydrogen atom through any angle; the purely imaginary field-dependent term reaches sharp turning points when $\sin \theta / \lambda = \pm 0.1202$ Å^{-1} and $f^{(0)} = 0.744$. First-order changes in scattered intensities are predicted only for crystals lacking centres of symmetry. Measurements might be used for (i) space group assignments, (ii) determination of absolute configurations, and (iii) obtaining structure factor phases. Approximate calculations indicate that a uniform field of 1000 e.s.u. would produce intensity changes of the order of 10^{-4}, which could be modulated with the field; with non-uniform fields, and in ferroelectrics, much larger changes could be induced. The theory is illustrated by application to the zinc blende crystal.

Introduction

The major difficulty that now hinders the successful and rapid determination of molecular structures through X-ray crystallography is the well-known 'phase-problem'. The observables are the positions and intensities of the scattered X-rays. The positions give the unit-cell dimensions as well as information about the space group, but because reflections from opposite faces are normally identical (Friedel's law) crystals can be unambiguously assigned by conventional X-ray analysis to only 70 of the 230 possible space groups. The scattered intensities are determined by the electron charge distribution within the unit cell; intensity measurements give the magnitudes, but not the signs, of the electric vectors of the scattered X-ray beams.

The intensity $I(hkl)$ of an X-ray beam scattered from the (hkl) plane of a single crystal is proportional to $|F(hkl)|^2$, where $F(hkl)$ is the *structure factor*, that is, the scattering power of a unit cell. The structure factor is dependent on the positions of the atoms within the cell and on the *atomic scattering factors* f,

$$F(hkl) = \sum_j f_j \exp [2\pi i (hu_j + kv_j + lw_j)] = \sum_j f_j \exp (iX_j) \tag{1}$$

where the summation is over all atoms j in the unit cell and u_j, v_j, w_j are numbers defining the position of the jth atom along the **a**, **b**, **c** axes of the unit cell (James, 1954). The effective electron density $\varrho(x, y, z)$ is the Fourier transform of the structure factor,

$$\varrho(x, y, z) = \frac{1}{V} \sum_{hkl} F(hkl) \exp \left[-2\pi i \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \right] \tag{2}$$

where V is the volume of the unit cell and the summation is over all positive, negative and zero values of h, k and l. The phase problem exists because intensity measurements give $|F(hkl)|$ and not $F(hkl) = |F(hkl)| \exp (i\alpha_{hkl})$, where α_{hkl} is the unknown phase of the structure factor.

If the atomic scattering factor $f_j = f_j' + i f_j''$, then from equation (1)

$$|F(hkl)|^2 = \sum_j (f_j' + i f_j'') \exp (iX_j) \sum_k (f_k' - i f_j'') \exp (-iX_k)$$

$$= \left[\sum_j f_j' \cos X_j \right]^2 + \left[\sum_j f_j' \sin X_j \right]^2$$

$$+ 2 \sum_{j,k} f_j' f_k'' (\sin X_j \cos X_k - \cos X_j \sin X_k)$$

$$+ \left[\sum_j f_j'' \cos X_j \right]^2 + \left[\sum_j f_j'' \sin X_j \right]^2. \tag{3}$$

For centrosymmetric crystals, the summations over equivalent atoms eliminate the terms in $\sin X_j$ in equation (3), giving

$$|F(hkl)|^2 = \left[\sum_j f_j' \cos X_j \right]^2 + \left[\sum_j f_j'' \cos X_j \right]^2. \tag{4}$$

Normally, X-rays of frequency far from atomic absorption frequencies are used, and then f_j is real and equation (3) simplifies to

$$|F(hkl)|^2 = \left[\sum_j f_j' \cos X_j \right]^2 + \left[\sum_j f_j' \sin X_j \right]^2 \tag{5}$$

so that $|F(hkl)|^2 = |F(\overline{hkl})|^2$, which is Friedel's law. This law is inapplicable when $f_j'' \neq 0$, and by using X-rays that were partly absorbed by one of the atoms, the polarity of zinc blende was determined (Coster, Knol & Prins, 1930), and absolute configurations found for optically active molecules (Bijvoet, Peerdeman & van Bommel, 1951). When f_j is real, the phase α_{hkl} is

---

$$\alpha_{hkl}=\tan^{-1}\left[\sum_j f'_j \sin X_j \Big/ \sum_k f'_k \cos X_k\right]\qquad(6)$$

which is 0 or π for centrosymmetric crystals.

