

BASIC X-RAY INTERACTIONS WITH MATTER

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1. Interaction processes

In the photon energy range below 1 MeV the electromagnetic interaction between x-rays and matter leads to the following processes:

- 1) Photoelectric absorption (true absorption). In this process a photon disappears and an electron is ejected from an atom. The electron carries away all the energy of the absorbed photon minus the energy binding the electron to the atom.
- 2) Coherent scattering (Rayleigh scattering). This is a process by which photons are scattered by bound atomic electrons and in which the atom is neither ionized nor excited. The scattering from different parts of the atomic charge distribution is then coherent, i.e. there are interference effects. For an assemblage of atoms the scattering from the different atoms may add up coherently or incoherently depending on the atomic arrangement.

It is often assumed that the Rayleigh scattering is elastic. However, the scattering from a free atom is never strictly elastic because of the recoil energy. In a crystal lattice the recoil is negligible because it is absorbed by the crystal as a whole. However, the interaction with the lattice vibrations (phonons) may give rise to inelastic thermal diffuse scattering. This scattering is at least partially coherent. In conclusion, the Rayleigh scattering from an assemblage of atoms may be coherent or incoherent and elastic or inelastic.

- 3) Incoherent scattering (Compton scattering). This process can be visualized as a collision between the photon and one particular electron. The photon loses some of its energy and its wavelength is accordingly modified. Thus the scattering is inelastic. No interference takes place between radiation scattered by different electrons of the material system.

The interaction processes also produce fluorescent x-ray and a number of emitted electrons, namely photo-electrons, Auger electrons and Compton recoil electrons. These x-rays and electrons can be analysed by spectroscopic methods and give information about the element composition and the electronic structure of the sample.

The total photon-atom interaction cross section can therefore be written

$$\sigma_{\text{tot}} = \tau + \sigma_{\text{coh}} + \sigma_{\text{incoh}} \quad (1)$$

where τ is the photoeffect cross section. The magnitudes of the cross sections are shown in Fig. 1 for germanium.

2. Rayleigh scattering

The high-energy limit of the atomic scattering factor, f_0 , for an atom of atomic number Z is defined as the matrix element

$$f_0(\vec{q}, Z) = \sum_{n=1}^Z \langle \psi_0 | \exp(i \vec{q} \cdot \vec{r}_n) | \psi_0 \rangle \quad (2)$$

where ψ_0 is the ground-state wave function of the atom and \vec{q} is the scattering vector. The atomic scattering factor may also be expressed as the Fourier transform of the electron density. In the forward direction one has $f_0(0, Z) = Z$ (Fig. 2).

Only in the case of the hydrogenic atoms (single electron) can the Schrödinger equation for the ground-state wavefunctions, ψ_0 , be solved in a simple analytic form. For many-electron atoms the Coulomb repulsion between the electrons prevents exact solutions, and so a variety of approximations have been used.

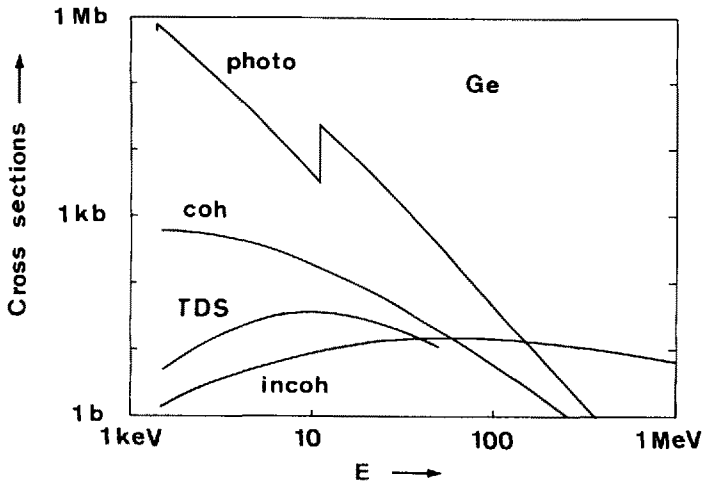


Fig. 1. Cross sections for the photoeffect, coherent and incoherent scattering, and thermal diffuse scattering in germanium. Data from Ref. 3.

