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A Method for Determining a Set of Experimental Spherically Symmetrical Form Factors from X-ray or Neutron-Diffraction Measurements

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A method is described for extracting a set of spherically symmetric form factors for the atoms in a structure, when a complete set of structure amplitudes for a single zone has been measured. The methods is applicable only when the atoms are resolved in projection. The calculation has been programmed for the digital computer EDSAC II.

Introduction

In recent years several workers have been using X-ray and neutron diffraction methods to determine form factors, appropriate to the scattering processes, for the atoms in crystalline solids; see for instance Weiss & De Marco (1958), Batterman (1959), Alperin (1961), Pickart & Nathans (1961), Alperin, Brown & Nathans (1963). The concept of an atomic form factor or atomic scattering factor is useful to describe the major variations of scattering power with angle; it provides a convenient basis for comparing theoretical calculations with experimental measurements and for assessing changes of scattering by similar atoms in different structures. It must however be realized that there is a severe limitation in applying the concept of an atomic scattering factor to the atoms of a solid, since to do so one must be able to decide to which atom each of the electrons of the solid belongs. Thus no unique description of a solid by means of atomic or magnetic form factors exists, and each of the many descriptions that are possible corresponds to a different apportionment of the electrons between atoms. One of the features of the method of deriving form factors which is described here is that the electrons are allocated amongst the various atoms of the crystal explicitly, by defining the boundary of each atom. This contrasts with the rather uncertain allocation of electrons which results when the form factors are computed, as they can be for simple structures, from simple combinations of the structure factors. This paper then suggests a method for extracting a set of spherically symmetrical form factors from measurements of a single zone of reflexions, which can be used successfully provided that the atoms do not overlap to any great extent in the projection, and that the set of measurements is complete to at least as high a value of $\sin\theta/\lambda$ as that to which the form factor is required.

Outline of the method

It is a well known and well used fact that the values of the scattering amplitudes for a complete zone of reflexions will give, on Fourier inversion, a map of the density of scattering matter in the unit cell projected down the zone axis. This density map, it must be emphasized, represents all the information that it is possible to obtain from the measurements. Any further analysis such as the present one can add nothing to this information although it may be of value in interpreting it. In order to derive spherically symmetric form factors from such a map one must first define the boundary of each atom. In this method it is assumed that all the electrons belonging to each atom in the projection lie inside a set of non-overlapping circles centred on the centres of the atoms. The equation for the electron density of a centrosymmetric structure is given by

$$\varrho(R)=\frac{1}{A}\sum_{\mathbf{K}}F(\mathbf{K})\,[\cos 2\pi(\mathbf{Q}.\mathbf{K}) +i\sin 2\pi(\mathbf{Q}.\mathbf{K})]\exp(2\pi i\mathbf{R}.\mathbf{K})$$

where $\mathbf{R}$ is the radius vector from the centre of an atom, vector distance $\mathbf{Q}$ from a centre of symmetry; the $F(\mathbf{K})$ are the structure factors referred to that centre as origin, corresponding to reflexions having reciprocal lattice vectors $\mathbf{d}^*=\mathbf{K}$, and A is the area of the unit cell in projection.

Then the total electron density projected into an elementary ring of radius R about the atomic centre is

$$P(R)\,dR=\frac{1}{A}\sum_{\mathbf{K}}F(\mathbf{K})\cos 2\pi(\mathbf{Q}.\mathbf{K}) \times\int_0^{2\pi}\exp(2\pi iRK\cos\theta)R\,dR\,d\theta$$

as all the terms in $F(\mathbf{K})\sin 2\pi\,(\mathbf{Q}.\mathbf{K})$ vanish on summation. Hence

$$P(R)\,dR=\frac{1}{A}\sum_{\mathbf{K}}F(\mathbf{K})\cos 2\pi(\mathbf{Q}.\mathbf{K})\,2\pi J_0\{R|K|\}R\,dR\,.$$

Now the atomic scattering factor is derived from the spherical charge density $U(r)$ by the relation

$$f(S)=\int_{r=0}^{\infty}\int_{\theta=0}^{2\pi}\int_{\varphi=\frac{1}{2}(-\pi)}^{\frac{1}{2}\pi} U(r)\exp(4\pi iSr\cos\theta)\times r^2\,dr\,d\theta\sin\varphi\,d\varphi$$

where $S=\sin\theta/\lambda$.