The purpose of the present paper is to investigate the effects of a strong electric field on the scattering of X-rays. Since the field might be expected to interact more strongly with the more polarizable atoms, phase differences should be induced, and if these were to have a measurable influence on the intensities, the method would provide new information on crystal polarity and a possible escape from the phase problem. Some early attempts were made to detect the effects of electric and magnetic fields on X-ray scattering (Compton & Allison, 1935) and although claims of small changes were made, these were probably not justified. This early work was aimed at displacing ions in an ionic lattice; however, in a field of 1000 e.s.u. (300,000 volts cm^{-1}) movements of only 10^{-3} Å would be expected. Also, if f is real, intensity changes arising from atomic displacements would be proportional to the *square* of the field strength. The idea behind the present paper is different — the object is to distort the electronic structure, thereby inducing changes in the atomic scattering factors and hence in the observed intensities; if the unit cell lacks a centre of symmetry, these changes are predicted to be proportional to the *first power* of the electric field strength.

The atomic scattering factor

For frequencies that are high compared with atomic absorption frequencies, the scattering factor for an atom in a quantum state Ψ is

$$f=\sum_j \int \Psi^* \exp(i\varkappa\mathbf{S}.\mathbf{r}_j)\Psi d\tau \equiv \sum_j \langle\Psi|\exp(i\varkappa\mathbf{S}.\mathbf{r}_j)|\Psi\rangle$$
$$=\sum_j \langle\Psi|\exp(i\mu r_j \cos\beta_j)|\Psi\rangle\qquad(7)$$

where $\mu=2\varkappa\sin\theta=4\pi\sin\theta/\lambda$, and the summation is over all electrons j in the atom; the vector $\mathbf{S}=\mathbf{s}-\mathbf{s}_0$ is the difference between the unit vectors in the directions of the reflected and incident beams, and $\mathbf{r}_j$ is the position vector of electron j relative to its nucleus, so $\mathbf{S}.\mathbf{r}_j=2r_j\sin\theta\cos\beta_j$; $2\theta=\cos^{-1}(\mathbf{s}.\mathbf{s}_0)$ is the angle of scatter, and β_j the angle between $\mathbf{r}_j$ and $\mathbf{S}$.

In the presence of an electric field $\mathbf{E}$ with components $E_\gamma(\gamma=x,y,z)$, atomic wave functions $\Psi^{(0)}$ become

$$\Psi=\Psi^{(0)}+E_\gamma \Psi_\gamma^{(1)}+O(E^2)\ .\qquad(8)$$

The electric field perturbs the electron distribution, inducing polarity through $\Psi_\gamma^{(1)}$. The polarizability tensor $\alpha_{\beta\gamma}$ of the atom is

$$\alpha_{\beta\gamma}=2\langle\Psi^{(0)}|m_\beta|\Psi_\gamma^{(1)}\rangle\qquad(9)$$

where $\mathbf{m}=-e\sum_j\mathbf{r}_j$ is the dipole moment operator, e being the protonic charge. From equations (7) and (8)

$$f=\sum_j \langle\Psi^{(0)}|\exp(i\mu r_j \cos\beta_j)|\Psi^{(0)}\rangle$$
$$+2E_\gamma\sum_j \langle\Psi^{(0)}|\exp(i\mu r_j \cos\beta_j|\Psi_\gamma^{(1)}\rangle+O(E^2)$$
$$=f^{(0)}+iEf^{(1)}+O(E^2)\ .\qquad(10)$$

Many unperturbed atomic scattering factors $f^{(0)}$ are well-known empirically and through calculations. For low-angle scattering, the exponentials in equation (10) may be expanded in powers of μ, and

$$f=Z-i\mu e^{-1}(m_S^{(0)}+\alpha_{S\gamma}E_\gamma)+O(\mu^2)+O(E^2)\qquad(11)$$

where Z is the total number of electrons in the atom, and $m_S^{(0)}$ the component of the permanent dipole moment of the atom in the direction of the vector $\mathbf{S}=\mathbf{s}-\mathbf{s}_0$. For atoms in S-states, $m^{(0)}=0$, $\alpha_{\beta\gamma}$ is isotropic and

$$f=Z-i\mu e^{-1}\alpha E+O(\mu^2)+O(E^2)\qquad(12)$$

where E is the component of $\mathbf{E}$ in the direction of the vector $\mathbf{S}$ for positive angles of scatter; the components of $\mathbf{E}$ perpendicular to $\mathbf{S}$ produce changes in f proportional to E^2. Henceforth it is supposed that the unperturbed atoms are spherical.

