Geometric Crystallography

An Axiomatic Introduction to Crystallography

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Preface

In the last decade mathematical crystallography has found increasing interest. Siginificant results have been obtained by algebraic, geometric, and group theoretic methods. Also classical crystallography in three-dimensional Euclidean space has been extended to higher dimensions in order to understand better the dimension independent crystallographic properties. The aim of this note is to introduce the reader to the fascinating and rich world of geometric crystallography. The prerequisites for reading it are elementary geometry and topological notations, and basic knowledge of group theory and linear algebra.

Crystallography is geometric by its nature. In many cases, geometric arguments are the most appropriate and can thus best be understood. Thus the geometric point of view is emphasized here. The approach is axiomatic starting from discrete point sets in Euclidean space. Symmetry comes in very soon and plays a central role. Each chapter starts with the necessary definitions and then the subject is treated in two- and three-dimensional space. Subsequent sections give an extension to higher dimensions. Short historical remarks added at the end of the chapters will show the development of the theory. The chapters are mainly self-contained. Frequent cross references, as well as an extended subject index, will help the reader who is only interested in a particular subject.

The author is grateful to many persons who have contributed to this note: First of all to my teacher Werner Nowacki who introduced me into crystallography. To Hans Wondratschek for his teaching me crystallographic orbits and four-dimensional space groups. To Wilhelm Plesken for his exposition on higher dimensional lattices at the Bielefeld symposium in summer 1985. To Hans Debrunner for his tutorial on Dehn's function.

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Peter Engel

Table of Contents

1. Basic Definitions

The regular shape of crystals suggests that within a crystal atomic building units, congruent to each other, are regularly arranged. Assuming the crystal to be infinite and the atoms to be points, an infinite discrete point set, called a discontinuum, results which plays an essential role in crystallography. Moreover, such point sets are of great importance in several branches of mathematics and physics. Whereas the existence of a continuum in nature cannot be shown, the discontinuum has an assured position in natural sciences. In this chapter some general properties of discrete point sets will be discussed.

1.1. Axioms of geometric crystallography

We consider a point set X in n-dimensional Euclidean space E^n which fulfils, following Hilbert (Hilb2), three conditions:

1.1. The point set X is discrete, that is, around each point of the set an open ball of fixed radius $r>0$ can be drawn which contains no other point of X.
1.2. Every interstitial ball, that is, every open ball which can be embedded into E^n such that it avoids all points of X, has a radius less than or equal to a fixed finite R.
1.3. The point set X looks the same if seen from every point of X.

The second condition ensures that the points are spread uniformly over the whole space. For example they may not lie all on one side of a hyperplane. This signifies that the number of points within any ball of radius $L > R$ increases with the n-th power of L.

A point set X which fulfils the first two conditions is called a discontinuum or, following Delaunay (Delo4), a (r,R)-system. This more general kind of point set is important in the theory of amorphous mater and of quasi-crystals.

Following Sohncke (Sohn2), the third condition can be made more precise if we consider the set of straight line segments drawn from any point of the set X to all the

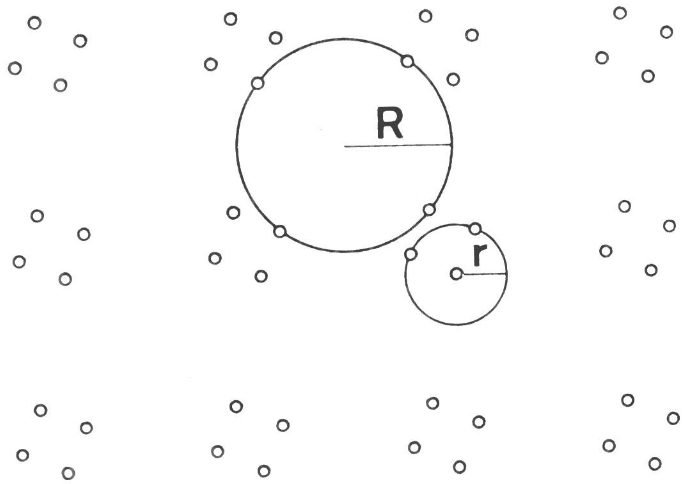

Figure 1.1. A fragment of a regular point system having plane group p4.

remaining points of X. The third condition requires that the line systems of any two points of X are directly or mirror congruent. That is ,for each pair of points we can find a rigid motion of the space which brings the two line systems and hence the whole point set X into self-coincidence.

The third condition ensures that a largest interstitial ball of radius R exists. In a (r,R)-system the radius R is the supreme of radii of all interstitial balls and a ball of radius R not necessarily exists.

