short communications

Integral lattices

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Most of the sharp peaks, recently reported by Constant & Shlichta [*Acta Cryst.* (2003), A**59**, 281–282], in the frequency distribution of known tetrahedral and hexagonal–rhombohedral inorganic compounds apparently correspond to integral lattices. These are characterized by an integral metric tensor of their basis vectors (up to a unit-length factor). Integral lattices also occur in molecular forms of axial-symmetric biomacromolecules, as illustrated by a RNA quadruplex. A general tendency in nature to reduce the number of structural free parameters is conjectured.

1. Introduction

An integral lattice is a lattice compatible with an integral metrics. It means that there is a unit of length such that the metric tensor of the scalar product of the basis vectors of the lattice has integral entries. This property does not depend on the lattice basis selected. Metric tensors for different choices of the unit length only differ by a positive constant factor and are considered to be equivalent. Accordingly, the rational case is equivalent to the integral one. In two dimensions, the square and the hexagonal lattices are integral, whereas the oblique, rhombic and rectangular lattices are not, at least not in the general case. In the conventional choice of the basis of the hexagonal lattice and with a unit of length given by the lattice parameter a, the metric tensor g_{ik} is rational: $g_{11} = g_{22} = 1$ and $g_{12} = g_{21} = -1/2$. By choosing $\sqrt{2}a$ as unit of length, one gets the integral case, the corresponding constant factor being $2a^2$. In three dimensions, only the cubic lattices are integral, whereas generic hexagonal ones are not. One only gets an integral hexagonal lattice for special values of the c/a ratio as, for example, in the hexagonal close-packing case (h.c.p. lattice) with $c/a = \sqrt{8/3}$. The corresponding metric tensor is rational, up to the constant factor a^2, so that the h.c.p. lattice is integral. Another well known integral lattice is the hexagonal 'cubic' lattice, considered by Frank (1965), also associated with a specific mode of packing, where the c/a ratio is $\sqrt{3/2}$. Despite their structural relevance, the special character of these hexagonal lattices does not affect their crystallographic characterization in terms of Bravais class, crystal class, holohedry and so on. Only within a general crystallography (Janner, 2001), where point groups of infinite order occur leaving a lattice invariant, is the symmetry of integral lattices, in general, larger than in the generic real case. This has been shown, in particular, in the case of ice (Janner, 1997). Within classical crystallography, integral lattices do have characteristic properties, for example in terms of diffraction patterns and of packing units, as discussed by Frank (1965) in the 'cubic' hexagonal case mentioned above, and analyzed further by other authors (Singh *et al.*, 1998; Lidin, 1998; Ranganathan *et al.*, 2002). As remarked by Frank (1965), and implicitly taken into account by the other authors, these properties are stable with respect to small deviations from the ideal case. Indeed, the integral lattice can be recovered from the real one by an affine transformation, which only has a perturbative effect on the properties of the ideal case.

Table 1
Frequency peaks of known inorganic hexagonal–rhombohedral crystals [according to Constant & Shlichta (2003), from Donnay & Ondik, (1973)].

Remark: the change in slope at $c/a = 1$ has been interpreted as a non-resolved peak.

Frequency $N(c/a, 0.1)$	Peak at c/a	Integral lattice c/a	Frequency $N(c/a, 0.1)$	Peak at c/a	Integral lattice c/a
390	0.9	$\sqrt{3}/2 = 0.86\ldots$	65	3.2	$2\sqrt{8/3} = 3.26\ldots$
280	1.0	1.0	35	3.7	$\sqrt{14} = 3.74\ldots$
145	1.2	$\sqrt{3/2} = 1.22\ldots$	40	3.9	$\sqrt{15} = 3.87\ldots$
130	1.4	$\sqrt{2} = 1.41\ldots$	25	4.3	$\ldots$
420	1.6	$\sqrt{8/3} = 1.63\ldots$	25	4.5	$\sqrt{20} = 4.47\ldots$
65	2.4	$\sqrt{6} = 2.45\ldots$	48	4.9	$3\sqrt{8/3} = 4.89\ldots$
80	2.7	$\sqrt{15/2} = 2.73\ldots$			

Table 2
Frequency peaks of known inorganic tetragonal crystals [according to Constant & Shlichta (2003), from Donnay & Ondik (1973)].

