conductive at such high temperatures and partly because of the difficulties in obtaining stable conductive coatings on the relatively porous ceramic disc. The latter inconvenience can, however, be overcome by shaping the condenser into a pressed tablet; inside this, two thin foils of platinum were placed with a thin layer of powder in between. Before pressing, a piece of platinum wire was welded to each foil to serve as electrical connexions. The measurement was made at 1 MHz with a Wayne Kerr transformer bridge. The preliminary measurement showed that the dielectric constant increases with temperatures up to *ca.* 1200°C where it reaches its peak and after which it decreases with further rise in temperature. Small anomalies were also observed at 700 and 850°C. The appearance of the curve indicates that the transition at 1170°C is either a ferroelectric to paraelectric transition or an antiferroelectric to paraelectric one. The fact that the tetragonal modification is of multiple cell type indicates an antiferroelectric modification since according to Megaw (1957) this is physically more likely than a ferroelectric for multiple cell perovskites. Resistivity data indicate that at temperatures above 1000°C the zirconate behaves as a semiconductor in the intrinsic range with a band gap of $\sim 2{\cdot}1$ eV. No anomality in the electrical conductivity was detectable at the transition at 1170°C.

It is of interest to note that the predictions made by Krainik regarding crystallographic transformations of pure $SrZrO_3$ are in good agreement with our findings. An extrapolation of Krainik's phase diagram to 100% $SrZrO_3$ shows that a transformation between a nonpolar and a paraelectric phase should take place at *ca.* 1100°C; this compares favourably with the one experimentally found between the cubic and the pseudotetragonal phase at 1170°C. Krainik's next transformation found between the nonpolar phases was to occur at *ca.* 700°C compared with our result between the two pseudotetragonal phases at 830°C. The lines in Krainik's phase diagram indicating the next transformation between a nonpolar and an antiferroelectric phase displays no straight part, making an extrapolation impossible. This transformation may correspond to the one at 700°C between the pseudotetragonal and orthorhombic phases. The sequence of phase transitions of $SrZrO_3$ shows marked differences compared with known features of other perovskites. If more than one tetragonal or pseudotetragonal phase appears, c/a values in other perovskites are generally both <1 or both >1. It is remarkable that the corresponding transformation in $SrZrO_3$ goes from one phase with $c/a<1$ to another with $c/a>1$.

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Linear Programming and the Refinement of Structures

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A new technique is developed for the perturbation of the coordinates of a structure away from a false least-squares minimum. The perturbation is a function of the accuracy of the individual components of the data. The technique could be used as an alternative method of refinement.

Introduction

The primary requirement of a well devised X-ray diffraction experiment is the collection of data, the individual components of which have a reasonably well defined error or standard deviation. Usually this information is only used to devise a least-squares weighting scheme and there are no explicit constraints to fit the calculated model to the data within the experimental errors. A question that should be asked is, does a calculated structure which has a low overall R index but a small number of structure factors that lie well outside the possible error limits for the observed structure factors give a reasonable representation of the structure? The purpose of statistics, of which the least-squares process is a part, is to provide a basis for further action, and the purpose of this paper is to indicate a possible mathematical tool whereby the above question can be answered. The larger than expected calculated errors in the structure factors obtained from the model may be due to one of two causes. There may be some unallowed for physical effect on the observed or calculated data or they may have been produced as a consequence of obtaining a mathematical minimum and be purely a mathematical artefact. If the former is the reason for the large error, and cannot be numerically corrected, then these structure factors can only be removed from subsequent refinement. If the latter is the reason then the model must be sufficiently perturbed so that they are brought within the expected experimental errors and refinement continued. They must not be removed from subsequent refinement.

The recent work of Donohue & Goodman (1967) on an alternative minimum to that obtained by Nordman & Schmitkons (1965) for the structure of adamantane shows the problem of false minima to be real. It is clear that the results of Donohue & Goodman give a better over-all fit to the observed data and also a more symmetric stereochemical model.