A point set X which fulfils all three conditions is called a regular point system by Sohncke (Sohn2) or a homogeneous discontinuum by Niggli (Nigg1).

Regular point systems have applications in the theory of ideal crystals. Any ideal crystal structure can be described as a union of one ore several regular point systems. Each regular point system corresponds to one atomic species.

1.2. Euclidean vector space

We will assume that the reader is familiar with standard linear theory of E^n and elementary topological notations. We also assume familarity with convex sets. The main purpose of this section is to give a brief survey of an Euclidean vector space. The following definitions are standard.

In order to describe the properties of a point set X in n-dimensional Euclidean space E^n, where n is finite, we have to introduce the concept of a real vector space. As origin we choose a point $O \in E^n$; it need not belong to the point set X. Then we consider the translation which carries O to some other point x. This translation can be identified with the vector $\vec{x}$ from the origin O to the point x. Selecting n linearly independent vectors $\vec{a}_1,\ldots,\vec{a}_n$ as basis vectors, every vector $\vec{x}$ is uniquely represented by its components $\xi_1,\ldots,\xi_n$ referred to this basis,

$$\vec{x} = \xi_1\vec{a}_1+\ldots+\xi_n\vec{a}_n,$$

The components $\xi_1,\ldots,\xi_n$ can also be considered as the coordinates of the point x.

The dimension n is defined as the maximal number of linearly independent basis vectors.

We represent a vector by a column:

$$\vec{x} := \begin{pmatrix} \xi_1 \\ \cdot \\ \cdot \\ \cdot \\ \xi_n \end{pmatrix} .$$

Defining the sum of two vectors to be

$$\vec{x} + \vec{y} = \begin{pmatrix} \xi_1 \\ \cdot \\ \cdot \\ \cdot \\ \xi_n \end{pmatrix} + \begin{pmatrix} \zeta_1 \\ \cdot \\ \cdot \\ \cdot \\ \zeta_n \end{pmatrix} := \begin{pmatrix} \xi_1 + \zeta_n \\ \cdot \\ \cdot \\ \cdot \\ \xi_n + \zeta_n \end{pmatrix}$$

and multiplication by a real scalar λ by

$$\lambda\vec{x} = \lambda \begin{pmatrix} \xi_1 \\ \cdot \\ \cdot \\ \cdot \\ \xi_n \end{pmatrix} := \begin{pmatrix} \lambda\xi_1 \\ \cdot \\ \cdot \\ \cdot \\ \lambda\xi_n \end{pmatrix},$$

a vector space V^n over the field of real numbers is defined.

The vector space V^n is called Euclidean if we define the scalar product of two vectors, referred to the coordinate system $\vec{a}_1,\ldots,\vec{a}_n$, to be

$$\vec{x}\bullet\vec{y} := (\xi_1,\ldots,\xi_n) \begin{pmatrix} c_{11}\ldots\ldots c_{1n} \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \\ c_{n1}\ldots\ldots c_{nn} \end{pmatrix} \begin{pmatrix} \zeta_1 \\ \cdot \\ \cdot \\ \cdot \\ \zeta_n \end{pmatrix} = \vec{x}^t C\vec{y},$$

and the length of a vector to be

$$|\vec{x}| := +\sqrt{\vec{x}^t C\vec{x}}\ .$$

The metric tensor $C=(c_{ij})$ is a symmetric matrix with coefficients

$$c_{ij} = |\vec{a}_i|\ |\vec{a}_j|\cos\alpha_{ij},$$

where α_{ij} is the angle between the basis vectors $\vec{a}_i$ and $\vec{a}_j$.

If the basis vectors $\vec{a}_i$ have unit length and are mutually perpendicular, then C is the identity matrix and it follows that

$$\vec{x}\bullet\vec{y} := \xi_1\zeta_1+\xi_2\zeta_2+\ldots\ldots+\xi_n\zeta_n.$$

such a basis is called a cartesian coordinate system.

In crystallography the periodicity of an ideal crystal is used to define a crystal coordinate system which, in general, is not a cartesian one.