For large angles of scatter it is not generally possible to perform the integrations in equation (10) precisely. However, for the ground state of a hydrogen-like atom with nuclear charge Ze, an exact calculation gives

$$\Psi=\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}e^{-Zr/a}\left[1-E\left(\frac{r^2}{2Ze}+\frac{ar}{Z^2e}\right)\cos\beta+O(E^2)\right]\qquad(13)$$

where $a=0{\cdot}5292$ Å is the Bohr radius. The polarizability $\alpha=\tfrac{9}{2}a^3Z^{-4}$ and

$$f=\left[1+\frac{a^2\mu^2}{4Z^2}\right]^{-2}$$
$$\times\left[1-iE\frac{9a^3\mu}{2eZ^4}\left(1+\frac{a^2\mu^2}{4Z^2}\right)^{-2}\left(1+\frac{a^2\mu^2}{12Z^2}\right)\right]+O(E^2)$$
$$=f^{(0)}\left[1-iE\frac{\mu\alpha}{e}\left(1+\frac{a^2\mu^2}{4Z^2}\right)^{-2}\left(1+\frac{a^2\mu^2}{12Z^2}\right)\right]$$
$$+O(E^2)\ .\qquad(14)$$

Fig. 1 shows the hydrogen atom scattering factors

$$f^{(0)}=\left(1+\frac{a^2\mu^2}{4Z^2}\right)^{-2}$$

and

$$f^{(1)}=-\frac{\mu\alpha}{e}\left(1+\frac{a^2\mu^2}{4Z^2}\right)^{-4}\left(1+\frac{a^2\mu^2}{12Z^2}\right)$$

plotted as functions of $\mu/4\pi=\sin\theta/\lambda$; $f^{(0)}$ has a maximum of unity (the number of electrons) at $\theta=0$ and falls with increasing angle of scatter. The field-dependent contribution $iEf^{(1)}$ is purely imaginary and $f^{(1)}$ vanishes, with a large slope of $-4\pi\alpha e^{-1}$, at $\theta=0$ and has turning points at $\mu=\pm1{\cdot}51$ Å^{-1}, which for $\lambda=1{\cdot}542$ Å ($K\alpha$ radiation from Cu) correspond to
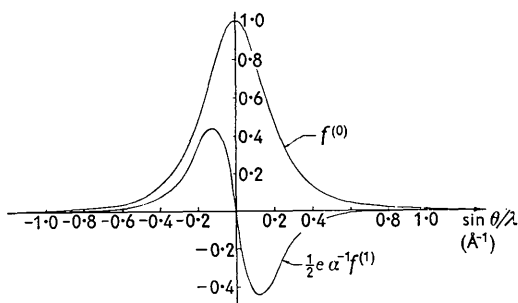
Fig. 1. The atomic scattering factor $f^{(0)}$ and the electric-field factor $f^{(1)}$ times $e/2\alpha$ for the ground state of the hydrogen atom.

scattering through $2\theta = \pm 21\cdot3°$. For heavier atoms, $f^{(0)}$ decreases from Z less rapidly with increasing θ, since tightly bound electrons are more successful in scattering X-rays through large angles — this is in accord with the $\mu^2 Z^{-2}$ factor in equation (14). Presumably $f^{(1)}$ also dies more slowly with increasing θ in heavier atoms.

Discussion

At the turning points in $f^{(1)}$, $f = 0\cdot744 \mp 1\cdot22 \times 10^{-7} iE$ for the ground state of the hydrogen atom, where E is in e.s.u. The effective field will differ from the actual field, and the Lorentz internal field is $[(\varepsilon+2)/3]E$, where ε is the static dielectric constant. In most crystals, ε is between 2 and 10, but in ferro-electric crystals like barium titanate, $\varepsilon \sim 10^4$ and the internal field effect can be very large. Very large local fields might also be obtained by using a sharp conductor on one face of a crystal on a flat conductor, producing a highly inhomogeneous field. Most atoms are more polarizable than hydrogen, but $f^{(0)}$ is also larger, and $f^{(1)}/f^{(0)}$ ratios may be similar to that of the hydrogen atom. An important practical point is likely to be our ability to modulate E at a low audio-frequency and to use a phase-sensitive scintillation detector.

