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Crystal nets as graphs: Terminology and definitions

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Abstract

Definitions from graph theory relevant to the nets of crystal chemistry are reviewed. This is followed by a summary of recent developments in the formal description of such structures.

Keywords: Graphs; Nets

1. Introduction

Since the first extended crystal structures were determined nearly 100 years ago, it has been commonplace to describe them as nets, which are special kinds of graphs. In recent years there has been an explosive growth of interest in the subject, as attested, for example, by the contributions to this issue of the *Journal of Solid State Chemistry*. In this paper, we give an informal account of recent developments in the description of such nets as graphs. The subject has developed sporadically, with contributions from chemists, crystallographers and mathematicians often working in ignorance of each other's contributions, and often using inconsistent terminology. Accordingly we first offer some definitions that represent an attempt to outline a logically consistent set that might serve as a starting point towards the adoption of a more formal agreed set of definitions and nomenclature in the future.

2. Basic definitions in graph theory

A useful compilation of definitions in graph theory has been given by Essam and Fisher [1]. Some of the definitions here are based on that more-comprehensive work.

A graph consists of *vertices* labeled $i, j, \ldots$ and *edges* corresponding to pairs of vertices (i, j). If the pair (i, j) is distinguished from (j, i) then the edges are *directed* and the graph is *directed*. A directed edge is sometimes called an *arc*. There may be more than one edge for a given pair of vertices; in that case the edges are no longer *simple* edges. A *loop* is a special kind of edge (i, i). A *simple graph* is one that has simple undirected edges and no loops.

Vertices connected by an edge are *neighbors*, and the set of neighbors of a vertex is the *neighborhood* of that vertex. (But notice that for an embedding of a structure, the term "neighbors" of a point usually refers to points the shortest distance away—usually the context makes the sense clear).

The *coordination number* of a vertex is the number of edges incident on the vertex. In graph theory the coordination number is also called the "valence" or "degree", but "valence" has a different meaning for chemists, so it is avoided. Conversely a graph with n-coordinated vertices is often called "n-connected" by chemists, but this term has a quite different meaning (see below) in graph theory and is also avoided. If all the vertices of a graph have the same coordination number, n, the graph is often called *n-regular*.

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A *path* (*chain*) is a sequence of vertices ($x_1, x_2, \ldots, x_n$) such that (x_1, x_2), (x_2, x_3)… (x_{n-1}, x_n) are directed (undirected) edges.

A *circuit* (*cycle*) is a closed path (chain) in which the first and last vertices are the same ($x_1, x_2, \ldots, x_{n-1}, x_1$). These are *elementary* if no edge or vertex occurs more than once. (For a circuit or cycle we count the beginning and end vertices as one). References to cycles below always means elementary cycles.

A *connected* graph is one in which there is at least one chain between all pairs of vertices.

Deletion of a vertex means removing that vertex and all edges incident upon it.

An *n-connected graph* is one with at least $n+1$ vertices for which there is no set of $n-1$ vertices whose deletion would leave the graph no longer connected.

The *adjacency matrix* for a finite graph containing n vertices is an $n \times n$ matrix in which the i, j element is 1 or 0 according to whether there is or is not an edge connecting vertices i and j.

An *embedding* of a graph is a realization of the graph (e.g., with coordinates for vertices) in Euclidean space. In a *faithful* embedding, edges are not allowed to intersect or to touch vertices other than those at their end points.

A *planar graph* has a faithful embedding in two dimensions.

An *automorphism* of a graph is a one-to-one correspondence between the vertices of the graph which induces a one-to-one correspondence between its edges.

The *graph group* of a graph is the abstract group formed from the set of automorphisms of the graph.

Two graphs are *isomorphic* if there is a one to one correspondence between the vertex sets that induces a one-to-one correspondence between their edge sets (Fig. 1).

