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The choice of the unit cell in the triclinic system.

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Introduction

With the extension of X-ray structure analysis and the accumulation of experimental data, several methods have been proposed for making a unique choice of the parameters for triclinic crystals (Barth & Tunell, 1933; Buerger, 1937, 1942, chap. 19; Crowfoot, 1935; Donnay & Melon, 1933; Donnay, Tunell & Barth, 1934; Donnay, 1943*a*, *b*; Peacock, 1937; Tunell, 1933). In a recent publication (Donnay & Nowacki, 1954, pp. 161–178), which included all published crystal data (up to 1951) for substances belonging to the triclinic system, the authors undertook the considerable labour of calculating all parameters according to one general system, namely that of the Russian mathematician Delaunay (1933), which was brought to the attention of crystallographers by Ito (1950, p. 189).

Application of the Delaunay reduction (*International Tables*, 1952, p. 530) gives the cell which has the three interaxial angles (α, β, γ) all non-acute, i.e. $\geq 90°$, and, within the limits imposed by this condition, the three translations, *a*, *b*, *c* the shortest possible. Unfortunately, in many cases (more than 20% of those presented by Donnay & Nowacki) the reduction causes some interaxial angles to deviate from 90° by more than 30° and sometimes by as much as 60°. Consequently, the axial translations are often much greater than the minimum possible and are therefore inconvenient to use in X-ray structure analysis.

In seeking improved rules for the choice of the unit cell, we take the following features of the triclinic system into account:

1. The triclinic system is the only one where the choice of cell is not imposed by the symmetry.
2. Any unit cell will in general have two solid angles in which all three plane angles are 'homogeneous', i.e. either (*a*) all acute (the unit cell is an acute parallelepiped) or (*b*) all obtuse (the unit cell is an obtuse parallelepiped).
3. No parallelepiped can be obtuse and acute at the same time. (A parallelepiped having a solid angle in which one or two plane angles are equal to 90° can be described as non-obtuse $(\alpha, \beta, \gamma \leq 90°)$, or non-acute $(\alpha, \beta, \gamma \geq 90°)$ parallelepiped. Following the crystallographic convention, this parallelepiped would be described as non-acute $(\alpha, \beta, \gamma \geq 90°)$ parallelepiped.)
4. In a parallelepiped (obtuse or acute) formed by three shortest translations each edge must be shorter than the diagonals of the faces bordering it.
5. The Delaunay reduction automatically gives the three shortest non-coplanar translations of the lattice if these form an *obtuse* parallelepiped.
6. The Delaunay reduction cannot give the three shortest non-coplanar translations of the lattice if they form an *acute* parallelepiped.
7. The reciprocal of an obtuse parallelepiped is an acute one, and, usually, vice versa.
8. The shortest possible a^*, b^* and c^* of the triclinic reciprocal lattice do not necessarily correspond to the shortest possible *a*, *b* and *c* of the corresponding direct lattice, as is the case in all other crystallographic systems (Buerger, 1942, p. 365).
9. In the absence of requirements imposed by the symmetry there is no preference for the choice of *a*, *b* or *c* in any particular direction, but the convention $a < b < c$ proposed by Buerger (1942, p. 366) seems more convenient for tabulation purposes than the labelling $c < a < b$ used by Donnay & Nowacki (1954, p. 138).

From the structural point of view it is more convenient (for graphical representation of the unit-cell contents) to have the shortest of the three axes towards the observer (this axis will thus, by convention, be labelled *a*). In the majority of tetragonal and hexagonal crystals, where (in contrast to the orthorhombic system) the *c* and *a* axes are fixed by convention, the ratio c/a is greater than unity. These considerations support Buerger's convention.