Frequently the reciprocal or dual basis $\vec{r}_1,\ldots,\vec{r}_n$ is used. For a vector $\vec{x}:=\xi_1\vec{a}_1+\ldots+\xi_n\vec{a}_n$ and a vector $\vec{y}:=\zeta_1\vec{r}_1+\ldots+\zeta_n\vec{r}_n$ we require that

$$\vec{x}\bullet\vec{y} = \xi_1\zeta_1+\ldots+\xi_n\zeta_n.$$

Thus the reciprocal basis $\vec{r}_1,\ldots,\vec{r}_n$ is obtained by the invers of C, $U:=C^{-1}$.

$$\begin{pmatrix} \vec{r}_1 \\ \cdot \\ \cdot \\ \cdot \\ \vec{r}_n \end{pmatrix} = \begin{pmatrix} u_{11} \ldots u_{1n} \\ \cdot \quad\quad \cdot \\ \cdot \quad\quad \cdot \\ \cdot \quad\quad \cdot \\ u_{n1} \ldots u_{nn} \end{pmatrix} \begin{pmatrix} \vec{a}_1 \\ \cdot \\ \cdot \\ \cdot \\ \vec{a}_n \end{pmatrix},$$

1.3. Rigid motions

A motion in E^n can be represented by a non-singular nxn matrix S and a shift vector $\vec{s}$; it transforms the coordinates of of a point $x\in E^n$ into those of another point $x'\in E^n$:

$$\begin{pmatrix} \xi'_1 \\ \cdot \\ \cdot \\ \cdot \\ \xi'_n \end{pmatrix} = \begin{pmatrix} s_{11} \ldots s_{1n} \\ \cdot \quad\quad \cdot \\ \cdot \quad\quad \cdot \\ \cdot \quad\quad \cdot \\ s_{n1} \ldots s_{nn} \end{pmatrix} \begin{pmatrix} \xi_1 \\ \cdot \\ \cdot \\ \cdot \\ \xi_n \end{pmatrix} + \begin{pmatrix} \sigma_1 \\ \cdot \\ \cdot \\ \cdot \\ \sigma_n \end{pmatrix}.$$

We assume that the point x is moved referred to a fixed coordinate system. Using the Frobenius symbol (Frob1) this equation can be abreviated as

$$x' := (S,\vec{s})\ x.$$

The matrix S is called the rotation part and the shift vector $\vec{s}$ is called the translation part of the motion $(S,\vec{s})$. Every motion that brings x into coincidence with x' has also to bring an arbitrary point $y\in E^n$ into coincidence with some point $y'\in E^n$.

For a rigid motion we require that the length of the vector $\overrightarrow{xy} = \vec{y}-\vec{x}$ is conserved:

$$|\vec{y}-\vec{x}|^2 = (\vec{y}-\vec{x})^t C\ (\vec{y}-\vec{x}) = |\vec{y}\,'-\vec{x}\,'|^2$$

$$= |S\vec{y}-S\vec{x}|^2 = (\vec{y}-\vec{x})^t S^t C S\ (\vec{y}-\vec{x})$$

This equation has to remain valid for all $\vec{x},\vec{y} \in E^n$ therefore, $C = S^tCS$. As a necessary and sufficient condition we have

$$c_{ij} = \sum_{h=1}^{n} \sum_{k=1}^{n} c_{hk}\, s_{hi}\, s_{kj}.$$

For a cartesian coordinate system the metric tensor C is the identity matrix and therefore, the following orthogonality relations hold,

$$\sum_{k=1}^{n} s_{ki}s_{kj} = \begin{cases} 0 \text{ if } i \neq j \\ 1 \text{ if } i = j \end{cases}$$

A rigid motion is also called an isometry.

Since det(C) equals $\det(S^tCS)=\det(C)\det^2(S)$ the result $\det(S) = \pm 1$ follows. The two values −1 and 1 for det(S) are connected to the chirality character of the isometry. In oder to understand the chirality character of an isometry $(S,\vec{s})$ we take a subset $M \subset E^n$ of at least n+1 points which not all lie in a hyperplane. In the two-dimensional case we take three points which determine a triangle R in the plane as shown in Figure 1.2. In general n+1 points determine a simplex in E^n. It is always possible to determine a simplex which exhibits chirality, that is, the mirror image of the simplex is not directly congruent to the original simplex. The simplex and its mirror congruent copy are said to be enantiomorph to each other. In Figure 1.2 the triangles R" and R"' are enantiomorh.

If det(S)=+1 then the isometry $(S,\vec{s})$ carries the simplex into a direct congruent copy. Such an isometry is called a proper isometry. Particularly S is called a proper rotation. If "I" designates the identity operation then $(I,\vec{s})$ is a translation.

Otherwise if det(S)=−1 then $(S,\vec{s})$ carries the simplex into a mirror congruent copy, that is, the chirality of the simplex changes. Such an isometry is called an improper isometry. Particularly S is called an improper rotation or a rotoreflection or, if it leaves a (n−1)-dimensional hyperplane fixed, a reflection.