Since f''_j in equations (3) and (4) is proportional to E, terms in $f''_j f''_k$ are of $O(E^2)$ and are therefore negligible in this calculation. Equation (4) requires that centrosymmetric unit cells do not produce intensity changes proportional to the first power of E. However, when

$$\sum_j f'_j \sin X_j \neq 0 \ ,$$

equations (3) and (10) lead to intensity changes $\delta I(hkl)$ given by

$$\frac{\delta I(hkl)}{I(hkl)} = \frac{2E \sum_{j,k} f_j^{(0)} f_k^{(1)} (\sin X_j \cos X_k - \cos X_j \sin X_k)}{\left[\sum_j f_j^{(0)} \cos X_j\right]^2 + \left[\sum_j f_j^{(0)} \sin X_j\right]^2} + O(E^2) \ . \quad (15)$$

Measurements of δI might be used for (i) space group assignments, (ii) determination of absolute configurations of optically active groups, and (iii) obtaining new information about $\sin X_j$ and $\cos X_j$ and hence about the phase α_{hkl} in equation (6). If only first order effects in E should be measurable, the technique would be restricted to crystals that lack centres of symmetry; however, centrosymmetric crystals normally yield to conventional methods of X-ray structure analysis. The method has something in common with work aimed at using anomalous dispersion to determine phases (Okaya & Pepinsky, 1956; Ramachandran & Raman, 1956).

As an illustration of the theory, consider zinc blende, whose unit cell contains Zn ions at the positions $000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$, and S ions at $\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}, \frac{1}{4}\frac{3}{4}\frac{3}{4}$. From equation (3),

$$|F(100)|^2 = 0, \quad |F(200)|^2 = 16(f_{Zn}^{(0)} - f_S^{(0)})^2, \quad |F(300)|^2 = 0 \ ,$$
$$|F(400)|^2 = 16(f_{Zn}^{(0)} + f_S^{(0)})^2 \ ;$$

$$|F(110)|^2 = 0, \quad |F(220)|^2 = 16(f_{Zn}^{(0)} + f_S^{(0)})^2, \quad |F(330)|^2 = 0 \ ,$$
$$|F(440)|^2 = 16(f_{Zn}^{(0)} + f_S^{(0)})^2 \ ;$$

$$|F(111)|^2 = 16[f_{Zn}^{(0)2} + f_S^{(0)2} + 2E(f_{Zn}^{(0)} f_S^{(1)} - f_S^{(0)} f_{Zn}^{(1)})] \ ,$$
$$|F(222)|^2 = 16(f_{Zn}^{(0)} - f_S^{(0)})^2 \ ,$$

$$|F(333)|^2 = 16[f_{Zn}^{(0)2} + f_S^{(0)2} - 2E(f_{Zn}^{(0)} f_S^{(1)} - f_S^{(0)} f_{Zn}^{(1)})] \ ,$$
$$|F(444)|^2 = 16(f_{Zn}^{(0)} + f_S^{(0)})^2 \ .$$

Hence the first and third order reflections from the (111) planes show the effects of the electric field, and these show equal and opposite changes.

References

BIJVOET, J. M., PEERDEMAN, A. F. & BOMMEL, A. J. VAN (1951). *Nature, Lond.* **168**, 271.

COSTER, D., KNOL, K. S. & PRINS, J. A. (1930). *Z. Phys.* **63**, 345.

COMPTON, A. H. & ALLISON, S. K. (1935). *X-rays in Theory and Experiment*, 2nd ed., p. 469. New York: Van Nostrand.

JAMES, R. W. (1954). *The Optical Principles of the Diffraction of X-rays*. London: Bell.

OKAYA, K. & PEPINSKY, R. (1956). *Phys. Rev.* **103**, 1645.

RAMACHANDRAN, G. N. & RAMAN, S. (1956). *Curr. Sci.* **25**, 348.