research papers

Remarkable features in lattice-parameter ratios of crystals. II. Monoclinic and triclinic crystals

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The frequency distributions of monoclinic crystals as a function of the lattice-parameter ratios resemble the corresponding ones of orthorhombic crystals: an exponential component, with more or less pronounced sharp peaks, with in general the most important peak at the ratio value 1. In addition, the distribution as a function of the monoclinic angle β has a sharp peak at $90°$ and decreases sensibly at larger angles. Similar behavior is observed for the three triclinic angular parameters α, β and γ, with characteristic differences between the organic and metal-organic, bio-macromolecular and inorganic crystals, respectively. The general behavior observed for the hexagonal, tetragonal, orthorhombic, monoclinic and triclinic crystals {in the first part of this series [de Gelder & Janner (2005). *Acta Cryst.* B**61**, 287–295] and in the present case} is summarized and commented. The data involved represent 366 800 crystals, with lattice parameters taken from the Cambridge Structural Database, CSD (294 400 entries), the Protein Data Bank, PDB (18 800 entries), and the Inorganic Crystal Structure Database, ICSD (53 600 entries). A new general structural principle is suggested.

1. Introduction

In the first part of this survey of crystal lattice-parameter frequency distributions (de Gelder & Janner, 2005), here denoted as Part I, crystals with high point-group symmetry (hexagonal, tetragonal and orthorhombic) were considered for three sets of crystal structures: the organic and metal-organic compounds, with entries from the Cambridge Structural Database (CSD), the bio-macromolecular crystals, with entries from the Protein Data Bank (PDB), and the inorganic crystals, with entries from the Inorganic Crystal Structure Database (ICSD).

Here, this survey is extended to the monoclinic and the triclinic crystals of these data banks. As in Part I, frequency denotes the number of cases fitting into a given δ interval of the lattice-parameter ratios considered, which is a δ coarse-grained distribution. For the lattice-parameter ratios, the value $\delta = 0.05$ has been adopted, because it represents a reasonable number of points (of the order of 100) in the relevant range.

While in all the crystals considered in Part I the angular lattice parameters were fixed by symmetry, this is not the case for monoclinic and triclinic crystals. Their values occur in the non-diagonal entries of the metric tensor of the corresponding lattices. Nevertheless, the concept of *integral lattice* also applies to monoclinic and triclinic lattices, where integral lattices allow a metric tensor with integral entries (non-integral lattices are here denoted as *generic lattices*). One can even show that integral monoclinic and triclinic lattices are rationally equivalent to orthorhombic lattices (Janner, 2004).

This means that each of them can be given as a centered orthorhombic integral lattice. It is, however, not always simple to express the integrality conditions in terms of the lattice parameters (four for the monoclinic lattice and six for the triclinic one). Moreover, it is not even said that doing so is structurally meaningful and one may wonder whether integral lattices play any role in these crystals. One of the aims of this paper is to give an answer to the last question. It is convenient to start with monoclinic crystals.

2. Monoclinic crystals

The monoclinic crystal data have been oriented in such a way that the unique axis is in the b direction, the β angle is larger or equal to 90° and $a \leq c$. The coarse-graining parameter chosen is $\delta_0 = 0.5°$ for the angular distribution and $\delta = 0.05$ for the length ratios. As in Part I, different behavior for the three types of crystals considered was observed: the organic and metal-organic (CSD), the bio-macromolecular (PDB) and the inorganic (ICSD) ones. This difference already appears in the angular distribution of the monoclinic crystals (Fig. 1): a broad characteristic peak for the organic and metal-organic compounds, which is practically reduced to a single sharp peak for the inorganic materials and shows several irregular peaks in the case of bio-macromolecular crystals. In the first two cases, the maximal distribution is at 90°, corresponding to pseudo-orthorhombic lattices. In PDB crystals, this peak is the second most important one. It is not clear why the highest peak occurs for β at *ca* 104°. In general, the frequency decreases for increasing angles (chosen to be $\geq 90°$).

Now we consider the frequency behavior as a function of the various ratios of the lattice parameters a, b and c. The interpretation of the plots depends on the ratio considered and the corresponding two-dimensional sub-lattice. The ratio c/a expresses properties of the sub-lattice in the monoclinic plain (a, c), whereas the c/b and b/a ratios determine the properties of the lattices in the axial planes (c, b) and (a, b), respectively, having the unique axis b in common.

2.1. Lattice in the monoclinic plane (a,c)

In the monoclinic plane the (a, c) lattice is oblique with a metric of the form

$$\begin{pmatrix} a^2 & ac\cos\beta \\ ac\cos\beta & c^2 \end{pmatrix} \simeq \begin{pmatrix} 1 & \frac{c}{a}\cos\beta \\ \frac{c}{a}\cos\beta & \left(\frac{c}{a}\right)^2 \end{pmatrix}. \quad (1)$$

An integral oblique lattice requires that both $(a/c)\cos\beta$ and $(c/a)^2$ are rational. These conditions also apply to the monoclinic lattice. As $(c/a)\cos\beta$ and $(c/a)^2$ are rational numbers, the oblique lattice is equivalent to an integral rectangular lattice. Indeed,

$$\tilde{S}g_{ob}S = \begin{pmatrix} 1 & 0 \\ 0 & (\frac{c}{a}\sin\beta)^2 \end{pmatrix} = g_r, \quad S = \begin{pmatrix} 1 & -\frac{c}{a}\cos\beta \\ 0 & 1 \end{pmatrix}. \quad (2)$$