Mathematical formulation

Kitaigorodskii (1957) has suggested that an appropriate measure of the accuracy of a structure determination is given by G, where

$$G^2=\frac{\Sigma\,\{|F_o(\mathbf{h})|-|F_c(\mathbf{h})|\}^2}{\Sigma\,|F_o(\mathbf{h})|^2}$$

rather than the conventional R index

$$R=\frac{\Sigma\,||F_o(\mathbf{h})|-|F_c(\mathbf{h})||}{\Sigma\,|F_o(\mathbf{h})|}\,.$$

It is easy to show that G is independent of symmetry, whereas R is symmetry dependent, and for reasonably well refined structures G and R are numerically very similar. Kitaigorodskii also points out that a much more sensitive function is

$$H^2=\left\langle\frac{\{|F_o(\mathbf{h})|-|F_c(\mathbf{h})|\}^2}{|F_o(\mathbf{h})|^2}\right\rangle.$$

It is worth remembering that the usual least-squares refinement expression takes the form

$$\Sigma\,w_i\Delta_i^2=\Sigma\,\frac{\{|F_o(\mathbf{h})|-|F_c(\mathbf{h})|\}^2}{|F_o(\mathbf{h})|^2}$$

for data obtained with a constant count technique (Killean, 1967), assuming no systematic errors and negligible statistical setting errors. The use of this expression should militate against obtaining false minima which have some large values of

$$\frac{||F_o(\mathbf{h})|-|F_c(\mathbf{h})||}{|F_o(\mathbf{h})|}$$

but it by no means assures that large values of this expression cannot be obtained.

There is, however, a more novel approach to the problem which by its very nature assures that large values of this expression cannot be obtained. In the usual way consider a set of trial coordinates, $\mathbf{r}_i$, which define the $(p-1)$th set of calculated structure factors and their associated small incremental shifts, $\partial\mathbf{r}_i$, which define the pth set of calculated structure factors.

Consider the most general form of the structure factor equation and let the subscript p refer to the pth set of calculated structure factors. For the purposes of this paper it is not required to treat perturbations in the scale or thermal parameters but it is a simple algebraic matter to include them if required. Under these conditions

$$\begin{aligned}|F_c(\mathbf{h})|_p^2=&\{\sum_i f_i(\mathbf{h})\cos 2\pi\mathbf{h}\,.\,(\mathbf{r}_i+\partial\mathbf{r}_i)\}^2\\&+\{\sum_i f_i(\mathbf{h})\sin 2\pi\mathbf{h}\,.\,(\mathbf{r}_i+\partial\mathbf{r}_i)\}^2\\\simeq&|F_c(\mathbf{h})|_{p-1}^2\\&-2A(\mathbf{h})_{p-1}\sum_i(2\pi f_i(\mathbf{h})\sin 2\pi\mathbf{h}\,.\,\mathbf{r}_i)\mathbf{h}\,.\,\partial\mathbf{r}_i\\&+2B(\mathbf{h})_{p-1}\sum_i(2\pi f_i(\mathbf{h})\cos 2\pi\mathbf{h}\,.\,\mathbf{r}_i)\mathbf{h}\,.\,\partial\mathbf{r}_i\end{aligned}$$

and

$$\begin{aligned}|F_c(\mathbf{h})|_p\simeq&|F_c(\mathbf{h})|_{p-1}\\&-\cos\varphi(\mathbf{h})_{p-1}\sum_i(2\pi f_i(\mathbf{h})\sin 2\pi\mathbf{h}\,.\,\mathbf{r}_i)\mathbf{h}\,.\,\partial\mathbf{r}_i\\&+\sin\varphi(\mathbf{h})_{p-1}\sum_i(2\pi f_i(\mathbf{h})\cos 2\pi\mathbf{h}\,.\,\mathbf{r}_i)\mathbf{h}\,.\,\partial\mathbf{r}_i\end{aligned}$$

where $\varphi(\mathbf{h})$ is the usual phase angle. But

$$\Delta_{i,p}^2=||F_o(\mathbf{h})|-|F_c(\mathbf{h})|_p|^2\,,$$

and by substitution and rearrangement

$$\begin{aligned}\Delta_{i,p}^2=&||F_o(\mathbf{h})|-|F_c(\mathbf{h})_{p-1}||^2\\&-2\{A(\mathbf{h})_{p-1}-|F_o(\mathbf{h})|\cos\varphi_{p-1}\}\\&\Sigma\,(2\pi f_i(\mathbf{h})\sin 2\pi\mathbf{h}\,.\,\mathbf{r}_i)\mathbf{h}\,.\,\partial\mathbf{r}_i\\&+2\{B(\mathbf{h})_{p-1}-|F_o(\mathbf{h})|\sin\varphi_{p-1}\}\\&\Sigma\,(2\pi f_i(\mathbf{h})\cos 2\pi\mathbf{h}\,.\,\mathbf{r}_i)\mathbf{h}\,.\,\partial\mathbf{r}_i\end{aligned}$$

which is linear in the variables $\partial\mathbf{r}_i$.

