Chapter 1
Introduction

This chapter introduces the spatial periodicity and the macroscopic scale symmetry properties which characterize crystals.

1.1. Crystal order

Depending on temperature and pressure, all materials take on three different states: solid (S), liquid (L) and gas (G) (Fig. 1.1). However, when looking at matter from a microscopic point of view, there are only two really distinct states: the ordered state (grey area on Fig. 1.1) and the disordered state. It is clear that a gas at low pressure, consisting of a set of molecules separated by distances that are large compared to their size, is totally disordered. In a liquid, the molecules are in contact with one another, like marbles packed in a bag. A liquid is not completely disordered: there is some order, but only at short range.

Furthermore, it is possible to go continuously from the gas state to the liquid state. At a temperature Θ between the temperature Θ_T of the triple point and that Θ_C of the critical point, a gas undergoing compression goes from the gas state (A) to the liquid state (B) through a sharp transition, liquefaction or condensation. But it is possible to go from A to B around the critical point, for instance by going from A to D at constant pressure, then from D to F at constant temperature, and then from F to B at constant pressure. In contrast, it is impossible to go from the disordered area to the ordered area without crossing the line, shown as a thick line on the figure, that clearly separates the ordered and the disordered domains. This line consists of two parts: one corresponds to sublimation (solid–gas transition) and to condensation for the inverse transformation, the other to melting (solid–liquid transition) and to solidification for the inverse transformation.

The equilibrium diagram of Figure 1.1 applies to most solids and their transition to a disordered state, either liquid or gas. However, for some solids, the liquid–solid transition is not sharp but continuous: this is the case for amorphous or glassy solids. When the temperature of such a material in liquid form is lowered, its viscosity increases, which means that its flow is more and

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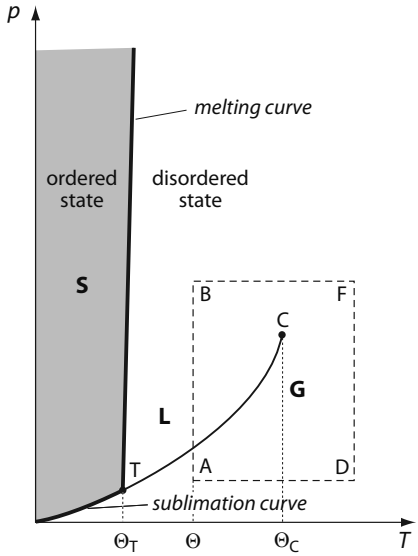

Figure 1.1: Equilibrium diagram for a pure substance, in a representation where pressure p is shown as a function of temperature T

more difficult. It forms a kind of paste, which ends up being solid but with a structure hardly more ordered than that of a liquid: it is a kind of set liquid – which corresponds to a metastable state.

This book deals only with crystalline solids, characterized by long-range order. The size of the ordered regions depends on the conditions in which crystallization occurs. If no special care is exercised when solidifying a pure liquid, microcrystals appear at various points of the liquid, grow and end up being contiguous. Each small crystal is perfectly ordered, but there is no reason for these crystals to have the same orientation. We get a polycrystal, *i.e.* a solid made up of small crystals (grains) with the same structure, but differently oriented. This is the most prevalent case for materials and in particular for metals (Fig. 1.2). However, some minerals occur in single crystal form, *i.e.* in a form where the solid is identically oriented over its entire volume. This is the case for the gems of jewelers, and for some beautiful minerals which can be found in private or public collections[1] (Fig. 1.3a). On the other hand, some crystals can be manufactured in the form of quite large single crystals. This is the case for silicon or quartz, which are produced as single crystals several tens of centimeters in size (Fig. 1.3b).

1. All museums of natural history have a section on minerals. If you visit Paris (France), you will enjoy in particular the mineral collection of Pierre & Marie Curie University (UPMC) and of the Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC), located at 4 place Jussieu, in the 5th district (arrondissement).

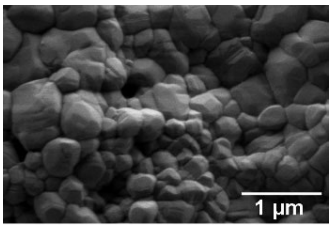

Figure 1.2: Scanning Electron Microscopy (SEM) image of the surface of a polycrystalline copper sample (courtesy Cyril Langlois)