This implies that an integral oblique lattice can be considered as the centering of a rectangular lattice. Indeed, the rationality of $(c/a)\cos\beta$ and of $(c/a)^2$ implies that of $[(c/a)\sin\beta]^2$. In a coarse-grained description, the rationality of $(c/a)\cos\beta$ is difficult to recognize, because the observed values are practically restricted to the interval 0–1 (see Fig. 2). Therefore, it is more convenient to replace this condition with that of $[(c/a)\sin\beta]^2$ and to look at the two frequency distributions as
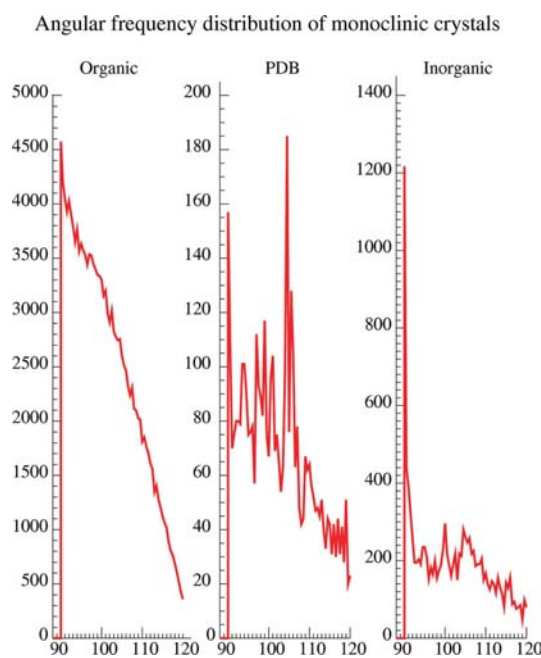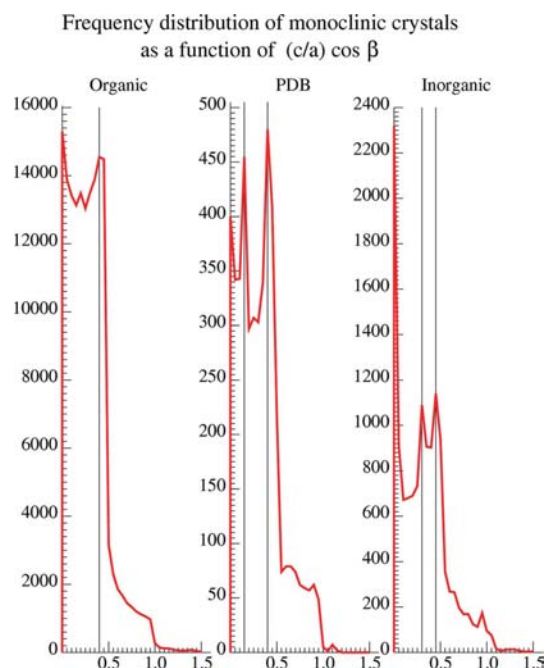

Figure 1
Frequency distributions of monoclinic crystals as a function of the β angle, with $\beta \geq 90°$ and the coarse-graining parameter $\delta_0 = 0.5°$. Left-hand side: organic and metal-organic crystals; center: bio-macromolecular crystals; right-hand side: inorganic materials.

