

Expanding the square and replacing $\exp(i\alpha_T)$ and $\exp(i\alpha'_T)$ by their expectation values, as in (5), one gets

$$F_o F'_o m m' \{ \exp [i(\alpha_B + \alpha'_B)] - \exp [i(\alpha_B + \alpha_B)] \\ - \exp [i(\alpha_B + \alpha'_B)] + \exp [i(\alpha_B + \alpha_B)] \} = 0. \quad (13)$$

Terms involving complex conjugates give the same result. Thus, (10) represents the final expression for $\sigma^2(\mathbf{x})$ in space group $P1$.

Other space groups

One can calculate $\sigma^2(\mathbf{x})$ for other space groups by a procedure similar to that used above. The main difference is that in (3), where Friedel mates are collected for space group $P1$, all symmetry mates have to be collected within the brackets, since they constitute the set of non-independent observations. A program that takes specific account of the space group is thus required. As a simple example, consider the space group $P2$. To make the notation more compact we introduce

$$\mathbf{W}_{\mathbf{h},\mathbf{x}} = \exp(2\pi i \mathbf{h} \cdot \mathbf{x}), \quad \Delta \mathbf{F} = \mathbf{F}_T - \mathbf{F}_B,$$

$\mathbf{h}' =$ symmetry mate of $\mathbf{h} = (-h, k, -l)$.

$$\Delta \rho^2 = (1/V^2) \left\{ \sum_{\text{sphere}} \Delta \mathbf{F} \cdot \mathbf{W}_{-\mathbf{h},\mathbf{x}} + \Delta \mathbf{F}^* \cdot \mathbf{W}_{\mathbf{h},\mathbf{x}} \right. \\ \left. + \Delta \mathbf{F}' \cdot \mathbf{W}_{-\mathbf{h}',\mathbf{x}} + \Delta \mathbf{F}'^* \cdot \mathbf{W}_{\mathbf{h}',\mathbf{x}} \right\} \\ \times (1/V^2) \left\{ \sum_{\text{sphere}} \Delta \mathbf{F} \cdot \mathbf{W}_{-\mathbf{k},\mathbf{x}} + \Delta \mathbf{F}^* \cdot \mathbf{W}_{\mathbf{k},\mathbf{x}} \right. \\ \left. + \Delta \mathbf{F}' \cdot \mathbf{W}_{-\mathbf{k}',\mathbf{x}} + \Delta \mathbf{F}'^* \cdot \mathbf{W}_{\mathbf{k}',\mathbf{x}} \right\}. \quad (14)$$

As before, consider only terms for which $\mathbf{k} = \mathbf{h}$. The general term is

$$\Delta \mathbf{F}^2 \cdot \mathbf{W}_{-2\mathbf{h},\mathbf{x}} + \Delta \mathbf{F}^{*2} \cdot \mathbf{W}_{2\mathbf{h},\mathbf{x}} + \Delta \mathbf{F}'^2 \cdot \mathbf{W}_{-2\mathbf{h}',\mathbf{x}} + \Delta \mathbf{F}'^{*2} \cdot \mathbf{W}_{2\mathbf{h}',\mathbf{x}} \\ + 2|\Delta \mathbf{F}|^2 + 2|\Delta \mathbf{F}'|^2 + 2\Delta \mathbf{F} \cdot \Delta \mathbf{F}' \mathbf{W}_{-\mathbf{h}-\mathbf{h}',\mathbf{x}} \\ + 2\Delta \mathbf{F} \cdot \Delta \mathbf{F}'^* \mathbf{W}_{-\mathbf{h}+\mathbf{h}',\mathbf{x}} + 2\Delta \mathbf{F}^* \cdot \Delta \mathbf{F}' \mathbf{W}_{\mathbf{h}-\mathbf{h}',\mathbf{x}} \\ + 2\Delta \mathbf{F}^* \cdot \Delta \mathbf{F}'^* \mathbf{W}_{\mathbf{h}+\mathbf{h}',\mathbf{x}}. \quad (15)$$

The first six terms represent twin sets of terms just like those in the $P1$ equation - one for each asymmetric unit. The remainder involves cross terms between the asymmetric units. Symmetry operations do not change the phase in $P2$. Setting $F_o = |\mathbf{F}_T|$ as before, and using (6)

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Improved values of the forward X-ray scattering factor for metallic aluminium. By J. H. BARKYOUMB and D. Y. SMITH, *Department of Physics, University of Vermont, Burlington, Vermont 05405, USA*

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Abstract

The real and imaginary parts of the forward X-ray scattering factor of metallic aluminium are reported for photon

