

The only two cases in (1) where confusion must be avoided are the last two: $P\bar{3}$ and $P3$ are now used to designate hexagonal space groups and thus cannot be applied to the rhombohedral P cell. Indicating by 1s the secondary directions in the rhombohedral lattice ($P\bar{3}1$ and $P31$), and both secondary and tertiary directions in the hexagonal lattice ($1P\bar{3}11$ and $1P311$), removes the ambiguity. The old hexagonal symbols $P\bar{3}$ and $P3$ will still be understood, as synonyms of $P\bar{3}11$ and $P311$. Only $P\bar{3}1$ and $P31$ can be the equivalent of $R\bar{3}$ and $R3$.

As to the old $P3_1$ and $P3_2$, they could be retained as such. (They can only represent hexagonal space groups, since screw axes are implicit in rhombohedral space groups.) But they would be the only trigonal hP symbols in which the secondary and tertiary directions would not be filled. For the sake of uniformity, it may be better to designate them $P3_111$ and $P3_211$.

In the hR notation there is no need to change the symbols $R\bar{3}$ and $R3$ to $R\bar{3}1$ and $R31$. The meaning of the letter R is by now well established. Everyone knows that the ' R ' centering' of a P hexagonal lattice reduces the symmetry from $6/m2/m2/m$ to $\bar{3}2/m$. (This, of course, is the reason why Bravais placed the hR ($=rP$) crystals in a *rhombohedral system* and

the hP crystals in the *hexagonal system*, since the point symmetry of the lattice was the basis of his classification.)*

The trigonal space groups are presented (Table 1) in such a way as to show the proposed modifications to the symbolism now in use.

The present proposal has been thoroughly reviewed by Professor E. Hellner, Dr H. Burzlaff, Dr W. Fischer and myself, preliminary to its adoption for use in our forthcoming Tables, *Space Groups and Lattice Complexes*. I am much indebted to my Marburg co-workers for this critical discussion. My thanks are also due to Professor A. Pabst for a critical reading of the manuscript.

* In contrast the present subdivision into 'trigonal' and 'hexagonal' systems looks trivial indeed; the only information these terms convey refers to the nature of the symmetry axis — 3 or $\bar{3}$ vs 6 or $\bar{6}$ (if this were the point to emphasize, the names of other crystal systems would have to be recast: monoclinic to 'digonal', orthorhombic to 'tridigonal', cubic to 'tetradigonal'). In our age of crystal-structure determinations, Bravais' classification based on the lattice acquires an enhanced significance, stressing as it does the triperiodicity, which is the dominant feature of a structure.

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Spurious peaks in electron-density maps. By EFFI HUBER-BUSER, *Institut für Kristallographie und Petrographie, Eidgenössische Technische Hochschule, Zürich, Switzerland*

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Certain commonly used data-rejection procedures can cause specific patterns of prominent spurious peaks and holes in electron density maps.

In a recent structure analysis of the nine-coordinated thorium tetrakis(γ -isopropyl tropolonate) monohydrate,* the highest peak in our difference electron-density map with coefficients sign Th ($F_{\text{obs}} - |F_{\text{calc Th}}|$) was eventually proved to be spurious. The positional parameters of the thorium atom were obtained from a three-dimensional Patterson map and were then subjected — together with an isotropic temperature factor, B , and a scale factor — to three cycles of full-matrix least-squares refinement, treating the thorium as an anomalous scatterer. Because of the microscopic size of the crystal no absorption corrections were applied. (A comparison of the final calculated structure amplitudes with the observed values confirmed that absorption was indeed negligible.) After this refinement the thorium atom settled within 0.02 \AA of its final position and the temperature parameter B deviated from the final average isotropic \bar{B}_{Th} ($= 4.28 \text{ \AA}^2$) by 0.3 \AA^2 . The spurious peak and an additional hole of approximately -17 e. \AA^{-3} could therefore not be explained by an inaccuracy in the heavy atom parameters used in the calculation of the structure factor ($F_{\text{calc Th}}$) entering the difference Fourier synthesis. Also these features were only slightly attenuated after the inclusion of all the light atoms in the structure factor calculation.

We then noted that the sites of the hole and the spurious peak are connected to the heavy atom site: their coordinates are three- and fivefold multiples respectively of the thorium

coordinates and a hole-peak pattern at odd multiples of the heavy atom position could be traced throughout the unit cell up to $n=25$ (see Fig. 1).