Two embeddings of a graph that can be deformed into each other are *ambient isotopic.* Note that at no point in the deformation may edges intersect or have zero length. Clearly ambient isotopy implies isomorphism (but not vice versa). See Fig. 1

The *complete graph* K_n has n vertices each connected to all the others.

A *tree* is a connected graph that contains no cycles.

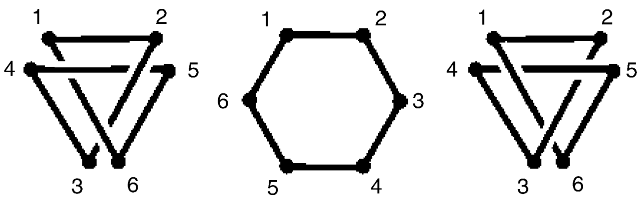

Fig. 1. Three embeddings of the same graph (i.e., the three graphs are isomorphic) that are not ambient isotopic. The left and right embeddings are chiral and of opposite hand.

A *spanning tree* of a connected graph is a tree in which all the vertices are connected by edges taken from the graph. If there are v vertices in the graph there are $v-1$ edges in a spanning tree.

A *Bethe lattice* is an infinite tree in which every vertex has the same coordination number (>2).

The *cyclomatic number* of a connected graph is the number of edges that have to be added to complete the full graph from a spanning tree. If there are e edges in the graph the cyclomatic number is $e-(v-1) = 1+e-v$.

The term *net* is commonly used in crystal chemistry, but rarely defined. We take it to mean a periodic connected simple graph.

An *n-periodic* net has a realization (which is not necessarily a faithful embedding) with translational symmetry in exactly n independent directions.

An n-dimensional net, or graph, permits a faithful embedding in n-dimensional space, but not in $n-1$ dimensional space. A planar graph, such as the graph of any convex polyhedron is 2-dimensional. K_5 is the smallest (i.e., least vertices) non-planar graph. All graphs have a faithful embedding in 3-dimensional Euclidean space.

One should not refer to an n-periodic net as "n-dimensional".

3. Rings, ring sums, and strong rings

Unfortunately the term "ring" in mathematics has a definite meaning in algebra, but the term is central to chemistry and the chemical sense is unavoidable. Unfortunately too, there is some disagreement among chemists on the meaning of the term and how best to identify rings in complex molecules. Molecular chemists [2] consider all cycles to be rings, but consider a molecule to be n-cyclic if n is the cyclomatic number of the molecular graph. Thus cubane, for example, is pentacyclic (Fig. 2).

It is convenient at this point to define a *cycle* (or *ring*) *sum*. The sum of two cycles is the set of all edges contained in exactly one of the cycles. A straightforward generalization is to the sum of a number of cycles as the set of all edges that occur an odd number of times in the set of cycles.

Solid state chemists define a *ring* as a cycle that has the property that there is no shorter path ("short cut") between two vertices on the cycle than the shortest one that is part of the cycle. This is equivalent to defining a ring as a cycle that is not the sum of two shorter cycles. (Fig. 2). An n-ring has n edges. Notice that the graph of cubane contains six 4-rings. The total number of distinct cycles in the cubane graph is 28 (the reader may enjoy identifying them), but they can all be derived as sums of one or more of a set of five face rings (the sum of all five is the sixth face), and this set of five is known as the

