If the unknown is more properly indexed as 642, then the ratio is

$$\frac{[hk+kl+lh]-[hk-kl-lh]}{[hk-kl-lh]-[hl-kl-kh]} = 1.66,$$

whereas if it is more properly 642, the ratio equals 1.25.

Values of 'a' were then calculated, using the average 'a' value by extrapolation against the Nelson-Riley factor with results as shown in Table 1. The theoretical density over the range of compositions varies only between 6.91 and 6.92; the measured values using the density bottle method gave values as shown in the Table.

From these results, it appears that 'a' and 'a' adjust themselves to give an almost invariant unit-cell volume. These results agree fairly well with those of Hagg & Hybinette shown in the Table.

The values found by Bowen & Morris-Jones (1931), also shown in the Table, are those obtained after conversion of kX units to Angströms, and are based on the assumption, also made by many others, that the unit cell is cubic, which is incorrect.

It would appear at first sight that the lattice parameter changes are so slight that for the whole range of compositions studied the movement of an atom from a position in the inhomogeneous ingot to its equilibrium position would have such a small effect on the X-ray diffraction lines as to be impossible to see. The largest reorganization is obviously the unit-cell angle and it is the range of these in the as cast ingot which blur the diffraction lines.

Extracted cuboids from a 14%Sb alloy quenched from the melt showed no well-defined high angle lines until they had been annealed for 200 hours at 250°C. The X-ray pattern then obtained showed lines corresponding to those for the alloy of composition approximately 42%Sb as expected from the phase diagram, but with associated rather diffuse haloes indicating shells of slightly different structure presumably on the cuboid surfaces.

It is interesting here to compare this compound with another intermetallic compound which occurs over a range of composition, namely electroplated NiSn. This shows a large change in density over the range of composition (Dutta & Clarke, 1968), in this case perhaps due to a capability to trap extra atoms in the basic nickel arsenide lattice. The basic antimony/tin structure is that of sodium chloride, which does not allow this, and it must be the fact that tin and antimony are neighbouring atoms in the Periodic Table which permits the compound to form.

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References


Tests of a Hankel Transform Method of Determining Electron Densities of Long Cylinders from Small-Angle X-ray Scattering Data*

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The Hankel transform method proposed by Fedorov & Aleshin (1966; Vysokomol. Soed. 8, 1506; English translation, 1967: Polymer Science USSR 8, 1657) for calculating the electron density of long cylindrical particles with circular cross section is tested with theoretical intensity functions for which the density can be found both by an exact calculation and by numerical integration. (In this method, the density is assumed to depend only on the distance from the cylinder axis.) The tests show how the degree of resolution obtained in the density curve is related to the largest scattering angle at which data are available. For the step function density corresponding to a cylinder with uniform electron density, the requirements are more severe than for continuously decreasing density functions. The possibility of obtaining useful results with the available scattering data from two biological macromolecules is discussed.

Fedorov & Aleshin (1966) have described a Hankel transform method which can be used with small angle X-ray scattering data to calculate the electron density of long cylindrical particles for which the cross section is circular and the density depends only on the distance from the cylinder axis. This method assumes that scattering data are available at all scattering angles. However, since data cannot be obtained at arbitrarily large

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scattering angles, the numerical evaluation of the transforms cannot be carried out with arbitrarily high accuracy. The limited extent of the data can often introduce errors in Fourier transforms used in analysis of the large-angle X-ray scattering data from liquids. Therefore, we felt that it would be of interest to investigate the analogous small-angle X-ray scattering Hankel transform calculation proposed by Fedorov & Aleshin, to see whether appreciable errors might sometimes result from the restriction of the angular range over which the integral transform was evaluated.

The particles are assumed to be identical and randomly oriented in a suspension which is so dilute that interparticle interactions do not affect the observed scattering. By hypothesis, the rods are long enough for the intensity to be inversely proportional to the scattering angle \( \theta \) at the smallest scattering angles for which data are available, and the electron density \( \varrho(r) \) of the rods depends only on the distance \( r \) from the axis of the rod. Then* (Fedorov & Aleshin, 1966, equation 12)

\[
\varrho(r) = (\varrho_0)^{-1} \int_0^\infty dh \frac{h^{3/2}I(h)}{\left[1 + h^2R^2\right]^{3/2}} J_0(hr)
\]

(1)

where \( I(h) \) is the scattered intensity, \( h = 4\pi\lambda^{-1} \sin(\theta/2) \), \( \theta \) is the scattering angle, \( \lambda \) is the X-ray wavelength, \( J_0(x) \) is the zero-order Bessel function of the first kind, and

\[
\varrho_0 = \int_0^\infty \frac{h^{3/2}I(h)}{\left[1 + h^2R^2\right]^{3/2}} dh.
\]

To test the effects of approximating the integral in (1) by an integral with a finite upper limit, we used three theoretical intensity functions for which the infinite integral (1) could be evaluated exactly to give simple density functions \( \varrho(r) \). The density was also calculated by evaluating (1) numerically with a computer, using different finite upper limits on the integral. The errors in the numerical calculations were determined by comparing the results with the exact calculation.