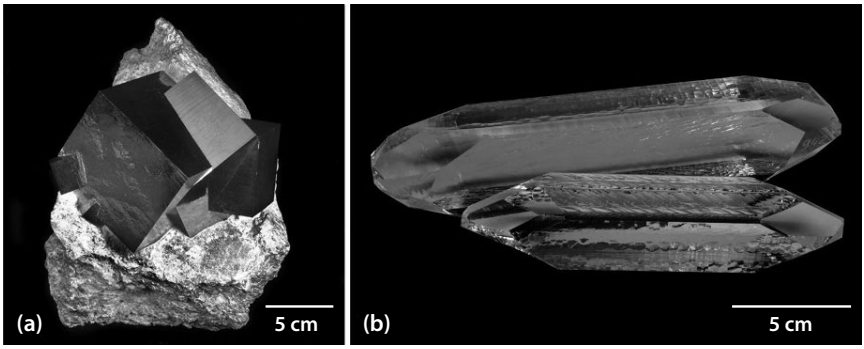

Figure 1.3: (a) A sample of pyrite (iron sulfide, FeS_2), mineral collection of Pierre & Marie Curie University (Paris 6) (photograph by Jean-Pierre Boisseau); (b) two bars of single crystal synthetic quartz produced by the SICN company (photograph by Alain Jeanne-Michaud)

1.2. Order on a macroscopic scale

The existence of crystal order was sensed in the 17th century at the macroscopic scale, and recognized at the beginning of the 20th century at the microscopic scale. For instance, Niels Stensen, or Nicolaus Stenonius, or Steno, a Dane, noticed as early as 1669 that the angles between faces of natural crystals of quartz and some other minerals have a well defined, constant value, independent of their origin. He then spelled out the law of constancy of angles, which was to be generalized to all crystals by Romé de l'Isle in 1783. This constancy of angles also shows up on the small crystals which form naturally during solidification.

The mineralogist René Just Haüy showed in 1784 how this regularity in angles can be explained. He had noticed that, when he would cleave[2] a crystal of calcite, he would obtain smaller and smaller rhombohedra, all with the same

2. When a crystal of calcite is broken, the fracture surface features perfectly plane areas, with a restricted number of orientations. If one attempts, using a cutting tool and a small hammer, to cleave the crystal, *i.e.* to break it along one of these special areas, one obtains, provided the blade is properly oriented and the experimentalist has some experience, two fragments separated by a beautiful plane suface known as a cleavage surface.

angles. He then imagined that a final stage, *i.e.* a small elementary rhombohedron which can no more be cut, should eventually be reached. He deduced that the macroscopic crystal should be formed from the regular stacking of small rhombohedra, all identical to this elementary rhombohedron which he called the "integrating molecule". He then showed, and this is the strong point of his theory, that he could reconstruct all external forms of crystals by stacking identical elementary parallepiped-shaped blocks into successive layers which he shifted by a constant, integral number of units at each layer (Fig. 1.4). The parameters defining the basic parallelepiped were characteristic of the crystal. The notions of periodicity and of crystal unit cell, which we will define later, thus appear.

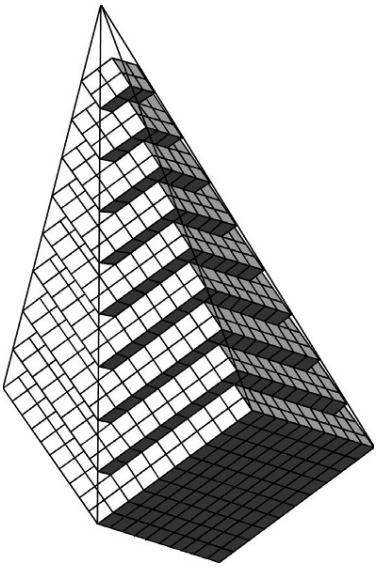

Figure 1.4: A stacking of layers of identical parallelepipeds, regularly shifted to reproduce the actual habit of the crystal

1.3. Order on a microscopic scale

After Haüy and until 1912 the concepts of symmetry and of internal periodicity in the crystal developed. However it was not evident, or at any rate not proved, that this internal order, *viz.* a triply periodic stacking, could exist in materials with any external shape.

It was in fact through the discovery of X-ray diffraction by Max von Laue in 1912, and thanks to the work of William and Lawrence Bragg, that the existence of a periodic stacking of atoms in solids, as predicted by Haüy, could be evidenced. They showed that X-rays are diffracted by crystals along special directions, forming a discrete set of spots which could be interpreted only

through a triply periodic stacking of the atoms. Thus crystalline solids can be represented using a crystal motif,[3] comprising a finite number of atoms, periodically repeated along three non-coplanar directions with periods along these directions respectively a, b and c.

Let us discuss a few examples to illustrate this notion of periodicity. Figure 1.5 shows a frieze formed by repeating, with period a, a motif. Figure 1.6 shows a sample of wallpaper featuring periodicity in two directions (periods **a** and **b**).