Figure 2
Frequency distributions as in the previous figure, here as a function of $(c/a)\cos\beta$, with $a \leq c$ and a coarse-graining parameter $\delta = 0.05$.
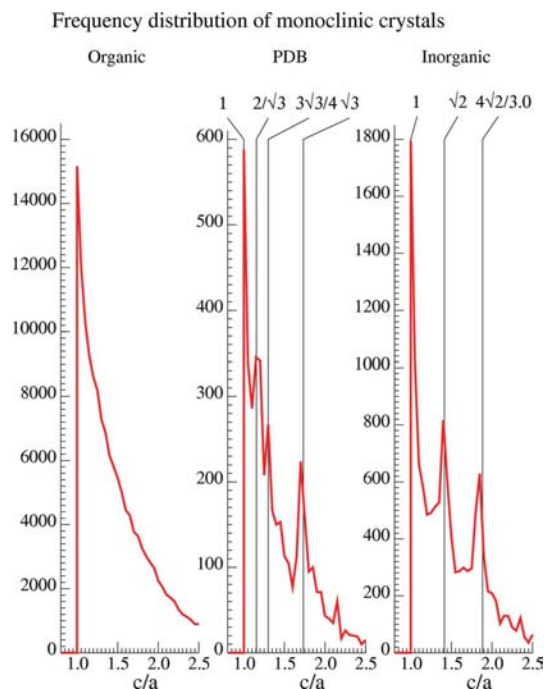
Figure 3
Frequency distribution of monoclinic crystals as a function of the oblique axial ratio c/a, with $a \leq c$ and $\delta = 0.05$ [as in Fig. 2 for $(c/a)\cos\beta$]. In all three cases (organic and metal-organic, bio-macromolecular and inorganic crystals) the largest peak occurs at the isometric ratio $c/a = 1$. The assignment of the peaks to the values indicated does not ensure that the corresponding lattices are integral.
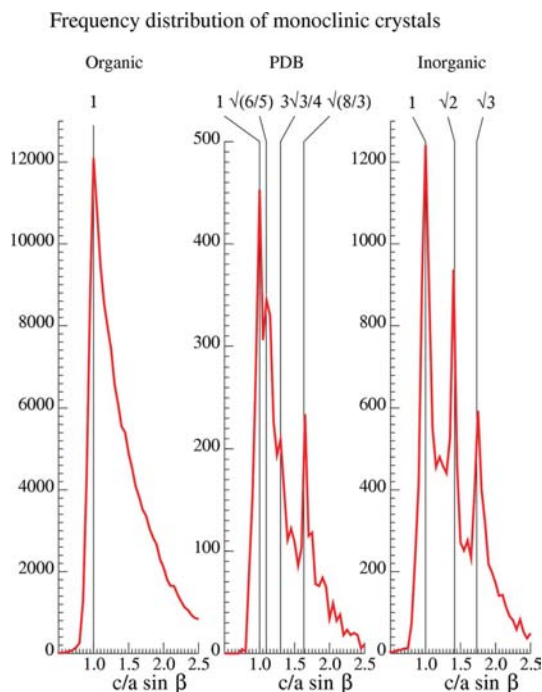
a function of c/a and of $(c/a)\sin\beta$, as shown in Figs. 3 and 4, respectively, for the CSD, the PDB and the ICSD monoclinic crystals. In all cases the general behavior is similar to that of the orthorhombic lattices presented in Part I as a function of c/b, which plays a similar role to c/a here. The following is found: a pure exponential decay from a maximum at the isometric ratio 1 for the CSD crystals (*cf.* Fig. 2 of Part I); the combination of an exponential decay with a number of peaks in the PDB case (*cf.* Fig. 4 of Part I), and finally more pronounced sharp peaks for the inorganic ICSD crystals (*cf.* Fig. 6 of Part I). In all cases, the isometric ratio $a = c$ gives rise to the highest peak. The occurrence of peaks at the same value of c/a and $(a/c)\sin\beta$ is due to the dominance of the $\beta = 90°$ angle observed in Fig. 1, which is also visible in Fig. 2. The peaks have been assigned to the square roots of simple rational numbers, but the identification does not ensure that the oblique lattices are integral, because to assign integrality one has to consider the intersection of each peak population of one plot with that of the peaks of the other plot. One can restrict the considerations to the integral rectangular lattices determined by the assignments indicated in Fig. 4, which occur as sublattices in the corresponding oblique lattices. In this respect, the three peaks at 1, $2^{1/2}$ and $3^{1/2}$ observed in the distribution of the inorganic monoclinic lattices as a function of $(c/a)\sin\beta$ are the most remarkable. It is hard to believe that these values are purely accidental, but, again, more studies are needed to substantiate this.
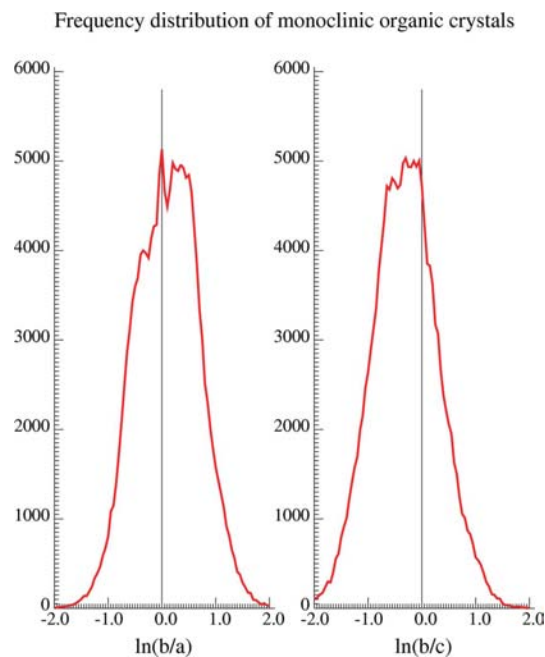

Figure 4
Frequency distribution of monoclinic crystals as a function of the rectangular axial ratio $(c/a)\sin\beta$, with $a \leq c$ and $\delta = 0.05$ (as in Fig. 3). The labeling of the peaks corresponds to the integral rectangular sublattices of the corresponding monoclinic ones.

Figure 5
Frequency distribution of monoclinic organic and metal-organic crystals as a function of $\ln(b/a)$ and $\ln(b/c)$, respectively. These curves imply that the rectangular sub-lattices in the corresponding axial planes (b, a) and (b/c) are generic (without specific relations of their lattice parameters). Nevertheless, also in this case, the maximal frequency occurs at the isometric ratio 1.

2.2. Lattices in the axial planes (b,a) and (b,c)

In the axial lattice planes, the two-dimensional (b, c) and (b, a) lattices are rectangular and angular dependence must not be taken into account (which nevertheless still plays a role in the three-dimensional monoclinic lattice). As in both cases ratios greater and smaller than 1 occur, it is better to plot the frequency distribution as a function of the logarithm of the lattice parameter ratios rather than as a function of the ratios themselves (the reason has already been explained in Part I). The general trend is as expected from Part I. There are virtually no peaks in the distributions of organic and metal-organic compounds (Fig. 5), and in the other cases the sharp peaks could be assigned to axial ratios of integral rectangular lattices. The difference in behavior between the bio-macro-molecular crystals (Figs. 6 and 7) and the inorganic crystals (Figs. 8 and 9) is less pronounced than in the three-dimensional hexagonal and tetragonal cases. Again, the isometric ratio 1 (at 0.0) is represented by one of the most important peaks of all these distributions.