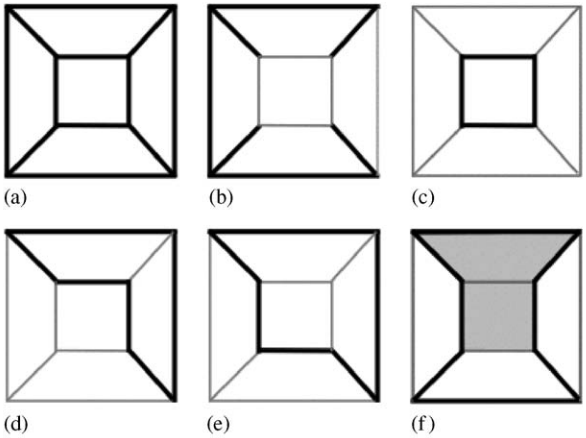

Fig. 2. Reference is to the heavy lines: (a) The graph of a cube; (b) a spanning tree of that graph; notice that cyclomatic number is 5; (c) a strong ring; (d) a 6-cycle that is the sum of two 4-rings, and hence not a ring; (e) a 6-cycle that is the sum of three smaller rings but not of two—it is therefore a ring, but not a strong ring; (f) an 8-cycle that is the sum of a 6-cycle (shaded: itself the sum two 4-cycless) and a 4-cycle and hence not a ring.

smallest set of smallest rings (SSSR).[1] Considerable effort has been devoted to devising efficient algorithms for identification of minimal sets of rings for molecules [3,4].

It might also be noticed that the graph of cubane also has 6-rings (Fig. 2 again) that are the sum of three 4-rings. Goetzke and Klein [5] make the useful distinction between rings (as defined here) and *strong rings* defined as rings that are not the sum of *any* number of smaller cycles. It is our belief that in discussing the topology of crystal graphs, one should focus mainly on the cycles that are strong rings. Strong rings have also been called *relevant cycles* in the molecular context [4].

4. Vertex symbols

For most of the periodic nets of fundamental importance in crystal chemistry, there are only a few different kinds of vertex (by a "kind of vertex" we mean a set of vertices related by symmetry operations, including translations), and the local topology is sometimes specified in terms of the size of the shortest rings or cycles at the angles of a vertex. For an n-coordinated vertex there are $n(n-1)/2$ angles and usually one of two kinds of symbol is used.

I. The *point symbol* [6] or *Schläfli symbol* [7] is of the form $A^a.B^b.C^c\ldots$ in which $A<B<C<\ldots$ and $a+b+c\ldots = n(n-1)/2$ and signify the length (A, B, $C\ldots$) and numbers (a, b, $c\ldots$) of the shortest cycles contained in each of the angles. Thus for the 4-coordinated diamond net for which all the shortest cycles are 6-cycles the symbol is 6^6. For the net of the 6-coordinated primitive cubic lattice the point symbol is $4^{12}6^3$.

II. The *vertex symbol* or *long symbol* [8,9]. Here the size of the shortest *ring* at each angle is given with a subscript to denote the number of such rings. Thus in the familiar 3-coordinated net of the Si atoms in the $SrSi_2$ structure, symbol **srs**, there are five 10-rings at each angle and the symbol is $10_5 \cdot 10_5 \cdot 10_5$, and for the net **ths** of the Si atoms in $ThSi_2$ structure, with two, four and four 10-rings at each angle, the symbol is $10_2 \cdot 10_4 \cdot 10_4$.

In the case of 4-coordinated nets there are six angles. The net of the 4-coordinated diamond structure, symbol **dia**, with two 6-rings at each angle has symbol $6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2 \cdot 6_2$. In the case of 4-coordinated nets only, the angles are grouped into three pairs of opposite angles in the sequence of a vertex symbol, and subject to that constraint, the smallest numbers come first. For the net of the 4-coordinated atoms in the feldspar structure the point symbol for both kinds of vertex is $4^2 \cdot 6^3 \cdot 8$ and the vertex symbols are $4 \cdot 6 \cdot 4 \cdot 6 \cdot 8_2 \cdot 10_{10}$ and $4 \cdot 6_2 \cdot 4 \cdot 8 \cdot 6 \cdot 6_2$. See [8,9] for more on these symbols which are the ones used e.g., in the *Atlas of Zeolite Framework Types* [10]. It is not necessary that all angles of a 4-coordinated net have rings. If there is not a ring an asterisk is inserted (in early work an infinity sign, ∞, was used). Thus for the 4-coordinated $CdSO_4$ net (this is the net of the Cd, S atoms with –O– links considered as edges), symbol **cds**, the vertex symbol is $6 \cdot 6 \cdot 6 \cdot 6 \cdot 6_2 \cdot *$.