In search of an explanation we found that in an electron-density map with one heavy atom per asymmetric unit and space group $P\bar{1}$ one can produce such a pattern with the

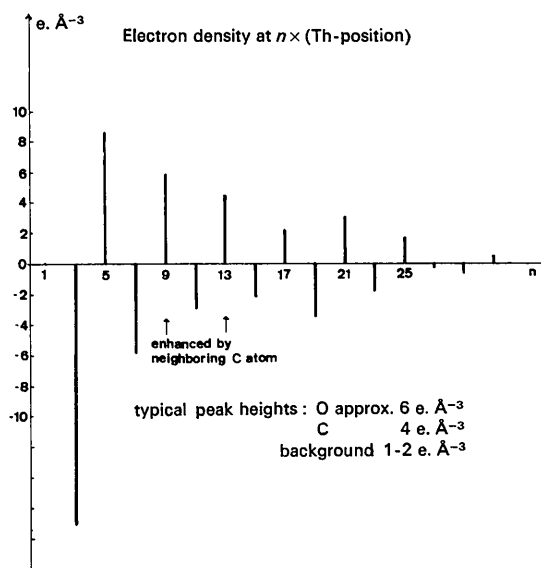


Fig. 1

* $\text{Th}(\text{C}_{10}\text{H}_{11}\text{O}_2)_4 \cdot \text{H}_2\text{O}$ plus one molecule of crystal solvent, either H_2O or a disordered CH_3OH ; space group $P\bar{1}$; one molecule per asymmetric unit; detailed description not yet published.

use of constant structure amplitudes and by attributing the sign of the heavy atom to them, that is, with a structure factor contribution of the form $\Delta F_h \sim \text{sign}(\cos 2\pi \cdot \mathbf{h} \cdot \xi)$, where $\xi = (x/a, y/b, z/c)_{\text{Th}}$. This can be seen as follows: if we introduce the Fourier expansion of

$$\text{sign}(\cos \alpha) = 4/\pi \sum_{m \geq 0} \frac{(-1)^m}{2m+1} \cos(2m+1)\alpha$$

we find that our

$$\Delta F_h \sim 4/\pi \sum_m \frac{(-1)^m}{2m+1} \cos(2\pi \cdot \mathbf{h} \cdot (2m+1)\xi)$$

corresponds formally to a structure factor contribution from atoms at sites $(2m+1)\xi$ with their numbers of electrons proportional to $(-1)^m/(2m+1)$.

The next question was, how can such a ΔF_h arise in our observed amplitudes? We propose the following explanation: in our data collection we rejected a reflexion as unobservable if the measured intensity (essentially scan count minus background count) was smaller than its standard deviation (essentially the square root of the sum of scan count plus background count). Any such criterion is biased – it tends to reject measured intensities with negative random errors and to retain those with positive random errors. Since we had relatively weak intensities (because of our small crystal) against a high background count, this bias must have affected a large percentage of our weak high-

order reflexions. This could be confirmed by remeasuring a sample of 49 weak reflexions. Of these, 13 were twice accepted, 10 twice rejected and 26 switched sides. On average, this bias acts like adding a positive term, ε , to the observed structure amplitudes and therefore, when ε is multiplied by the heavy-atom sign, it produces the pattern described above. Unfortunately, this kind of bias will be present with any rejection procedure and cannot be completely eliminated, but it was argued that it should be possible to reduce it by throwing out data with large standard deviations in the structure amplitudes, F . Since $\sigma(F) \sim \sigma(I)/\sqrt{I}$, this would reduce both the average value of ε and the number of marginal data (the weakest reflexions tend to have the highest estimated standard deviations). Indeed, when such a stronger rejection criterion was applied, reducing the number of observed reflexions from 2037 to 1407, the hole-peak pattern almost completely vanished from our difference electron-density map.

Our example corresponds to the simplest possible case. Higher symmetries and more than one heavy atom complicate the pattern considerably, but it can be worked out by similar methods.

As a conclusion we would like to point out that it can be imprudent to suppress negative electron densities in the electron-density map: holes may furnish crucial information for the identification of spurious peaks. Moreover, one can miss genuine atomic peaks if they coincide by chance with a hole produced by the described heavy atom effect.

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The role of intensity measurement projects: Correction. By A. MCL. MATHIESON, *Division of Chemical Physics, CSIRO Chemical Research Laboratories, Melbourne, Australia*

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A correction to *Acta Cryst.* (1969), A **25**, 264

Owing to a slip in proof correction, an error was introduced into the acknowledgment, p. 273, of the original paper (Mathieson, 1969). The necessary change in the first sentence of the relevant paragraph is ‘... my colleagues, Drs J. K. Mackenzie and V. W. Maslen ...’ and in the third

sentence ‘... my Commission colleagues, Drs S. C. Abrahams and W. C. Hamilton ...’.

Reference

MATHIESON, A. MCL. (1969). *Acta Cryst.* A **25**, 264.