The problem is now formulated as minimizing the linear quantity in $|\partial\mathbf{r}_i|$

$$\Sigma\,w_i\Delta_{i,p}^2\geq 0$$

subject to linear constraints in $|\partial\mathbf{r}_i|$

$$0\leq\Delta_{i,p}^2\leq\tau_i(\mathbf{h})$$

where the $\tau_i(\mathbf{h})$ are assessed from the experimental accuracy.

Mathematical solution

The neglecting of second and higher order terms in the expansion of $|\partial \mathbf{r}_i|$ imposes a limitation on the allowed shifts if the formulation of the problem is to retain its physical meaning. This, of course, is the same restriction as applies to the least-squares technique where unfortunately it is not possible to allow for it. Let

$$\partial \mathbf{r}_i = \partial x_i \mathbf{i} + \partial y_i \mathbf{j} + \partial z_i \mathbf{k}\ ,$$

where, because of the restriction on the shifts,

$$\begin{aligned} \varepsilon_{i,1} &\ge \partial x_i \ge -\varepsilon_{i,1} \\ \varepsilon_{i,2} &\ge \partial y_i \ge -\varepsilon_{i,2} \\ \varepsilon_{i,3} &\ge \partial z_i \ge -\varepsilon_{i,3}\ . \end{aligned}$$

Define new variables,

$$\begin{aligned} \partial u_i &= \partial x_i + \varepsilon_{i,1} \\ \partial v_i &= \partial y_i + \varepsilon_{i,2} \\ \partial w_i &= \partial z_i + \varepsilon_{i,3} \end{aligned}$$

so that

$$\begin{aligned} 2\varepsilon_{i,1} &\ge \partial u_i \ge 0 \\ 2\varepsilon_{i,2} &\ge \partial v_i \ge 0 \\ 2\varepsilon_{i,3} &\ge \partial w_i \ge 0\ . \end{aligned}$$

The problem is now one of optimization subject to a set of linear constriction with all variables being positive and was originally solved by Dantzig (1951). It is not necessary to outline the method of solving these inequalities to obtain a minimum in $\Sigma\, w_i \Delta^2_{i,p}$ as there can be few computers for which linear programming programs do not exist, such is its importance in the theory of economics.

It is worth noting that there are numerous strategies for the use of this technique. It is by no means necessary to have one inequality for each structure factor and they could be grouped together to give inequalities for various regions of reciprocal space or for various ranges of intensity, always, of course, treating separately those which had values $w\Delta^2$ which differed appreciably from experimental prediction.

Conclusion

It has been shown that the linear programming technique of minimizing the linearized function $\Sigma\, w_i \Delta_i^2$ has certain advantages to offer in deciding the accuracy of a given structure model over that of the conventional least-squares technique which does not use the maximum information derivable from the data. It is to be expected that for a refined structure using high quality data ($\tau_i(\mathbf{h})$ all small) the two techniques in the limit would give the same minima. It is dubious if this would be true if the $\tau_i(\mathbf{h})$ values are large.

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A Comparison of Experimental X-ray Structure Amplitudes for Sodium Chloride

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Recent X-ray structure amplitude data for sodium chloride are divided into a consistent majority and an inconsistent minority by statistical methods. A set of mean value estimates of the structure amplitudes is derived from the consistent data.

X-ray structure amplitudes (at room temperature) for sodium chloride have been measured many times in recent years (Table 1). Considerable differences occur, so that it is difficult to extract useful information about, say, the electron distribution and thermal motion in this alkali halide. The purpose of the present note is to compare the different experimental results for reflexions with $h^2+k^2+l^2 \le 48$ and to show that these results may be grouped into a consistent majority and an inconsistent minority.

The comparison has been restricted to this range of low-order reflexions for several reasons. Firstly, the range is common to most experiments. Secondly, the experimental measurements of these low-order reflexions are not very sensitive to those differences in experimental techniques which lead to different rates of fall-off, with angle, of the higher order reflexions. Thirdly, accurately known structure amplitudes for this range would provide a great deal of information about the electron distribution. With this in mind, a set of mean value estimates of the structure amplitudes has been derived from the consistent data and is presented in Table 3.

Brief details of the data to be compared are given in Table 1; mosaic single-crystal data published before 1952 have been excluded since, as Renninger (1952)