Example 1.1: A triangle R in the plane E^2 is shown in Figure 1.2. The rotation part S rotates the triangle R into R' through the rotation angle σ around the rota-

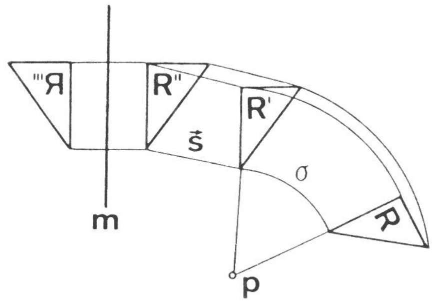

Figure 1.2. Rigid motions in the plane

tion point p. The translation part $\vec{s}$ carries R' into R". Both motions are proper isomteries. The triangle R" is enatiomorph to the triangle R"' hence, there exists no proper isometry in the plane which maps R" onto R"'. However, this can be achieved by a reflection in the mirror line m.

1.4. Symmetry operations

Let M be any subset of E^n. We look at the isometries which map M onto itself.

Definition 1.1: A symmetry operation acting on a set M is an isometry which maps M onto itself.

The symmetry operations of a set M have two important properties:

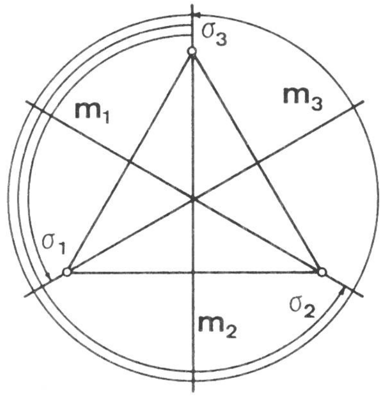

Figure 1.3. Symmetry operations of a set $M \subset E^n$

1. A symmetry operation $(S_1,\vec{s}_1)$ followed by a second symmetry operation $(S_2,\vec{s}_2)$ is again a symmetry operation $(S_3,\vec{s}_3)$ of M.

$$x'' = (S_2,\vec{s}_2)x' = (S_2,\vec{s}_2)(S_1,\vec{s}_1)x$$

$$= S_2S_1x+S_2\vec{s}_1+\vec{s}_2$$

$$= (S_3,\vec{s}_3)x,$$

with

$$S_3 := S_2S_1 \text{ and } \vec{s}_3 := S_2\vec{s}_1+\vec{s}_2.$$

2. The symmetry operation $(S_3,\vec{s}_3):=(S_1,\vec{s}_1)^{-1}$ which reverses another symmetry operation is again a symmetry operation of M and the result is the identity operation $(I,0)$.

$$(S_3,\vec{s}_3)\ (S_1,\vec{s}_1) = (S_3S_1,S_3\vec{s}_1+\vec{s}_3) = (I,0).$$

It follows that

$$S_3 = S_1^{-1} \text{ and } \vec{s}_3 = -S_1^{-1}\vec{s}_1.$$

Hence, the totality of symmetry operations of a set M generates a group in the mathematical sense.

Symmetry groups correspond to linear representations of abstract groups in Euclidean vector spaces. Thus we consider $(S,\vec{s})$ as a representation in E^n. We note that different symmetry groups may correspond to different representations of the same abstract group (cf. section 6.6).

<u>Definition 1.2:</u> Every group P of symmetry operations acting on a set M and which leaves at least one point $z \in E^n$ fixed is called a point group.

Example 1.2: Let Δ be the equilateral triangle shown in Figure 1.3. There exist six symmetry operations which map Δ onto itself. These are three rotations S_1, S_2, and S_3 having rotation angles σ_1, σ_2, and σ_3 respectively and three reflections in the mirror lines m_1, m_2, and m_3. The center of gravity of the triangle Δ remains fixed under all these symmetry operations.

We now look at the symmetry operations of a regular point system X. By the regularity condition 1.3 there exists for every pair $x,y \in X$ a symmetry operation $(S,\vec{s})$ which carries x into y and thereby maps X onto itself. It follows that all $x \in X$ are connected through symmetry operations acting on X. If this is fulfilled we say that the group of symmetry operations acts transitively on X.

<u>Definition 1.3:</u> Every group G of symmetry operations acting transitively on a regular point system in E^n is a n-dimensional space group.

Synonymous with space group also crystallographic group is used.

<u>Definition 1.4:</u> The set of all symmetry operations of a group Γ which map a set M onto itself is called the stabilizer of M in Γ.

Synonymous with stabilizer also site symmetry group or isotropy group are used.