2.3. Pseudo-orthorhombic and pseudo-tetragonal monoclinic lattices

In the angular distribution of monoclinic crystals, the $\beta = 90°$ angle gives rise to the most important peak (Fig. 1). As already mentioned, this peak corresponds to pseudo-

Figure 7
Frequency distribution of the same set of monoclinic crystals as in the previous case (Fig. 6), now as a function of $\ln(b/c)$. As in Fig. 6, the values assigned to the more pronounced peaks indicate the axial ratio of the corresponding integral rectangular sub-lattice in the plane (b, c).
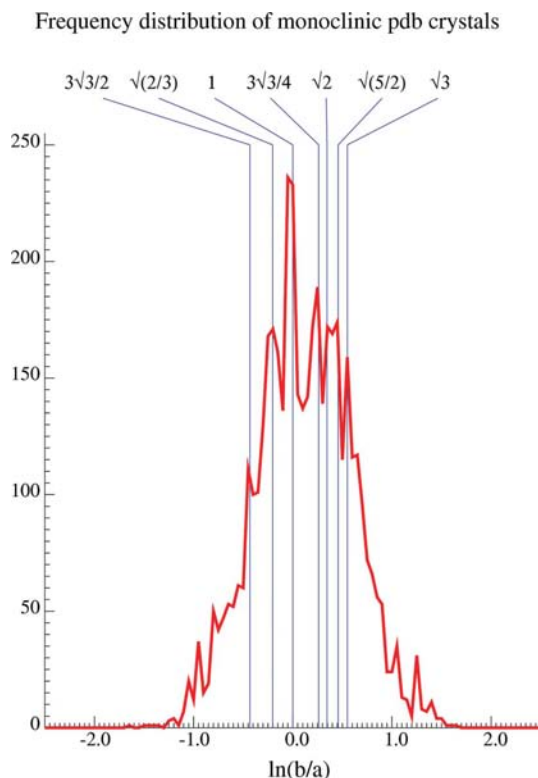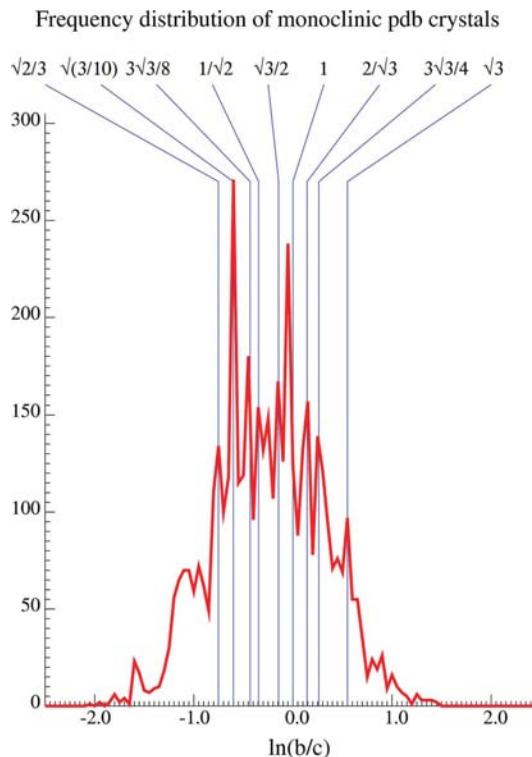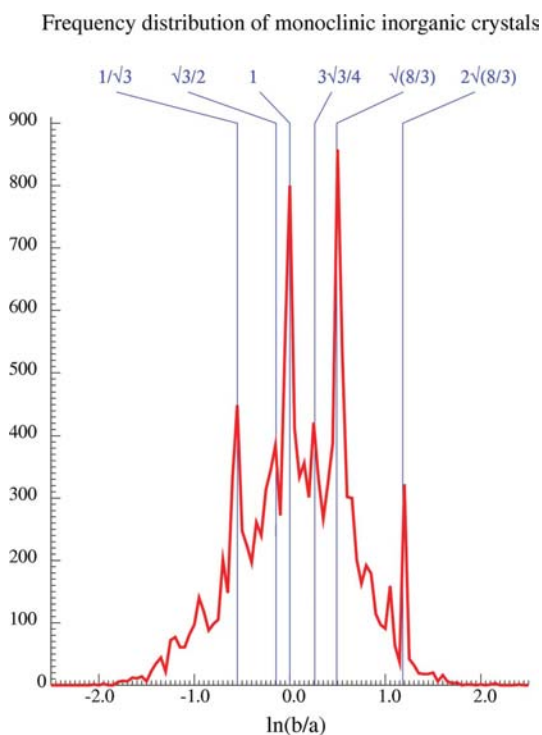

Figure 6
Frequency distribution of monoclinic bio-macromolecular crystals as a function of $\ln(b/a)$. In addition to a background contribution similar to that of the organic case (Fig. 5), a number of peaks appear, which can be assigned to integral lattices. The rectangular sub-lattice in the (a, b) plane is characterized by the axial ratio indicated.