For the theoretical intensity functions,

\[
I_1(hR) = 4(hR)^{-3} \left[J_1(hr)\right]^2,
I_2(hR) = (hR)^{-1} \left[1 + h^2R^2\right]^{-3},
I_3(hR) = (hR)^{-1} \exp\left(-h^2R^2/2\right),
\]

the respective density functions calculated from (1) are (Magnus & Oberhettinger, 1954):

\[
\begin{align*}
\varrho_1(r/R) &= 1, & 0 < r/R < 1, \\
\varrho_2(r/R) &= \frac{1}{2}, & r/R = 1, \\
\varrho_3(r/R) &= 0, & 1 < r/R, \\
\varrho_4(r/R) &= \exp\left(-r/R\right), & \\
\varrho_5(r/R) &= \exp\left(-r^2/R^2\right).
\end{align*}
\]

The parameter \( R \) determines the effective particle radius—that is, the magnitude of the \( r \) values for which the density is appreciably different from zero.

* Our equation (1) is obtained by multiplying equation (12) of Fedorov & Aleshin by a constant, after the latter equation has been corrected for a minor typographical error.

The calculations were done on a CDC 3600 computer at the University of Wisconsin Computer Center. In the numerical evaluation of the integral in (1), we used the trapezoidal rule, with different upper limits. In the integration, the increment \( \Delta h \) was equal to 0.005 or 0.010 \( \text{Å}^{-1} \). The exact value of the normalization constant, \( \varrho_0 \), was used in all calculations, regardless of the value of \( x_m \).

Fig. 1 shows density functions, \( \varrho_i(r/R) \) calculated with four different upper limits, \( h_m \), for the integral in (1). The quantity

\[
x_m = h_m R.
\]

is used to express the upper limits. Only the curve for \( x_m = 15 \) is a reasonable approximation to the exact density \( \varrho_i(r/R) \), which is a step function. Calculations were also made for several \( x_m \) values between 15 and 50. As expected, the \( \varrho_i(r/R) \) curves approached the exact step function more closely as \( x_m \) increased. The calculations of \( \varrho_i(r/R) \) indicate that (1) is useful for finding densities for cylinders with uniform electron density and radius \( R \) only when data are available at angles large enough that \( h_m R \geq 15 \).

As the curves in Fig. 2 indicate, good agreement with the exact density function can be obtained with smaller \( x_m \) values for \( I_3(hR) \) than for \( I_1(hR) \). For example, for \( r/R > 0.3 \), the curve for \( x_m = 5 \) is in reasonable agreement with the exact curve. When \( x_m = 10 \), errors are negligible except for \( r/R < 0.1 \). Therefore, the curve for \( x_m = 10 \) is not drawn for Fig. 2.

The curves for \( I_3(hR) \), which are summarized in

Fig. 1. The exact density function \( \varrho_i(r/R) \) (solid line), with corresponding curves calculated from (1) for \( x_m \) equal to 5 (crosses), 8 (squares), 10 (circles), and 15 (triangles).
Fig. 3, agree well with the exact density for even smaller $x_m$ values than were necessary for $I_2(hR)$. Within the accuracy with which Fig. 3 is plotted, the results for $x_m \geq 5$ coincided with the exact density function at all points at which calculations were made.

Comparison of $\rho_2(r/R)$ with $\rho_2(r/R)$ and $\rho_3(r/R)$ shows that $x_m$ must be considerably larger to resolve the discontinuous drop in $\rho(r/R)$ than is necessary to give density curves which agree well with the continuously varying exact density functions $\rho_2(r/R)$ and $\rho_3(r/R)$.