One sometimes see long symbols used for higher coordination, but as the number of angles increases as the square of the coordination number, they soon become cumbersome; the vertex symbol for the 6-coordinated net of the primitive cubic lattice is $4 \cdot 4 \cdot 4 \cdot 4 \cdot 4 \cdot 4 \cdot 4 \cdot 4 \cdot 4 \cdot 4 \cdot 4 \cdot 4 \cdot * \cdot * \cdot *$. A 12-coordinated net has $(12 \times 11)/2 = 66$ angles!

5. Vector representation and quotient graph

The topology of a periodic net is completely given by specifying the edges in the repeat unit (primitive cell) [8]. These edges may be given in the form i, j, u, v, w signifying that the edge connects vertex i in the reference cell to vertex j in the cell displaced from the reference cell by $u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$ (here $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ are primitive lattice vectors). In the diamond net (Fig. 3) there are four edges specified by 1 2 0 0 0, 1 2 1 0 0, 1 2 0 1 0, 1 2 0 0 1. Note that this string of integers *completely* specifies the net and that all topological properties (e.g., ring sizes and combinatorial

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[1] The enumeration of cycles is not entirely trivial, and doing it will indicate the difficulty of the problem for large structures. The number of distinct ways of selecting at least one from a set of g is 2^g-1. Thus for the cube with $g = 5$ independent cycles this is 31. But three combinations correspond to pairs of disjoint 4-cycles (opposite faces) so there are only 28 distinct cycles.

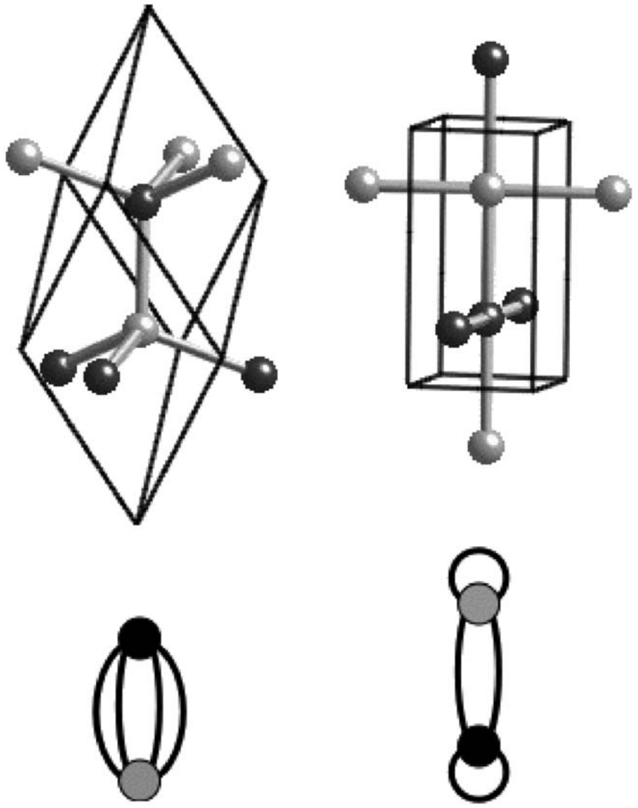

Fig. 3. Top: units of the dia (diamond, left) and cds ($CdSO_4$, right) nets. Below their quotient graphs. The graphs are unlabeled in this instance as the edges must be 0 0 0, 1 0 0, 0 1 0, 0 0 1 (notice that a loop cannot be 0 0 0).

symmetry) can be obtained from it [11]. This is the *vector representation* of a periodic net. What we have described is the analog, for a periodic graph, of the adjacency matrix for a finite graph.