This integral can be made to depend on $P(R)dR$ by changing to cylindrical coordinates so that

$$f(S)=\int_{R=0}^{\infty}\int_{\theta=0}^{2\pi}\frac{P(R)}{2\pi}\exp(4\pi iSR\cos\theta)\,dR\,d\theta\,.$$

Substituting for $P(R)$ and integrating with the assumption that $P(R)$ is zero outside radius R_0 this yields

$$f(S)=\frac{1}{A}\sum_{\mathbf{K}}F(\mathbf{K})\cos 2\pi(\mathbf{Q}.\mathbf{K})\frac{2\pi R_0}{(4S^2-K^2)}\times[2SJ_0(2\pi KR_0)J_1(4\pi SR_0)-KJ_0(4\pi SR_0)J_1(2\pi KR_0)]$$

from which $f(S)$ can be calculated without explicit calculation of a density distribution. The expression for the form factor for a non-centrosymmetric structure is exactly similar except that $F(\mathbf{K})\cos 2\pi(\mathbf{Q}.\mathbf{K})$ is replaced by $A(\mathbf{K})\cos 2\pi(\mathbf{Q}.\mathbf{K})-B(\mathbf{K})\sin 2\pi(\mathbf{Q}.\mathbf{K})$ where $A(\mathbf{K})$ and $B(\mathbf{K})$ are the real and imaginary parts of the structure factor.

Numerical calculation of the form factor

The calculation of $F(S)$ has been programmed for the digital computer EDSAC II in Cambridge. The sum is computed term by term and one special case has to be considered. This occurs when $(4S^2-K^2)=0$, in which case the term to be added to the sum is

$$(1/A)F(\mathbf{K})\cos 2\pi(\mathbf{Q}.\mathbf{K})\pi R_0\{J_0^2(KR_0)+J_1^2(KR_0)\}$$

and the program includes an appropriate test for this contingency.

There are three major possible sources of error in the method, apart from experimental error. These are, firstly errors caused by atoms overlapping in projection, secondly (and intimately connected with the first) effects which arise when the electron density belonging to an atom is not all enclosed within the radius R_0, and lastly series termination errors.

Overlap errors

In order to get some idea of the radii at which overlap will become serious for d electron wave functions a set of structure factors was calculated for an imaginary structure containing iron atoms with one $3d$ electron having the distribution calculated by Freeman & Watson (1961) and with their centres at the points of a cubic lattice of side 3 Å. The value of $f(0)$ for this electron, which gives the fraction of one electron inside the radius R_0, was calculated for a range of values of R_0 up to 1·5 Å; this is illustrated in Fig. 1 and it can be seen that there is no significant increase in the number of electrons enclosed after 1·15 Å. One may conclude that if the atomic centres are further apart than 2·3 Å overlap effects will be negligible.

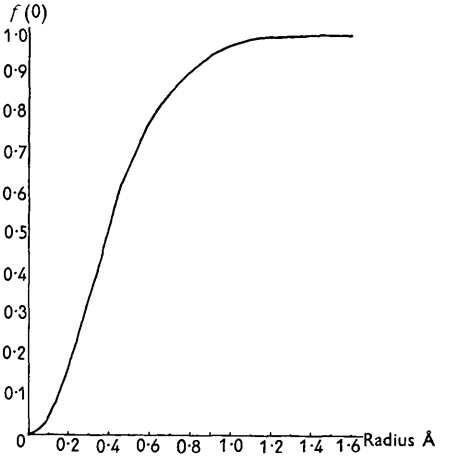

Fig. 1. Normalized $f(0)$ against radius for the iron $3d$ form factor as calculated by Freeman & Watson (1961).