With these points in view the following rules are proposed:

Rules for choice and evaluation of the unit cell in the triclinic system

1. The unit cell should be primitive (i.e. it should have the smallest volume).
2. The cell edges should be labelled in the following order:

$$a < b < c\,.$$

3. The interaxial angles α, β and γ should be 'homogeneous' (that is either *all acute* or *all obtuse*).
4. The Delaunay reduction is applied in direct space to any primitive cell obtained experimentally.
5. The edges *a*, *b* and *c* of the cell obtained after operation (4) are tested to determine whether they are shorter than the diagonals of the faces bordering the cell.
6. If this test reveals a diagonal shorter than an edge, it must be concluded that the shortest translation a_0, b_0 and c_0 form the *acute* parallelepiped: the Delaunay reduction should be applied in reciprocal space to the values a^*, b^*, ... etc.
7. From the reduced parameters a_0^*, b_0^*, ... etc. obtained after operation (6), the corresponding values a_0, b_0, ... etc. are calculated and accepted as parameters of the direct lattice.
8. When one or two interaxial angles are equal to 90°, under the conditions of the experiment, the unit cell should be presented as the non-acute $(\alpha, \beta, \gamma \geq 90°)$ parallelepiped. For the sake of completeness it may be classed as an obtuse parallelepiped.

By the application of the above rules, all triclinic lattices (direct space) will therefore be divided into two groups, for one of which the unit cell is an obtuse parallel-

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epiped and for the other of which the unit cell is an acute parallelepiped.

In the former case the translations a_0, b_0 and c_0 of the unit cell are the shortest possible. In the latter case, the translations a_0, b_0 and c_0 are not necessarily the shortest possible, but they will usually be so, and the interaxial angles will usually be not greatly different from 90°. Moreover, they have a unique definition and are automatically derived by the application of the Delaunay reduction in reciprocal space.

The application of the above rules thus avoids the inconvenient values of lattice parameters obtained in many cases when the Delaunay reduction is carried out in one (direct or reciprocal) space only.

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The Laue goniometer and its use as a proportional diffractometer.

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The Laue goniometer has long been used for the study of symmetry and lattice distortion, principally by metallurgists. Exact analysis is rendered difficult because two variables (wavelength and lattice spacing) are associated with each diffraction spot, and estimates of unit-cell size are generally only approximate. If the diffracted image were to be investigated by a proportional counter and multichannel pulse-height analyser then direct knowledge of the wavelengths and relative intensities associated with each spot could be obtained.

As the rate of arrival of X-ray quanta is governed by the Poisson distribution, and the effective integrated intensity (N) is a differential count between background (B) and $N+B$, then the variance associated with a count N is $N+2B$.

The coefficient of variation is $\{100\sqrt{(N+2B)}\}/N$, and if N is greater than B (as is usual except for very weak spots) we must have $N > 10^4$ if this coefficient is to be less than 1%.

Cochran (1950) reports a standard deviation of only 1–2% in I_{hkl} values for Geiger-counter measurements, compared with 12–18% for photographic recording.

Channel-selection considerations limit the maximum rate of arrival of quanta to 1600 per sec. (Hutchinson & Scarrott, 1951), which means that an intensity measurement with a coefficient of variation of 1% may be obtained in about 6 sec.

The pulse-height variance $(\sigma_p)^2$ for mono-energetic radiation absorbed in an argon-filled proportional counter can be expressed (Curran, Angus & Cockroft, 1949) by

$$\sigma_p^2 = \bar{p}^2(\alpha+\beta)/\bar{N} ,$$

where

$\bar{p}$ = mean pulse height,
$\bar{N}$ = E/W_k = number of ion pairs initially produced,
E = energy of incident quanta,
W_k = energy required to produce one ion pair = 27 e.V. for argon (Valentine, 1952),
$\alpha = \beta = \frac{2}{3}$.

Thus in the region of $\lambda = 1$ Å, $E = 12340$ e.V. and the coefficient of variation is 5·35%.

Lang (1952) assumes a Gaussian pulse-height distribution so that the standard error of the mean, expressed as a percentage of the mean, is

$$115/\sqrt{(\bar{N}N)} .$$

Thus if $\lambda = 1$ Å, and $N = 10^4$ the standard error of the mean is 0·05%.

The performance is limited by the stability of the grid potential in the amplitude analyser, which restricts the number of available channels to 120 and the maximum counting rate to 1600 counts per sec. (Titterton, 1953).

The preceding shows that a typical measurement of intensity and wavelength could be made in less than 10 sec. with the following degrees of accuracy:

Intensity: coefficient of variation 1%;
Wavelength: standard error 0·05% (expressed as a percentage fraction of the mean).

Furthermore, the harmonic content of the radiation may also be quantitatively measured if the pulse-height