For a finite graph of n vertices there are $n!$ ways of numbering the vertices and the problem of deciding whether two adjacency matrices represent different topologies is far from trivial; indeed it is not even known how difficult it is [12] although for certain types of molecular graph it can be solved in polynomial time [13]. The problem appears to be more acute for periodic graphs as, in addition to the freedom of numbering vertices in the repeat unit, there are also different possible choices of basis vectors (in principle an infinite number of these); however, for nets that permit equilibrium placements (see below) an algorithm has been devised to allow determination in polynomial time [14] of a unique *canonical form* for the string of integers specifying the net, and this is encoded in the program Systre [11] so the problem of determining whether two nets are the same or different is solved in this case (but note, as indicated in the next section, at present Systre only deals with nets that admit barycentric coordinates without collisions).

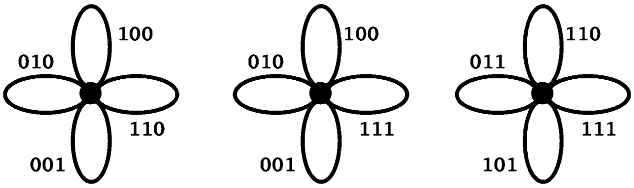

Fig. 4. The quotient graphs for three 8-coordinated nets. Left: the primitive hexagonal lattice (*hP*). Center: the body-centered cubic lattice (*cI*). Right: a rhombohedral net described in the text.

In an important paper, which appears to be the first to indicate how to specify the topology of a periodic net using vector representations, Chung et al. [15] describe the *quotient graph* which is a labeled graph derived as follows. The vertices are the vertices of a repeat unit and the edges are all the edges of the repeat unit labeled *uvw*. Thus for the diamond net, there are four edges linking vertices 1 and 2, labeled respectively 0 0 0, 1 0 0, 0 1 0, 0 0 1. The quotient graph may have loops and multiple edges (Fig. 3).

The cyclomatic number of the quotient graph of a periodic net has been called the *genus* of the net [16]. Beukemann and Klee [17] observe that the minimum genus of an n-periodic net is n and define nets of minimal genus as *minimal nets*. These authors also enumerate all minimal nets of genus 2–4.

In the absence of labels, a quotient graph will, in general, belong to more that one net. Fig. 4 illustrates this point for the simple case of three 8-coordinated nets with one vertex per unit cell. The first two of these are 8-coordinated lattices (hexagonal and body-centered cubic), but notice that structures with one vertex in the repeat unit are not necessarily the nets of lattices. The third quotient graph is for a rhombohedral $\left(R\bar{3}m\right)$ structure **ilc** in which the edges are not shortest distances—for unit edge length and minimum density the unit cell has $a = 0.8165$ and $\propto = 104.48°$. In this last structure there are six vertices at a distance of 0.8165 from a given vertex, and eight more, linked by edges to that vertex, at a distance of 1.0.

6. Barycentric coordinates and displacements

A net is a purely topological construct, completely specified by the set of edges. However for many purposes it is convenient to derive a *placement*, or assignation of coordinates, to the vertices. A way, that can be shown [14] to be unique once one vertex is set at the origin, is to use dimensionless center-of-mass (barycentric) coordinates expressed as fractions of the translation vectors [11]. Such a placement has several advantages. In particular the coordinates are all rational and therefore can be expressed exactly as a ratio of integers, and the combinatorial symmetries relating vertices and edges can be determined. A possible disadvantage is that, for certain topologies, pairs of vertices may have identical barycentric coordinates (*collide*), however nets with such collisions have proved to be very rare in crystal chemistry so far.

As a simple example consider the net, **dia**, of the diamond structure (discussed in the previous section) with two vertices in the primitive cell. Let atom 2 be at the origin 0, 0, 0. Atom 1 at x, y, z is bonded only to atoms labeled 2 at 0, 0, 0; 1, 0, 0; 0, 1, 0; 0, 0, 1. The average of these is 1/4, 1/4, 1/4; accordingly these are the values of x, y, z. Notice that a placement of this sort needs no metric (unit cell size and shape) and follows immediately from the vector representation.

It should be clear that vertices that have the same neighbors will have the same barycentric coordinates (collide).