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and (7), we have

$$\sigma^2(\mathbf{x}) = (1/V^2) \sum_{\text{all } \mathbf{h}} F_o^2 [1 - m(\mathbf{h})^2] \\ + (1/V^2) \sum_{\text{all } \mathbf{h}} F_o^2 \{ m_2(\mathbf{h}) \exp [i\alpha_2(\mathbf{h})] \\ - m(\mathbf{h})^2 \exp [2i\alpha_B(\mathbf{h})] \} \exp (-4\pi \mathbf{h} \cdot \mathbf{x}) \\ + (1/V^2) \sum_{\text{all } \mathbf{h}} F_o^2 \{ m_2(\mathbf{h}) \exp [i\alpha_2(\mathbf{h})] \\ - m(\mathbf{h})^2 \exp [2i\alpha_B(\mathbf{h})] \} \exp [-2\pi(\mathbf{h} + \mathbf{h}') \cdot \mathbf{x}] \\ + (1/V^2) \sum_{\text{all } \mathbf{h}} F_o^2 \{ m_2(\mathbf{h}) \exp [i\alpha_2(\mathbf{h})] \\ - m(\mathbf{h})^2 \exp [2i\alpha_B(\mathbf{h})] \} \exp [-2\pi(\mathbf{h} - \mathbf{h}') \cdot \mathbf{x}]. \quad (16)$$

Crystal and Friedel symmetries have been used to re-expand the summation limits to a full sphere. For high-symmetry space groups the formula for $\sigma^2(\mathbf{x})$ will clearly contain many terms. However, the calculation is easily compressed and fully tractable.

Discussion

As yet little direct experience has been gained with the error function. However, a number of uses come readily to mind. High- and low-quality regions of electron-density maps may be distinguishable, giving guidance about chain tracing through difficult regions. In the case of non-crystallographic averaging, the factor $1/\sigma^2(\mathbf{x})$ provides the correct weight for each point in the average. Hitherto, unit weights have been used. For a set of points related by non-crystallographic symmetry, substantial disagreement between the $\sigma^2(\mathbf{x})$ values and the actual variance of the average could serve as a warning about a possibly misplaced symmetry operator. More speculatively, combining the Fourier transforms of the modified density and the concomitantly modified $\sigma^2(\mathbf{x})$ could allow one to phase the probability density function used in generating the coefficients for the map in the next cycle.

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energies from 10 to 10^4 eV. The imaginary part of the scattering factor $f_2(\omega)$ was derived from the absorption database of Shiles, Sasaki, Inokuti & Smith [*Phys. Rev. B* (1980). **22**, 1612-1628] with the addition of solid-state struc-

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ture near the K edge. The real part of the scattering factor $f_1(\omega)$ was determined by a self-consistent dispersion (Kramers-Kronig) analysis. This analysis predicts a substantially smaller value for f_1 at the K -edge minimum than do previous studies. It also predicts that the strong anomalous dispersion associated with the $L_{II,III}$ edge drives $f_1(\omega)$ negative between 68 and 93 eV.

We have determined the real and imaginary parts of the forward X-ray scattering factor for metallic aluminium at room temperature for energies from the infrared to 10^4 eV. Our absorption database was obtained by incorporating fine structure near the K edge of crystalline aluminium as reported by Kiyono, Chiba, Hayasi, Kato & Mochimaru (1978) into the composite optical absorption covering infrared to X-rays developed by Shiles, Sasaki, Inokuti & Smith (1980). A self-consistent dispersion analysis was performed on the resulting composite absorption spectrum to obtain (Barkyoub & Smith, 1990) the refractive index and complex dielectric constant $\hat{\epsilon} = \epsilon_1 + i\epsilon_2$. The real and imaginary parts of the forward X-ray scattering factor f_1 and f_2 , respectively, were then obtained from ϵ_1 and ϵ_2 using the optical theorem (Jackson, 1975). Consistency of the measured spectrum with general theory was checked by applying the f sum rule to the composite absorption and by using partial oscillator strength sums to compare the absorption of individual shells with the known electronic occupation (Shiles, Sasaki, Inokuti & Smith, 1980; Smith & Shiles, 1978).

Fig. 1 shows $f_1(\omega)$ and $f_2(\omega)$ for photon energies from 10 to 10^4 eV. Note that the analysis predicts $f_1(\omega)$ to be negative in the vicinity of the $L_{II,III}$ edge between 68 and 93 eV. This is a result of the strong anomalous dispersion at the $L_{II,III}$ edge combined with the relatively small contribution of valence and conduction electrons to the total scattering at these photon energies. The minimum value of f_1 at the $L_{II,III}$ edge obtained from the present analysis is -4.4 at 72.7 eV.

At the K edge, we obtained a minimum of $+1.9$ for f_1 (Fig. 1) compared to the value of $+4.3$ at 1560 eV determined from the Shiles database (Shiles, Sasaki, Inokuti & Smith, 1980). This is a consequence of including the near-

edge structure in the absorption spectrum for metallic aluminium in the present study. This structure in the K -edge absorption has several effects on $f_1(\omega)$. The well known EXAFS oscillations produce corresponding oscillations in $f_1(\omega)$ from the K edge to approximately 200 eV above the edge. The large difference in $f_1(\omega)$ at the K -edge minimum is due to the large 'white-line-like' absorption at the core-hole excitation threshold (Fig. 2). This resonance, which has been observed previously (Deslattes, 1969), is almost certainly due to a transition from the K shell to one or more localized final states. This phenomenon is discussed further in other publications (Barkyoub & Smith, 1990; Bradley, Wroge, Dozier & Gibbons, 1985).