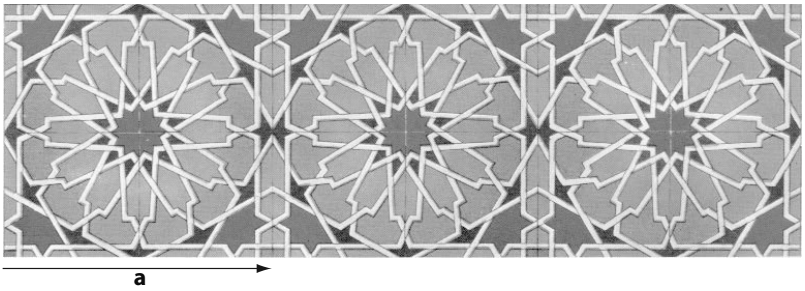

Figure 1.5: A decorative pattern from Arabic art, after J. Bourgoin, *Arabic Geometrical Pattern and Design* (Dover Publications, New York, 1973)

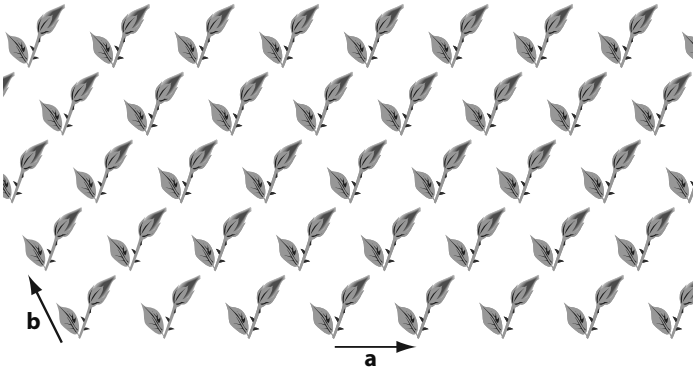

Figure 1.6: A sample of wallpaper

A crystal is thus formed from a motif consisting of a set of atoms. Repeating the motif through a translation **a** leads to a kind of linear crystal. If this linear crystal is submitted to a translation by a vector **b** (not collinear with **a**), then by 2**b**, 3**b**, etc., a plane crystal is obtained. To obtain the global crystal, the plane crystal is then thought to be submitted to a translation by a vector **c** not coplanar with plane (**a**, **b**), then by 2**c**, 3**c**, etc.

3. *Motif* is the French word for pattern. It is adopted in crystallographic English, with the present meaning.

1.4. Basic assumptions of geometrical crystallography

In order to describe crystal structures, we make three assumptions:

1. The crystal is assumed to be infinite. This assumption is reasonable, since the order of magnitude of the lengths a, b and c of the period vectors is a few angströms (1 Å = 10^{-1} nm). A small crystal with dimensions of the order of a micrometer, for example, contains linear sequences several thousands of periods long.
2. The thermal vibrations of atoms about a perfectly defined average position is neglected. Our description assumes that the atoms are fixed at these average positions.
3. The crystal is assumed to be perfectly triply periodic, *i.e.* not to feature any defect. Crystal defects can then be described with respect to the perfect crystal. The study of crystal defects is a broad subject, outside the scope of this book. A brief introduction to one type of defect, the dislocation line, is given in Complement 13C.

1.5. Anisotropy of physical properties

The beautiful crystal faces that can be observed in natural minerals and in some synthetic crystals are related to the very strong anisotropy of the growth rates as a function of growth direction. Figure 1.7 explains how the only faces that remain after some growth has occurred are those perpendicular to the directions where the growth rate is much smaller than in other directions. We consider, at time $t = 0$, three face orientations denoted as 1, 2 and 3, with one of them (noted 2) growing at a velocity v_2 twice larger than the two others (faces 1 and 3). We see that at time t all faces are present, whereas, at time $2t$, face 2 has disappeared.

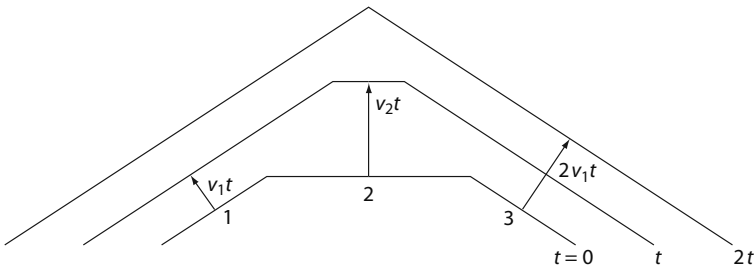

Figure 1.7: Growth at different rates of crystal faces. Face 2, with growth velocity v_2 twice larger than that, v_1, of faces 1 and 3, ends up disappearing.