For periodic nets without collisions, the combinatorial symmetry including translations is isomorphic to the maximum achievable symmetry of a realization (which is not in all cases a faithful embedding) of the net [18]. If this maximum symmetry is chiral (consists solely of rotations and translations) there is no embedding that is not chiral, and the graph is *intrinsically chiral.*

Notice that the coordinates in an equilibrium placement are independent of the size or shape of the unit cell (i.e., the metric).

7. Tilings and nets

In this section, we are concerned exclusively with 3-periodic tilings of Euclidean space. The tiles are generalized polyhedra or *cages* in which some vertices may have just two edges incident upon them. A tiling is a filling of space by tiles sharing faces ("face-to-face"). The vertices and edges of the tiling form a net and we say that the net is *carried* by the tiling. The *face symbol* of a tile is of the form $[M^m.N^n\ldots]$ which indicates that there are m faces that are M-gons, n faces that are N-gons etc.

For a tiling with t tiles, f faces, e edges and v vertices per repeat unit [19]:

$$t - f + e - v = 0. \tag{1}$$

Although the net carried by a tiling is uniquely determined, the converse is not true; indeed an infinite number of tilings may carry the same net. Thus a new tiling can be derived from the old one by fusing pairs of tiles that have a common face; alternatively, if the original tiles have more than three faces, they can be dissected into smaller tiles. Some nets have catenated rings and it may not be possible to find any tiling for such nets.

In general though, it appears that for the nets of interest in crystal chemistry, there is a *natural* tiling which is one that has the property that the tiles are the smallest possible that conserve the full symmetry of the net and for which the faces are all strong rings. In rare instances there may be more than one natural tiling. Notice that the tiles of a natural tiling have the properties: (a) There is not just one face that is largest (has the most edges); the cycle corresponding to this face would be the sum of the other smaller cycles associated with the other faces and hence not a strong ring; and (b) There is no strong ring of vertices of the tile that is not a face and does not cross any of its symmetric copies on the same tile [20].

The faces of the tiles are the *essential rings* of the structure. In the rare examples of a degeneracy (multiplicity) in choice of natural tiling, there is an ambiguity about the identification of essential rings. We remark that the same problem arises in molecular structures [2].

Associated with every tiling is a dual tiling obtained as follows. A new vertex is placed in the center of each old tile and new vertices in tiles sharing a face are connected by a new edge that passes through that old face. To complete the definition we note that the old tiling is also the dual of the new one. Sometimes the new and old tilings are the same; then we say that the tiling is *self-dual*. It should be noted that the dual of a natural tiling may not be (indeed often is not) a natural tiling [16,21].

As a net has infinitely many tilings, there are infinitely many nets carried by the duals of those tilings. However, one likes to consider the "dual" of a net; this should be construed to mean the net of the tiling dual to the natural tiling of the net. For an important class of nets the natural tiling is self-dual, and we refer to such nets and tilings as *naturally self-dual.*

The genus of the net of the tiling is $1+e-v$ and the genus of the net of the dual tiling is $1+f-t$; it follows from Eq. (1) that these two genera are equal.

For a tiling with p kinds of vertex, q kinds of edge, r kinds of face and s kinds of tile, the *transitivity* is $pqrs$. The dual tiling has transitivity $srqp$. Notice that it is a necessary, but not sufficient, condition for a tiling to be self-dual that its transitivity be palindromic.

Tilings with one kind of tile ($s = 1$) are tile-transitive or *isohedral*. Vertex-transitive nets ($p = 1$) are sometimes called *uninodal.*

Dual tilings carry a lot of information about the original tiling. Consider a tile of the dual tiling that encloses one of the vertices of the original tiling. If this tile has n vertices, then n original tiles meet at that original vertex. Each face of the dual tile corresponds to an edge of the original tiling, so the coordination number of the vertex is the number of faces of the dual tile. The number of tiles meeting at an edge is the number of vertices on the corresponding face of the dual tile.

Acknowledgments

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