Figure 8
Frequency distribution of monoclinic inorganic crystals, plotted in the same way as in Fig. 6.

Frequency distribution of monoclinic inorganic crystals

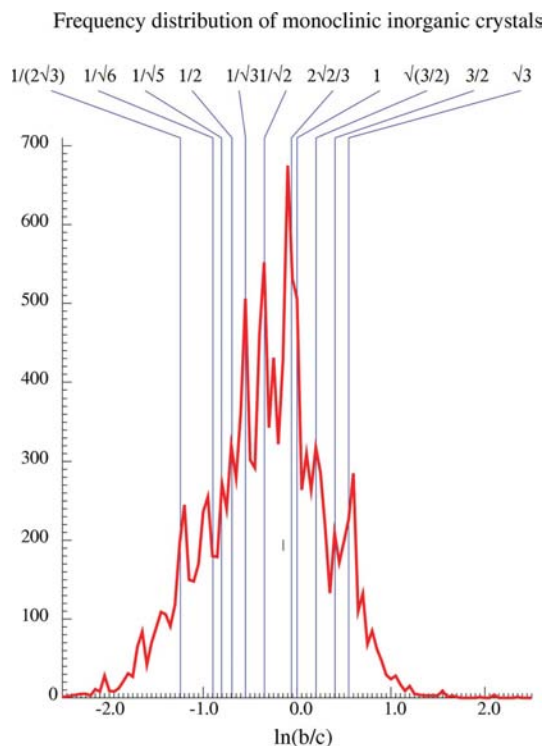1/(2√3)   1/√6   1/√5   1/2   1/√3 1/√2   2√2/3   1   √(3/2)   3/2   √3

Figure 9
Similar plot as in Fig. 7 for the frequency distribution of monoclinic inorganic lattices with respect to the axial plane (b, c).

orthorhombic lattices (with $90 \leq \beta \leq 90.5°$). Approximately 10% of all inorganic monoclinic crystals have such a pseudo-orthogonal lattice. This percentage drops to 4% for the biomolecular crystals and to 3% for the organic and metal-organic crystals.

In addition, in practically all the two-dimensional lattices analyzed above (Figs. 3–9) it is the square lattice which gives rise to the most important peak. One may therefore expect that pseudo-tetragonal lattices will appear above the level of statistical fluctuations, at least for the CSD and the ICSD collections, which have a sufficiently large number of monoclinic crystals (15 600 and 13 000, respectively). Fig. 3 shows that among the organic and metal-organic compounds, 15 164 monoclinic crystals satisfy the condition of having the ratio $1.0 \leq c/a \leq 1.05$, for any value of β. This represents 9.7% of the monoclinic population. For the inorganic crystals the corresponding figures are 1795 and 13.7%. These figures drop to 967 (0.6%) and 311 (2.4%), respectively, when the additional condition $90 \leq \beta \leq 90.5°$ is imposed. In both cases, the frequency distribution of the pseudo-tetragonal monoclinic lattices shows a number of peaks, which could be brought into correspondence with tetragonal integral lattices. Moreover, as in Part I, the exponential component is fairly important for the organic and metal-organic compounds (Fig. 10) and practically absent in the case of the inorganic crystals (Fig. 11). These observations strengthen the argument that the distributions

Frequency distribution of monoclinic organic crystals with pseudo-tetragonal lattice

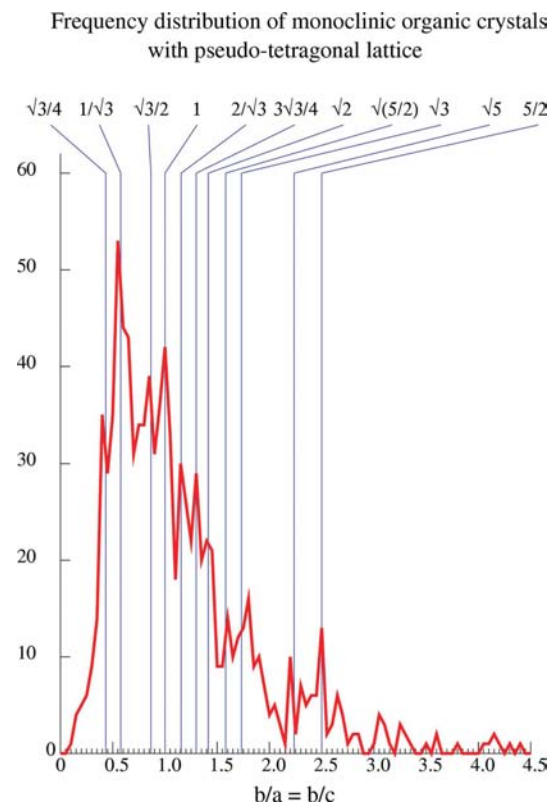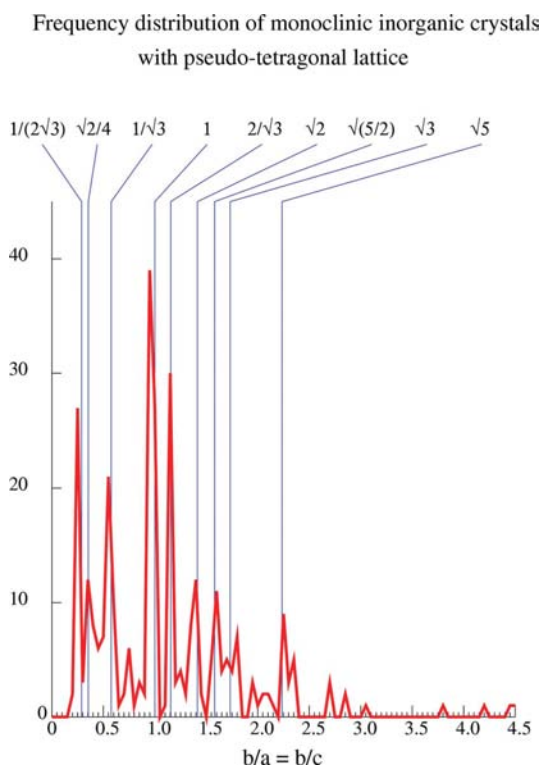√3/4   1/√3   √3/2   1   2/√3 3√3/4   √2   √(5/2)   √3   √5   5/2