Hydrogenic solutions can be obtained by assuming each electron of the atom to move in a hydrogen-like field reduced from the nuclear field by a screening constant, with the screening constant different for each electron group. In the self-consistent-field method each electron is assumed to move in the field of the nucleus and in an average field due to the other electrons. The most successful such one-electron scheme is the Hartree-Fock method in which the total wave function is written as a determinant of one-electron wavefunctions.

The differential scattering cross section is given by

$$d\sigma_{\text{coh}}/d\Omega = r_e^2 f_0^2 \sin^2 \alpha = f_0^2 (d\sigma^{\text{Th}}/d\Omega) \quad (3a)$$

where r_e is the classical electron radius, α the angle between the observed direction and the electric field of the incident wave, and σ^{Th} the cross section for a free electron according to the classical Thomson formula. For unpolarized radiation one obtains

$$d\sigma_{\text{coh}}/d\Omega = r_e^2 f_0^2 \cdot \frac{1}{2} (1 + \cos^2 \theta) \quad (3b)$$

where θ is the scattering angle.

In a condensed matter the coherence can extend to electrons of different atoms and give rise to more striking interference effects, such as Bragg-law diffraction by crystal lattices. The amplitudes of the crystalline reflections is described by the structure factor F:

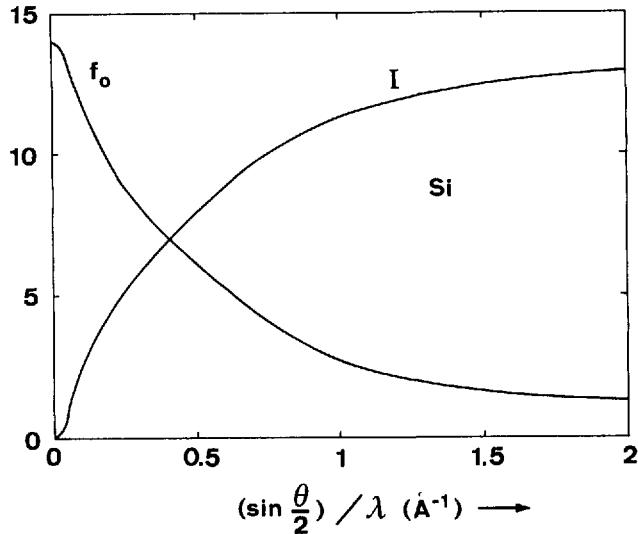


Fig. 2. The atomic scattering factor, f_0 , and the incoherent scattering function, I , for silicon.

$$F = \sum_n f_n \exp(i \vec{q} \cdot \vec{r}_n) \quad (4)$$

where the summation over n involves the positions \vec{r}_n of the different atoms in the unit cell. The Bragg condition implies that the scattering vector \vec{q} equals a reciprocal lattice vector. In a position in which no Bragg reflection occurs, the total Rayleigh scattering from a crystal is in general much less than the sum of intensities scattered by the individual atoms. The observed intensity is in this case due to all deviations from crystal periodicity (thermal vibrations, impurities etc.).

3. Anomalous scattering and absorption

Dispersion corrections to the atomic scattering factor have to be taken into account because of the interaction between the perturbing electromagnetic field and the excited states of the electrons. In non-relativistic quantum mechanics one has

$$f = f_0 + f' + i f'' \quad (5)$$

where f' and f'' are related through a Kronig integral:

$$f'(\omega) = \frac{2}{\pi} \int_0^{\infty} \frac{\omega' f''(\omega')}{\omega^2 - \omega'^2} d\omega' \quad (6)$$

According to relativistic quantum mechanics there will be an additional, real term on the right-hand side of equation (5)^{1,2}.

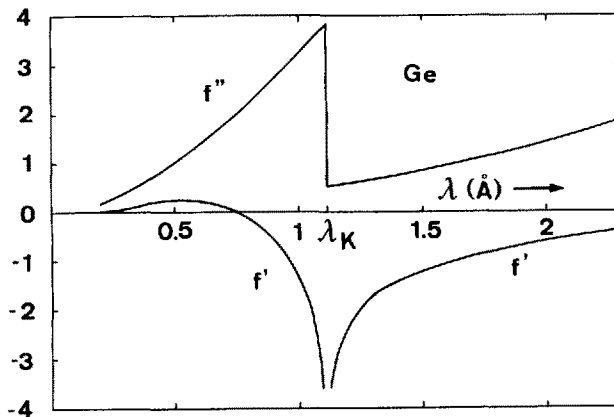


Fig. 3. Anomalous dispersion corrections of germanium, Data from Ref. 1.