Frequency $N(c/a, 0.05)$	Peak at c/a	Integral lattice c/a	Frequency $N(c/a, 0.05)$	Peak at c/a	Integral lattice c/a
62	0.35	$1/2\sqrt{2} = 0.35\ldots$	32	1.85	$\ldots$
96	0.55	$1/\sqrt{3} = 0.57\ldots$	73	1.95	2.0
104	0.7	$1/\sqrt{2} = 0.70\ldots$	60	2.13	$3\sqrt{2}/2 = 2.12\ldots$
106	0.86	$\sqrt{3}/2 = 0.86\ldots$	25	2.45	$\sqrt{6} = 2.45\ldots$
125	1.05	$3\sqrt{2}/4 = 1.06\ldots$	9	2.8	$2\sqrt{2} = 2.82\ldots$
37	1.2	$\sqrt{3/2} = 1.22\ldots$	19	3.15	$\sqrt{10} = 3.16\ldots$
65	1.4	$\sqrt{2} = 1.41\ldots$	19	3.3	$7\sqrt{2}/3 = 3.3\ldots$
45	1.6	$\sqrt{5/2} = 1.58\ldots$	12	5.9	$\sqrt{35} = 5.91\ldots$

2. Crystal lattice parameters

Recently, Constant & Shlichta (2003) reported on the variation in abundance of known inorganic crystalline compounds as a function of lattice constants, on the basis of the data tables of Donnay & Ondik (1973). A plot of the frequency as a function of c/a of hexagonal–rhombohedral and of tetragonal compounds shows a number of sharp peaks (Constant & Shlichta, 2003). One of these, at $c/a \simeq 1.6$, corresponds to the h.c.p. lattice discussed above. The aim of the present communication is to support the idea that more peaks occurring in Figs. 1 and 2 of their paper can be associated with integral lattices. The correspondence is given in Tables 1 and 2, where all the important peaks observed are listed, including those that are probably due to statistical fluctuations and not to integral lattices. The

frequencies and the c/a values reported in the tables are approximations deduced from the plots published. $N(c/a, 0.1)$ and $N(c/a, 0.05)$ indicate the number of compounds within each 0.1 and 0.05 range of c/a, respectively. The assignment indicated in the tables is not unique because it is approximate. Structurally relevant are only the square roots of reduced fractions with small entries (involving a few prime factors like 2, 3, 5 and 7). But even in this case, the assignment has purely geometric implications (like characteristic lattice–sublattice scaling relations) and it allows but does not guarantee properties like a higher point-group symmetry or a specific type of packing. A preliminary investigation, in collaboration with R. de Gelder of the Institute for Crystallography of the University of Nijmegen, reveals a similar behavior in the frequency distribution of crystals of small organic molecules, of crystals of biomacromolecules and of a larger class of inorganic crystals representing together about 40 000 hexagonal and tetragonal entries.

3. Molecular forms

The molecular forms of axial-symmetric proteins and of helical nucleic acids also point out the possible structural importance of integral lattices. In these cases, the inner and outer envelopes of the molecule can be chosen with vertices at points of a lattice possibly having a larger point group than the symmetry of the molecule. As illustration, the case of the RNA guanosine-5′-phosphate quadruplex is presented (Zimmerman, 1976). More examples will be reported elsewhere. This RNA forms a quadruple helix generated by a planar arrangement of four rG nucleotides (Zimmerman, 1976), which is the molecular unit considered here. The envelope of this molecule is tetragonal. The basis square of the outer envelope is scaled by a factor 6 with respect to the square of the inner envelope, which is that of the central channel (Fig. 1). This channel defines an integral tetragonal lattice with parameters a and $c = 2a$, a sublattice of the cubic lattice. The value of the cubic parameter is given by the minimal atomic distance of the guanine O(6) atom from the fourfold axis ($a = r = 2.28$ Å). With respect to the cubic basis, the indices of point-group representatives of the vertices of the molecular form are [100], [102] for the inner envelope and [600], [602] for the outer envelope. An intermediate tetragonal form with vertices at [330] and [332] separates the four bases guanine from the backbone of the sugar–phosphate molecules.