Figure 10
Frequency distribution of monoclinic organic crystals with a pseudo-tetragonal lattice ($a \simeq c$, $\beta \simeq 90°$). Many sharp peaks, which do appear in Fig. 5 because they all belong to a common part of the two plots, can be assigned to tetragonal integral lattices.

Frequency distribution of monoclinic inorganic crystals with pseudo-tetragonal lattice

1/(2√3)   √2/4   1/√3   1   2/√3   √2   √(5/2)   √3   √5

Figure 11
Similar plot to that shown in Fig. 10, but for the inorganic crystals with a pseudo-tetragonal monoclinic lattice (with $a \simeq c$, $\beta \simeq 90°$). These peaks are hidden in the common part of Figs. 8 and 9. The exponential component which occurs in those two plots no longer appears, as already observed for pseudo-tetragonal orthorhombic crystals (Fig. 16 of Part I).

reflect real properties and are not simply accidental. This could be the case for each individual peak, assigned or not to an integral lattice.
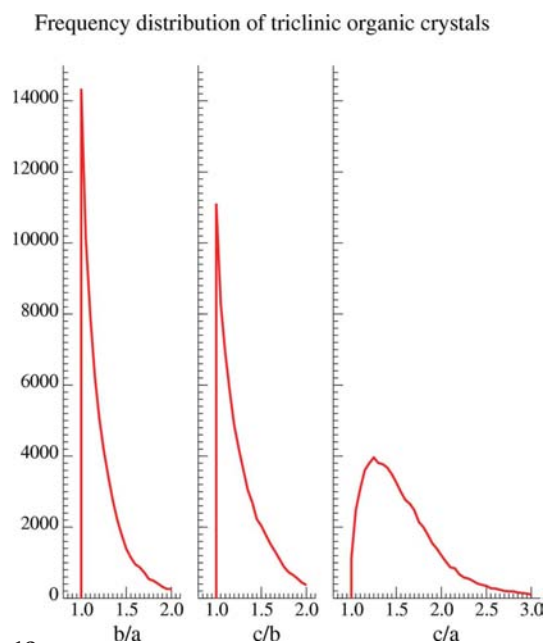

Figure 12
Frequency distribution of triclinic organic and metal-organic lattices. These plots are similar to those presented in Part I for the corresponding orthorhombic crystals (see Figs. 1, 2 and 3 of Part I). The peaked component is practically absent.
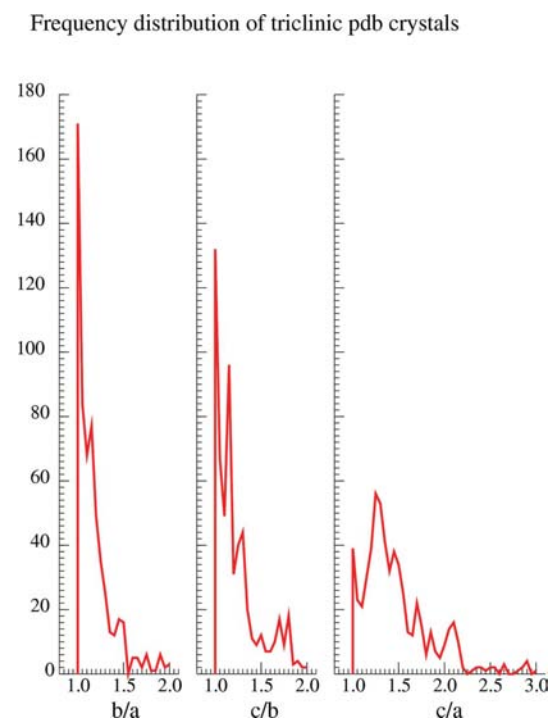

Figure 13
In the frequency distribution of triclinic bio-macromolecular crystals as a function of the three possible ratios, there are peaks in addition to the exponential component, as in many other cases. These peaks cannot be labeled by the corresponding ratios of integral lattices, because of the hidden dependency from the angular parameters.