The errors caused by overlap are plotted as a function of $\sin\theta/\lambda$ in Fig. 2, which is a graph of the difference between the form factor derived from the program and that from which the structure factors were calculated, for the same imaginary structure but for three different cell sides 3·5, 2 and 1·6 Å; in each case the value of R_0 taken was one half of the cell side. In all three cases the error is oscillatory, although for the 3·5 Å cell it does not amount anywhere to more than 1/100 of one electron. It can be seen that the maximum error does not necessarily occur at $S=0$.

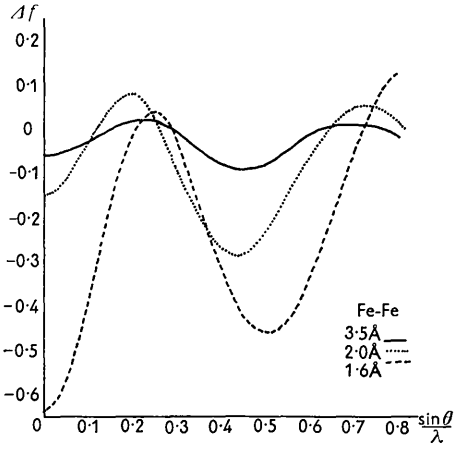

Fig. 2. The overlap error as a function of $\sin\theta/\lambda$ for the iron $3d$ form factor for three values of the interatomic distance.

The effect of temperature vibration on the degree of overlap has not been considered in the example given, since the temperature factor is normally

eliminated in measurements of magnetic scattering amplitudes made with polarized neutrons, or in measurements with unpolarized neutrons in which the data have been put on an absolute scale by comparison with the nuclear intensities. If the temperature factor can not be reliably eliminated it will, of course, increase the amount of overlap, and decrease the importance of the series termination effects discussed in the next section.

Series termination errors

The effects of series termination errors were examined for the X-ray scattering factor for technetium, as this is a case for which they would be important

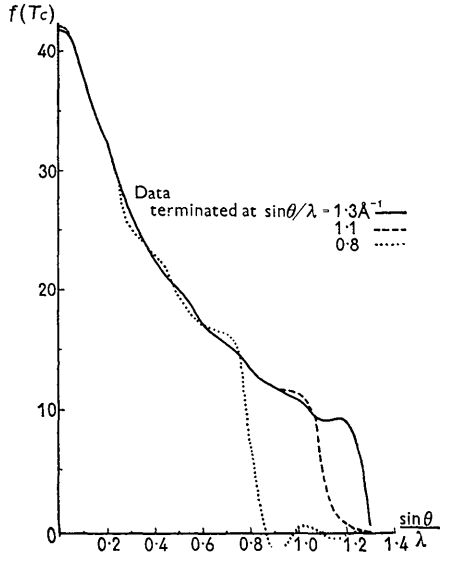

Fig. 3. The effect of series termination on the X-ray scattering factor of technetium.

at the limits of experimental data. Fig. 3 shows the effects of terminating the data at $\sin\theta/\lambda = 0{\cdot}8$, 1·1 and 1·3 Å^{-1}. If these curves are compared with the form factor which was used to make the calculations it can be seen that for termination at 1·1 and 1·3 Å^{-1} series termination effects do not become important until 0·9 and 1·1 Å^{-1} respectively, but for the data terminated at 0·8 Å^{-1} an appreciable error is introduced even at $S=0$.

Conclusion

In conclusion it may be said that this method of extracting form factors can be used successfully for 3*d* electrons if the atoms are more than 2 Å apart in the projection used. For other form factors suitable criteria for resolution must be developed. Series termination errors will not be important at angles well below the angle of cut-off if the value of the form factor at the cut-off is less than about 0·3. The major limitation of the method is likely to arise because the atoms are not resolved in projection, in which case recourse can be made to three-dimensional data to which a similar process can be applied.

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