The imaginary part f'' is directly related to the photoeffect cross section:

$$f''(\omega) = (\omega/4\pi r_e c)\tau(\omega) \quad (7)$$

Theoretical cross sections have been calculated rigorously using relativistic wave-functions by Cromer and Liberman¹, Storm and Israel³ and others. On the other hand relatively simple formulae for the calculation of hydrogen-like photoeffect cross sections have been communicated by Wagenfeld⁴. These formulae provide not only the possibility of a fast and easy calculation of the normal photoeffect cross section but also of the angular dependent term, $F''_{hk\ell}/F''_{000}$, governing the anomalous absorption of wave-fields in perfect crystals (Borrmann effect).

Hydrogen-like photoeffect cross sections in a medium energy range (5 to 25 keV) have been published by Hildebrandt, Stephenson and Wagenfeld⁵ for silicon and germanium and then expanded⁶ to all elements in the range $Z = 6$ to $Z = 54$. Later Stephenson⁷ has added further data for weaker energies. The agreement between theoretical and experimental cross sections is very satisfying in the medium energy range. For higher energies the hydrogen-like cross sections turn out to be somewhat too large, whereas the agreement between the measured cross sections and those of Storm and Israel is remarkably good as shown by Gerward and Thuesen⁸.

Experimental values of τ over a large enough frequency range will then allow the determination of f' by integrating equation (6). The additional term, which should appear at the right-hand side of equation (5) according to relativistic quantum mechanics, cannot be determined from photoelectric absorption measurements². It can only be determined by an experiment where the total real part of the atomic scattering factor is measured directly, for example by measuring the x-ray refractive index. However, very few accurate experiments of this kind have been performed⁹⁻¹⁵.

3.1. EXAFS

Absorption spectra from molecules, solutions and condensed matter show a modulation of the absorption coefficient above the absorption edges of the constituent atoms. This modulation is observed for several 100 eV above the edge and is called extended x-ray absorption fine-structure or EXAFS. The normalized EXAFS spectrum $\chi(k)$ is defined in terms of the x-ray absorption coefficient μ by

$$\chi(k) = (\mu - \mu_0)/\mu_0 \quad ; \quad k = (2m E/\hbar^2)^{\frac{1}{2}} \quad (8)$$

where μ_0 is the smoothly varying average absorption coefficient and E is the energy of the photoelectron, measured relative to the absorption edge.

The basic mechanism of the EXAFS is the interference between the outgoing photoelec-

tron wave from the x-ray absorbing atom and the backscattered waves from the surrounding atoms. Fourier analysis of the EXAFS data can locate the positions of the atoms surrounding the absorbing atom¹⁶⁻¹⁸. Since EXAFS measures the immediate environment of a given type of atom it does not require that the sample be single crystal or even crystalline. With the recent availability of x-ray synchrotron radiation, there has been a renewed interest in the use of EXAFS studies.

3.2. The Borrmann effect

According to the dynamical theory of diffraction a number of wavefields are produced in a perfect crystal set for Bragg diffraction. The effective absorption coefficient of a particular wavefield depends on the polarization state and the deviation from the exact Bragg condition. The absorption coefficient of the wavefield having minimum absorption is given by

$$\mu_{\min} = \mu(1 - \epsilon)/\cos \theta_B \quad (9)$$

where $\epsilon = |F''_{hkl}/F''_{000}|$ (centrosymmetric structure assumed) and θ_B is the Bragg angle. This phenomenon, known as the Borrmann effect, can be used for the imaging of lattice defects, such as dislocations.

The factor ϵ has been calculated by Wagenfeld⁴ using hydrogen-like photoeffect cross sections. In the case of perpendicular polarization one has

$$\epsilon^\perp = a \left[1 - 2(\tau^Q/\tau) \cdot \sin^2 \theta_B \right] \cdot \exp(-M) \quad (10)$$

where a is a geometrical factor, which equals unity when all atoms scatter in phase, and τ^Q the quadropole component of the photoeffect cross section.

