Neither space group is a subgroup of the other, however, both are subgroups of $Pm3m - O_\gamma$, which is also the space group of $BaTiO_3$ at high temperature. Thus the relevant group-subgroup relationships are $Pm3m \rightarrow R3m$ and $Pm3m \rightarrow Amm2$. Both, $R3m$ and $Amm2$ are translationengleiche (though not maximal) subgroups of $Pm3m$ and therefore only twin domains and no antiphase domains are allowed in the $R3m$ and $Amm2$ forms of $BaTiO_3$.

References


Analytic Approximations for the Incoherent X-ray and Electron Intensities of Light Atoms and Ions

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It has been found that the incoherent scattered X-ray and electron intensities of light atoms, with 2 to 18 electrons, and of light ions, with 2 to 28 electrons, can be accurately approximated by an analytical formula containing six parameters.

The incoherent intensities of the first 36 atoms calculated by Tavard, Nicolas & Rouault (1967) have been fitted analytically by Hajdu (1971, 1972), those of the atoms of higher atomic numbers (from Ca to Am) were approximated by Pálinkás (1973) with the numerical values of Cromer (1967, 1969).

In these works, the validity of the approximations had been tested in the scattering-variable range available for X-ray diffraction, $0 \leq s = \sin \theta / \lambda \leq 1.5 \text{ Å}^{-1}$.

In the present paper, a new analytical expression with six parameters is proposed for similar purposes. Its applicability is demonstrated in two somewhat different domains:

(1) for light atoms of atomic numbers 2 to 18 over a wide range of the scattering variable: $0 \leq s \leq 4.0 \text{ Å}^{-1}$,

(2) for all the ions ($2 \leq Z \leq 30$) for which numerical incoherent-intensity tables were available. The scattering-variable range of these published tables extends to $s = 1.1 \text{ Å}^{-1}$, so the fit could not be checked beyond this limit in the case of the ions.

We endeavoured to find an approximating formula with good analytic behaviour. By the use of such a function, physical quantities determined by the incoherent scattering function, e.g. the exchange energy, and the contribution to the electron-electron correlation function (Bartell & Gavin, 1964), can also be expressed analytically.

We have found that an expression meeting these conditions and yielding a good approximation can be composed of terms similar to the function describing
the incoherent scattering of the hydrogen atom:

\[ I_I(S)/I_T \equiv S(S) = N \left[ 1 - \sum_{i=1}^{3} \frac{\gamma_i}{(1 + \lambda_i s^2)^n} \right] \]  

(1)

where \( I_I(S) \) is the X-ray incoherent intensity, \( I_T \) is the Thomson formula, \( N \) is the number of electrons of the atom or the ion, \( \gamma_i \) and \( \lambda_i \) are independent parameters, and the power \( n \) of the denominator is 4 in the case of atoms and ions with \( 2 < Z \leq 20 \), and \( n = 1 \) for the ions with \( 21 < Z \leq 29 \).

The parameters \( \gamma_i \) and \( \lambda_i \) have been determined by a least-squares program, fitting the formula to the tabulated numerical intensities, i.e. the expression

\[ \sum_{i=1}^{M} \delta_i^2 = \sum_{i=1}^{M} [S_{\text{fit}}(s_i) - S_{\text{tab}}(s_i)]^2 \]

was minimized where \( i \) refers to the discrete \( \sin \theta/\lambda \) points and \( M \) is the number of tabulated values.

The goodness of the fits is characterized in our tables by the percentage error defined as

\[ \varepsilon = 100 \frac{\sqrt{\sum_{i=1}^{M} \delta_i^2}}{S(s_M)} / (M-1). \]  

(2)

Since the incoherent scattered electron intensities can be expressed – within the validity range of the first Born approximation – in terms of the corresponding X-ray intensity function (Morse, 1932), incoherent scattered electron intensities can also be expressed from (1) as

\[ I_I = \frac{4}{a_0^6} \frac{S(s)}{(4\pi s)^4} \]  

(3)

where \( a_0 \) is the Bohr radius.

**Light neutral atoms with atomic number 2 to 18**

Incoherent scattering functions of the atoms have been determined by Cromer (1967, 1969), based on the Waller–Hartree theory with the use of the numerical HF SCF wave functions of Mann (1967). On the basis of Cromer’s tables we have obtained a good analytic fit for the atoms with 2 to 18 electrons by applying equation (1) with \( n=4 \). Table 1 contains the parameter values and the errors.

The exchange energies determined by the expression (5), and the corresponding HF SCF values (Kim & Gordon, 1974) are compared for a few atoms in Table 2.

**Ions with atomic numbers 3 to 30**

It has been found that better fits could be attained by separating the ions in two groups for which power \( n \) in (1) was fixed differently. For the ions with \( 2 < Z \leq 20 \), \( n=4 \), for those with \( 21 < Z \leq 29 \), \( n=1 \) proved to be optimal.

Numerical values of the incoherent intensities of ions with \( 2 < Z \leq 20 \) have been taken from the International Tables for X-ray Crystallography (1962) and those for \( Z > 20 \) from the paper of Freeman & Watson (1961).

Tables 3 and 4 show the best parameters found for the two groups of ions and the percentage errors of the fits. The exchange energies as calculated from the analytic expression, contain a certain error especially in the case of heavy ions, probably because the fit is poorer in the range above \( s > 1.1 \text{ Å}^{-1} \).
Table 3. Parameters (×10^4) of the analytic fits of S(s) for ions with atomic numbers 3 to 20

<table>
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<tr>
<th>N</th>
<th>γ₁</th>
<th>γ₂</th>
<th>λ₁</th>
<th>λ₂</th>
<th>λ₃</th>
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Note: Table 4 has been published on the analytic approximation for the incoherent scattering function of atoms (Smith, Thakkar & Chapman, 1975; Balyuzi, 1975). The merit of the first one is to give an analytic formula of correct asymptotic behaviour, approximating the incoherent scattering functions of atoms over a wide s range. It is easy to show, that our analytic expression (1) has also a correct asymptotic behaviour at both high and low values of s. It can be verified, by comparing the corresponding percentage errors (ε) pertaining to atoms common in both papers, that the present approximation is a better fit. The approximating formula, however, referred to in the second paper is valid only up to s=1.5, and its asymptotic behaviour is not correct. Standard deviations given by the author have to be treated with criticism because they relate to the function Z - Iₙ(s) instead of the incoherent intensities themselves. Having converted them to the suitable form, we could establish that the percentage errors (ε) in the range 0<s≤1.5 were similar to ours.

References


Discussion

We have given an expression of good analytic behaviour for the approximation of incoherent X-ray and electron intensities of light atoms and ions. For the first 18 atoms this approximation is more accurate than the previous ones, and fits the numerical values uniformly over a wide range of the scattering variable.

For the ions, accurate approximations of the incoherent X-ray intensities have not been published up to the present. The present work is primarily intended for use in X-ray and electron diffraction studies on ionic solutions.

In both cases the mean errors are of the same order of magnitude, or even smaller than those of the fits of the corresponding coherent intensities.