The variation of the total forward scattering $|f|^2 = f_1^2 + f_2^2$ as a function of photon energy is shown in Fig. 3. The minimum in the total scattering below the $L_{II,III}$ edge occurs when $f_1(\omega) \approx 0$ and $f_2(\omega)$ is small. This minimum in $|f|^2$ is 0.18 at 67.0 eV. The minimum in the total scattering at the K edge is 6.0 at 1560 eV. These values are to be compared

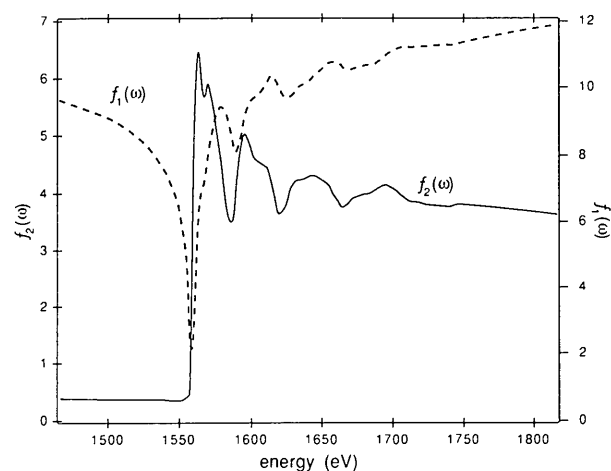


Fig. 2. $f_2(\omega)$ (solid line) and $f_1(\omega)$ (dashed line) at the aluminium K edge.

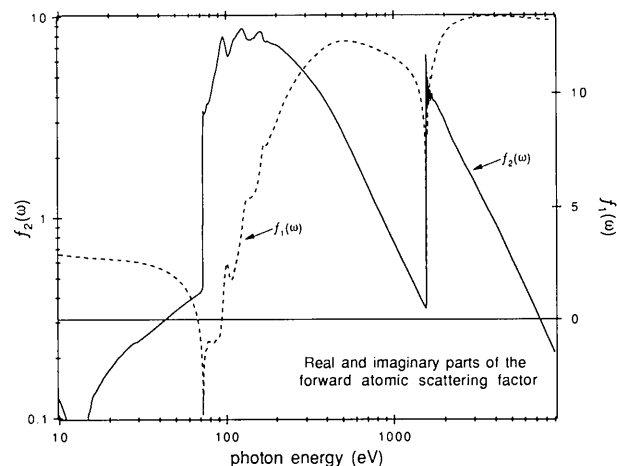


Fig. 1. The real (dashed line) and imaginary (solid line) parts of the forward atomic scattering factor of metallic aluminium.

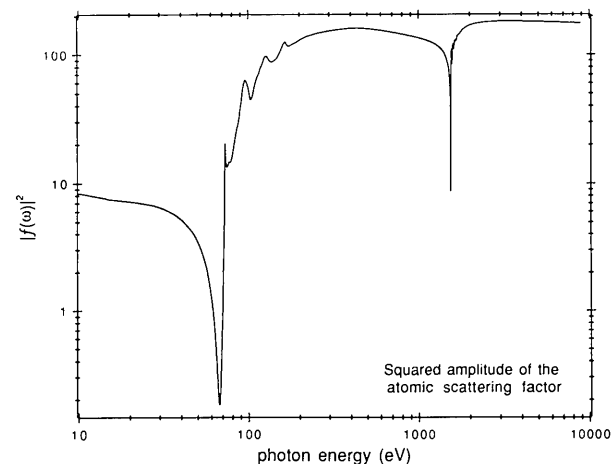


Fig. 3. The square of the amplitude of the forward atomic scattering factor of metallic aluminium, $f^2(\omega) = f_1^2(\omega) + f_2^2(\omega)$, as a function of energy.

with the square of the Thomson value, Z^2 , where Z is the atomic number. Apart from small relativistic corrections (Smith, 1986, 1987; Wang, 1986), this is the limit of $|f|$ at high frequencies and equals 169 for aluminium.

For spectral regions far from absorption edges, the present results for f_1 agree well with theoretical predictions. For example, at the Cu $K\alpha$ line, our value of f_1 differs from that reported by Cromer & Liberman (1970) and by Waseda (1984) by no more than 0.5%. However, in regions of anomalous dispersion near absorption edges, these and other analyses (Henke, Lee, Tanaka, Shimabukuro & Fujiikawa, 1981) that do not explicitly include edge structure yield values of the atomic scattering factor which differ substantially from ours.

A tabulation of the real and imaginary parts of the scattering factor for aluminium along with its square amplitude is available from the authors. This tabulation has also been deposited with the AIP Auxiliary Publication Service.*

* See American Institute of Physics document PAPS PLRAA-41-4863-07 of scattering factors and their square amplitude for aluminium. Order from American Institute of Physics, Physics Auxiliary Publication Service, 335E. 45 St, New York, NY 10017, USA, by giving PAPS number and citing Barkyoumb & Smith (1990). This material also appears in the monthly *Current Physics Microform* edition of *Phys. Rev. A* (1990), **41**, 4863.

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