4. Compton scattering

The basic theory of this effect, assuming the electron to be initially free and at rest, is that of Klein and Nishina¹⁹. Over most of the region in which Compton scattering is a major part of the total cross section, the Klein-Nishina theory is directly applicable. The electron binding effects are taken into account by writing the differential scattering cross section as

$$d\sigma_{\text{incoh}}/d\Omega = I(\vec{q}, Z) d\sigma^{\text{KN}}/d\Omega \quad (11)$$

where σ^{KN} is the Klein-Nishina cross section and $I(\vec{q}, Z)$ the incoherent scattering function. For large scattering vector $I(\vec{q}, Z)$ approaches Z (Fig. 2).

References to text-books dealing with one or more topics of the present review.

R.W. James, *The Optical Principles of the Diffraction of X-rays*, Bell, London 1950, Chap. I, III and IV.

B.E. Warren, *X-Ray Diffraction*, Addison-Wesley, Reading 1962, Chap. 1 and 11.

L.V. Azároff (Editor), *X-Ray Spectroscopy*, McGraw-Hill, New York 1974, Chap. 6.

L.V. Azároff (Editor), *X-Ray Diffraction*, McGraw-Hill, New York 1974, Chap. 1.

L.H. Schwartz and J.B. Cohen, *Diffraction from Materials*, Academic Press, New York 1977, Chap. 4.

References to recent tabulations of scattering factors, cross sections and attenuation coefficients.

International Tables for X-ray Crystallography Vol. III (1962); Vol. IV (1974), Kynoch Press, Birmingham.

J.H. Hubbell, Vm. J. Veigele, E.A. Briggs, R.T. Brown, D.T. Cromer and R.J. Howerton, *J. Phys. Chem. Ref. Data* 4, 471-538 (1975); erratum in 6, 615-616 (1977).

J.H. Hubbell and I. Øverbø, *J. Phys. Chem. Ref. Data* 8, 69-105 (1979).

References in the text.

1. D.T. Cromer and D. Liberman, *J. Chem. Phys.* 53, 1891 (1970).
2. L. Gerward, G. Thuesen, M. Stibius Jensen and I. Alstrup, *Acta Cryst. A* (in press).
3. E. Storm and H.I. Israel, *Nuclear Data Tables* A7, 565 (1970).
4. H. Wagenfeld, *Phys. Rev.* 144, 216 (1966).
5. G. Hildebrandt, J.D. Stephenson and H. Wagenfeld, *Z. Naturforsch.* 28a, 588 (1973).
6. G. Hildebrandt, J.D. Stephenson and H. Wagenfeld, *Z. Naturforsch.* 30a, 697 (1975).
7. J.D. Stephenson, *Z. Naturforsch.* 30a, 1133 (1975).
8. L. Gerward and G. Thuesen, *Z. Naturforsch.* 32a, 588 (1977).
9. C. Malgrange, E. Velu and A. Authier, *J. Appl. Cryst.* 1, 181 (1968).
10. U. Bonse and H. Hellkötter, *Z. Physik* 223, 345 (1969).
11. D.C. Creagh and M. Hart, *phys. stat. sol.* 37, 753 (1970).
12. U. Bonse and G. Materlik, *Z. Phys. B* 24, 189 (1976).
13. C. Cusatis and M. Hart, *Proc. R. Soc. Lond. A* 354, 291 (1977).
14. T. Takeda and N. Kato, *Acta Cryst. A* 34, 43 (1978).
15. T. Fukamachi and S. Hosoya, *Acta Cryst. A* 31, 215 (1975).
16. E.A. Stern, *Phys. Rev. B* 10, 3027 (1974).
17. F.W. Lytle, D.E. Sayers and E.A. Stern, *Phys. Rev. B* 11, 4825 (1975).
18. E.A. Stern, D.E. Sayers and F.W. Lytle, *Phys. Rev. B* 11, 4836 (1975).
19. O. Klein and Y. Nishina, *Z. Physik* 52, 853 (1929).