3. Triclinic crystals

The fairly large number of parameters needed for the characterization of a triclinic lattice (three lengths a, b and c, and three angles α, α and γ) require ordering and a simple presentation. The ordering adopted is $a \le b \le c$, with angles not smaller than $90°$. Moreover, the frequency distribution has been considered for the ratios b/a, c/b and c/a, dismissing their statistical correlation, due to the relation $c/a = (c/b)(b/c)$, and to the ordering adopted, so that $c = a$ implies $c = b$. This last fact is reflected in the different behavior of the c/a distribution with respect to the two others. To make comparison easier, the frequency distributions as a function of the three ratios, for each of the triclinic crystal sets (CSD, PDB and ICSD), have been included in one single figure, and plotted at the same scale independently of the height of the peaks. The same rules have been adopted for the frequencies as a function of the three angular parameters.

The frequency distributions decay, as expected, exponentially as a function of (increasing) b/a and c/b ratios, from a maximum at the isometric ratio 1 (Figs. 12, 13 and 14). This is no more so for the ratio c/a (as in the orthorhombic case of Part I), because of the additional restriction imposed on b at the initial point $c = a$. The isometric peak is higher for $b = a$ than for $b = c$. The reason for this is not clear, but it must reflect a general law, because the same can be said for all the 70 000 triclinic crystals involved. In the distributions of the inorganic and the bio-macromolecular crystals there are additional sharp peaks, whereas these peaks are absent (as usual) in the organic and metal-organic distributions. No
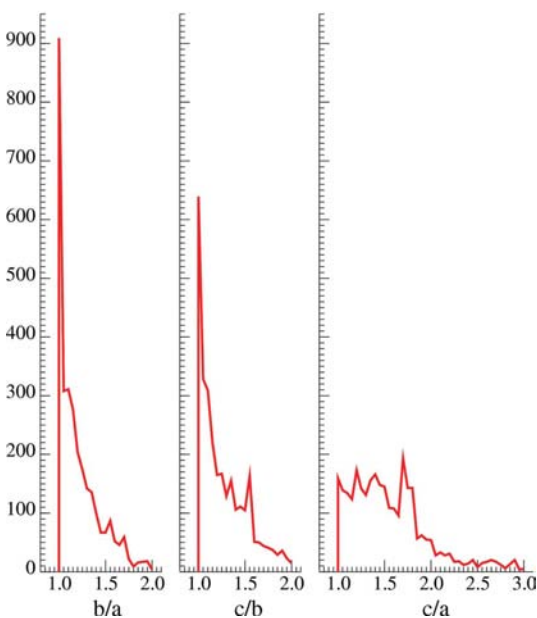

Figure 14
Frequency distributions of triclinic inorganic crystals as a function of lattice-parameter ratios. These distributions are similar to those of the previous figure. The same comment also applies here.

attempt has been made to assign the sharp peaks to integral lattices. Such an assignment would require a transformation of the corresponding data to (centered) orthorhombic lattices.
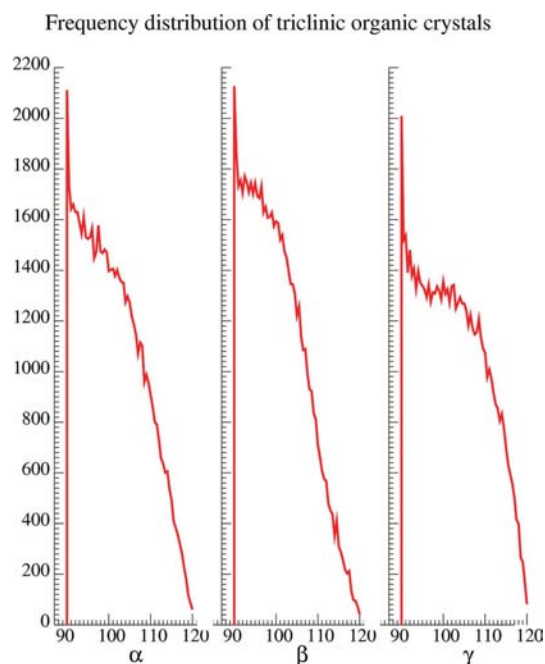

Figure 15
Frequency distribution of triclinic organic and metal-organic crystals as a function of the three angular parameters. Note the similar behavior of the three triclinic angles to the one of the monoclinic distribution (Fig. 1, left-hand side).
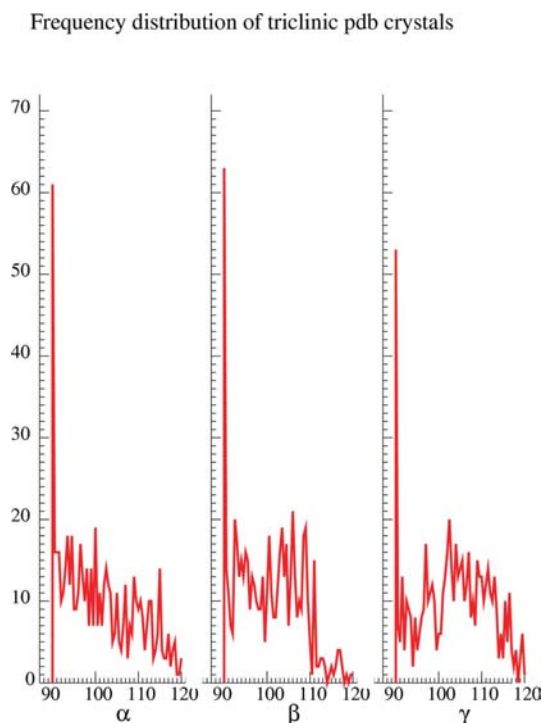

Figure 16
Angular frequency distribution of triclinic bio-macromolecular crystals, again showing similar behavior, but somewhat different from the corresponding monoclinic angular distribution (Fig. 1, central plot).