In an attempt to improve the agreement between the approximate and exact densities, an 'artificial temperature factor' (Furukawa, 1962) was used. In these calculations, the integrand was multiplied by a Gaussian $\exp(-b^2h^2)$, in which the constant $b$ was chosen so that the Gaussian was of the order of 0.1 when $h=hm$. Although this factor removed some of the ripples in the curve for $hmR=15$, for lower values of $hm$ the factor did not improve the agreement between the exact and approximate densities. Thus, our tests indicate that while the artificial temperature factor can refine the $\rho_2(r/R)$ curves when $hmR$ is sufficiently large, the factor cannot compensate for the effects of $hmR$ values being much too small.
Special attention should be given to the curves for $x_m = 5$ and $x_m = 8$ in Fig. 1. The former curve roughly resembles the density $q_5(r/R)$. Thus, when a value of $x_m$ that is much too small is used with $I_1(hR)$, one is tempted to say that the density function is approximately of Gaussian form. Similarly, when $x_m = 8$, $q_5(r/R)$ might be interpreted as a cylinder with a low-density region near the axis. At first glance these densities might appear reasonable if the true density were not known. The use of $x_m$ values that are much too small thus leads to errors in $q_4(r/R)$ that are difficult to detect and which are much less obvious than the ripples occurring when $x_m$ is larger but still not large enough to give essentially perfect agreement with the exact $q_4(r/R)$ curve.

Fedorov & Aleshin (1966) have tested their method with the small angle X-ray data obtained by Luzzati, Nicolaieff & Masson (1961) for solutions of deoxyribonucleic acid (DNA). The density curve shown by Fedorov & Aleshin appears similar to our density function $q_5(r/R)$. The data of Luzzati, Nicolaieff & Masson extend to $h$ values of about 0.3, and from the graph of Fedorov & Aleshin, $R$ is approximately equal to 10. Thus, $h_m R \approx 3$. Our tests have shown that this value of $h_m$ is sufficient to give a reliable density function if the density is a Gaussian function, and the errors will not be large if the density is an exponential function. However, for $h_m R = 3$, a density function like the curve shown by Fedorov & Aleshin would also be obtained if the particle were a cylinder with uniform electron density. Our tests therefore suggest that the data of Luzzati, Nicolaieff & Masson may not be available at large enough angles to give much information about the detailed form of the density function. Computations with larger values of $h_m$ would be required to resolve the uncertainty.

Numerous electron micrographs show that tobacco mosaic virus is a long cylinder with a radius of about 75 Å. For such a large particle, short-range structure of the order of 1 to 5 Å will not affect the X-ray scattering in the angular region needed for use of (1), and to a good approximation the electron density can be considered continuous. As Malmon (1957) obtained scattering data at angles through about 0.03 radians, $h_m R \approx 9$. For a uniform cylinder, as Fig. 1 indicates, for $x_m = h_m R = 8$, $q_4(r/R)$ has a low-density region near $r/R = 0$. Our tests thus suggest that Malmon's data may permit resolution of only the coarse features of the density.

The calculation proposed by Fedorov & Aleshin assumes that the electron density is continuous and depends only on the distance from the cylinder axis. The method thus neglects density fluctuations of the order of interatomic dimensions and also does not take account of any structure along the particle axis. If this structure can be neglected, the scattered intensity from an oriented sample should have appreciable small angle scattering only along the equator of the diffraction pattern. When diffraction patterns from oriented samples are available, they can be used to justify the neglect of structure along the axis.

While short-range density fluctuations may have a very small effect on the small-angle scattering from relatively large particles like tobacco mosaic virus, these fluctuations cannot be neglected for a particle such as deoxyribonucleic acid, which has a radius of about 10 Å. For the DNA samples studied by Bram & Beeman (1969), in which data were obtained for $h$ values as large as 1.4 Å$^{-1}$, the scattering in the region of the secondary maxima and minima appears to be at least partially determined by the internal structure of the molecule, including structure along the axis. Thus, even for large values of $x_m$, the density computed by equation (1) may not be a good approximation to the actual charge distribution in these particles.

When densities are calculated from (1), the proper sign must be chosen for the square root of the intensity when the intensity curve has zeros, as is true for $I_1(hR)$. For this test function, there is no problem in selecting the sign, since the choice $|I_1(hR)| = 2(hR)^{-3/2} J_1(hR)$ automatically gives $q_4(r/R)$. (There is no ambiguity of sign with $I_2(hR)$ and $I_3(hR)$, since these intensities are never zero.) However, with experimental curves the choice of sign can present real difficulties. These ambiguities can sometimes be resolved by the trial and error technique of comparing the results from calculations of the density for several choices of sign.

The information which we obtained in our tests leads us to recommend that when the density is calculated by the method of Fedorov & Aleshin, precautions should be taken to ensure that the features in the calculated density curve represent the structure in the actual density and are not merely artifacts caused by the choice of upper limit in (1). Whenever possible, the density should be computed for several values of $h_m$, in order to see how much the calculated density depends on the choice of $h_m$.

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