4. Conclusions

The integral lattices observed can be placed in the more general context of a tendency in nature to reduce the number of free parameters, within a given equivalence class of structures. So, for example, the two unit-cell parameters a and c of the tetragonal and the hexagonal system, respectively, are reduced to a single one (say a) in the corresponding integral lattice cases. The general situation can be analyzed further according to facts (the *what*), properties (the *which*) and reasons (the *why*). The main facts underlying the present note are:

– sharp peaks in the frequency distribution of crystals as a function of lattice parameters;

– rational axial ratios a^2/c^2 for most of the pronounced peaks in the distribution of crystals and for a number of axial-symmetric biomacromolecules (one case only is reported here);

– intrinsic properties of integral lattices (independent of their point-group symmetry), currently investigated in mathematics as integral quadratic forms (positive definite and indefinite ones).

Only a few of the properties of these facts have been taken into account from a crystallographic point of view, like:

– lattice–sublattice relations (revealed *e.g.* in zones of crystal diffraction);

– connection with packing of given structural units (anions, cations, atomic clusters, small or large single molecules, and so on);

– relations between the position of a diffraction spot and its intensity and phase (beyond general and special extinction rules and direct methods).

In order to recognize whether a given integral lattice is interesting or not, one needs, in addition to the properties, an insight into the possible reasons for the phenomena observed. These reasons could be:

– purely accidental (an appropriate statistical analysis is required for avoiding what is commonly denoted as *numerology*);

– due to perturbative effects (lattice parameters are less sensitive to small shifts in the atomic positions than point-group and space-group symmetries);

– based on clear geometrical principles (like close packing or rational approximants of quasicrystals);

– due to hidden symmetries (often expressible in a higher-dimensional description as for the Frank phase and/or in terms of non-Euclidean symmetries, like crystallographic scaling);

– still unknown geometrical principles.

A number of the integral lattices indicated in Tables 1 and 2 are possibly uninteresting, other ones are as expected to occur, but worth investigating further. Some intriguing cases remain that could change the conceptual frame of crystallography. For the author, most mysterious is the molecular case, where polygrammal scaling, lattice–sublattice relations and rational axial ratios involve integral lattices of various dimensions.
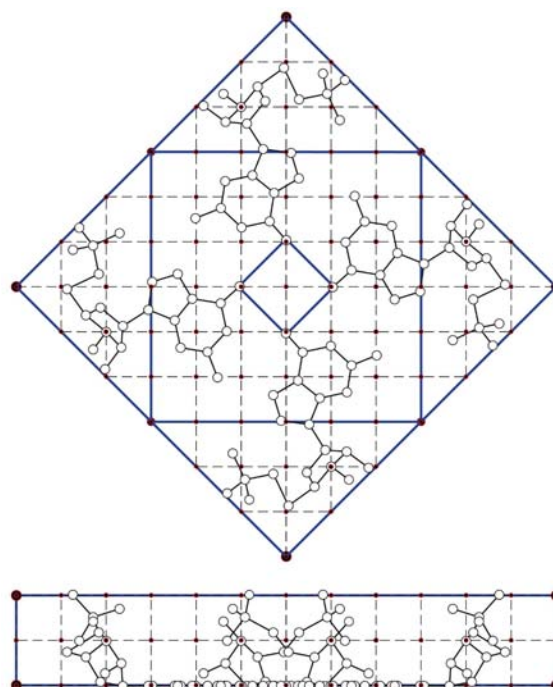

Figure 1
Tetragonal and cubic molecular form lattices of RNA guanosine-5′-phosphate quadruplex. The cubic lattice parameter a is given by the minimal axial distance of the guanine O(6) atom ($a = r = 2.28$ Å).

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