This is in principle possible, because integral triclinic lattices are rationally equivalent to orthorhombic ones, as explained in another paper (Janner, 2004). However, before doing so, it is desirable to have a better insight into the relation between crystal structures and integral lattices.

The angular distribution as a coarse-grained function of α, β and γ, does not seem to reflect the ordering of the remaining lattice parameters $a \leq b \leq c$. In all cases the dominant peak occurs at an angle of $90°$. For each of the angles this largest peak represents *ca* 2100 lattices in the organic and organo-metallic case, which corresponds to 3% (see Fig. 15), 60 lattices for the bio-macromolecular crystals (10%, Fig. 16) and 300 lattices (also 10%) for the inorganic crystals (Fig. 17). The general behavior is the same for the three angular distributions of a given class of crystals and correspondingly similar to the angular distribution observed for the monoclinic crystals (see Fig. 1). Again, these similarities strengthen the confidence in the existence of general laws underlying the observed distributions.

4. Conclusions

The basic features of the frequency distributions as a function of lattice-parameter ratios reported in Part I for the hexagonal, tetragonal and orthorhombic crystals also occur for monoclinic and triclinic crystals, *i.e.* an exponential decay by increasing ratios and sharp peaks, possibly due to integral lattices, with one of the most important peaks at the ratio
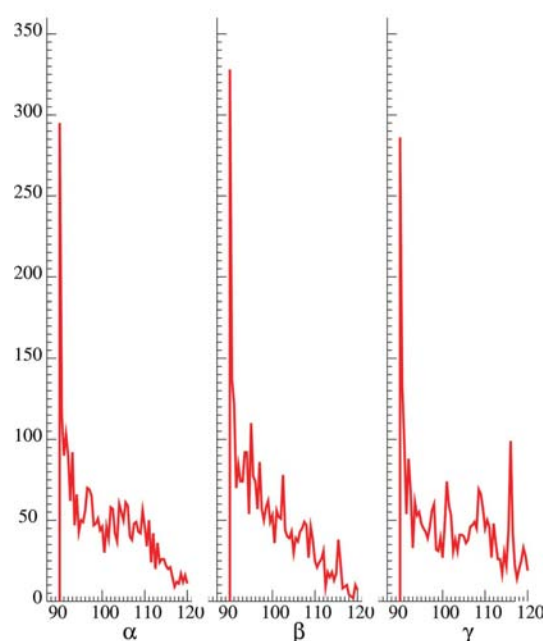

Figure 17
Frequency distribution of triclinic inorganic crystals, as a function of the three angles. In this case, the monoclinic and triclinic angular distributions show similar behavior, characterized by one single important peak at $90°$ and a relatively small noisy component for larger angles.

value 1. This implies that these properties have a general validity, independent of specific details not taken into account in the data plotted, such as lattice centering and/or choice of reduced cell.

The new element of this second part is represented by the angular parameters. The corresponding frequency distributions show similar behavior as a function of the various angles α, β and γ. They are essentially different for the organic and metal-organic crystals with respect to the bio-macromolecular and inorganic crystals. In nearly all cases, the maximum distribution observed is at an angle of $90°$.

The facts mentioned have been interpreted as being due to general geometrical properties, without, however, being able to give any structural support outside the crystallographic properties of the lattice systems involved. In particular, the following interpretation has been adopted:

(i) The exponential component is due to generic lattices, as usually considered.

(ii) Each important peak is associated with integral lattices having (approximately) the same axial ratio.

(iii) The number of relevant peaks can be fairly large (say between 10 and 20). In this case the assignment to integral lattices is more a guess than a property.

(iv) There are distributions showing only a few important peaks at integral-lattice ratios, which can barely be accidental. The ratios indicated determine the (approximate) geometrical properties of all the crystal lattices of the given peak, independent of whether this value is accidental or structural. Examples of the geometrical properties of integral lattices have been studied elsewhere for a number of hexagonal and tetragonal cases (Janner, 2004).

Most of these features do not follow from classical crystallographic principles. Some of these properties can be interpreted on the basis of a general crystallography, where crystallographic scaling and point groups of infinite order were considered (Janner, 2001). Possibly additional structural principles are needed to explain the observations. One is conjectured here and tentatively formulated as follows:

> **Principle of minimal number of structural parameters**: Within a given equivalence class of structures, there is a natural tendency to reduce the number of free parameters.

Most of the properties presented in this survey can be seen as a consequence of this general principle. For example, an isometric ratio (and, in general, a ratio implying an integral lattice) reduces the number of lattice parameters required by one. For the monoclinic and triclinic lattices, this is also the case if an angle is $90°$ and not generic.

The challenging crystallographic properties observed in a number of axial-symmetric proteins (Janner, 2005a,b,c) are also compatible with this principle.

A symmetry principle does not substitute for a theory. However, such a theory is still missing and is needed.

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