The habit, *i.e.* the very regular special shape, of crystals thus shows that the growth velocity is much smaller along certain directions, finite in number, than in all other directions. This is one of the expressions of the anisotropy of the physical properties of crystals. In this case, anisotropy is discontinuous while, for most other physical properties, it is continuous, meaning that the value of a physical quantity such as the expansion of a material along a given direction, under the influence of a rise in temperature, varies continuously as direction is varied. This anisotropy of their physical properties is a characteristic of crystals. Describing it involves the use of tensors. This will be the topic of the second part of this book, starting with Chapter 9.

1.6. Remarks on the scope of this book : topics left out

The aim of this book is to describe the structure and properties of perfectly ordered crystalline solids. We have seen that we therefore leave aside glasses or amorphous solids, the structure of which is close to that of a liquid set at a given instant [1]. Neither shall we mention liquid crystals or mesophases [2]. They often consist of rod-shaped molecules, which assemble parallel to one another, forming plane layers. In a given layer, the molecules may be ordered only at short range, as in a liquid, but the existence of these parallel layers denotes partial order, whence the term crystal.

Neither will we deal with quasi-crystals, discovered in 1984 [3] (see also [4]). They can be obtained through ultra-fast quenching of metallic alloys (e.g. Al–Mn–Si or Al–Fe–Cu). They do not feature the triple periodicity of crystals. They do however, like crystals, feature orientation symmetry: all properties observed along a given direction are reproduced along the directions deduced from the former through the action of the symmetry elements in the point group of the quasi-crystal. Because there is no translation symmetry, these point groups are different from those that are consistent with the crystalline state.

Complement 1C. Crystal growth

This complement is no more than a glimpse into the fascinating art and science of crystal growth. The variety of techniques and of characterization methods it encompasses is exemplified by a recent handbook of crystal growth (see Further reading): it comprises over 1800 pages, with a short table of contents spanning 14 pages and a detailed table of contents of 30 pages.

1C.1. Natural growth of single crystals

The largest producer of single crystals is nature. Large (centimeter-range) single crystals of many naturally occurring compounds, usually called minerals, have long been valued for their beauty and have raised many questions that led to understanding the structure of matter. Their characteristic habits, with well-developed natural faces, occur when their growth process involves isotropic enough an environment as well as enough space. The typical process, hydrothermal growth, is based on the slow deposition of a solute as the temperature of the solution changes, and it is often associated with high pressures. Among the most popular examples of minerals are quartz SiO_2 (rock crystal), calcite $CaCO_3$ (Iceland spar), diamond C, pyrite FeS_2 (fool's gold, Fig. 1.3a). They may well, through their beauty, have kindled the reader's interest for crystals and symmetry. Other materials crystallize very easily, at room pressure and room temperature, from solutions: this is the case for sodium chloride NaCl (rocksalt), or copper sulfate $CuSO_4$. Crystallization is then a convenient way of purifying the material.

1C.2. Crystal growth for scientific purposes

Growing single crystals is an important support activity for basic research. A meaningful investigation of anisotropic macroscopic properties, for example magnetism, electrical or heat conduction, or the ferroelectricity (see Sect. 15.2) of materials, requires single crystals, where the directional properties are the same throughout the sample. The growth must then be followed by the precise determination of the orientation of the crystal, so that a sample with well-defined crystal directions can be cut out. The laboratory techniques cover a broad range of approaches, depending on the chemical properties, melting temperature, etc. of the material. Thus soluble materials can often be made to crystallize in a controlled way by slow evaporation of the solvent, while refractory materials will have to be molten in an induction furnace, often in the form of a levitating drop without contact with a crucible to avoid contamination, and cooled in a temperature gradient. The Bridgman method provides for cooling of a larger molten sample, in contact with a small crystal used as a seed, in a temperature gradient. Another broadly used technique is the Czochralski method, where the seed is dipped into the melt and slowly pulled out at the same time that it is rotated. In the flux-growth method, the material to be crystallized is molten together with another material which is

not incorporated in the solid but lowers the melting temperature; with proper setting of the temperature evolution over days or weeks, good crystals can be obtained.

From another point of view, single crystals are necessary for many structure determinations using X-ray or neutron diffraction techniques. However, detailed examination of the validity of the usual data processing procedures ("kinematical approximation", if necessary with corrections) indicates that the crystals should not be big. Typical optimal sizes are tenths of a millimeter for X-rays, and a few millimeters for neutrons. Furthermore, nearly perfect crystals are not desirable for this kind of study, so that the requirements are, happily, close to what crystal synthesis produces. The preparation of single crystals of biological material, such as proteins, in their native hydrated form, is a crucial step toward the determination of their structure. The approach usually consists in trying many recipes at the same time, using boxes with tens of compartments which are filled with drops of the material with various values of the pH or other possibly relevant parameters. The growth of crystals of biomaterials was investigated in microgravity conditions in satellites, in order to eliminate the influence of convection. A similar quest is the motivation for crystal growth in gels.

1C.3. Industrial crystal growth

It may appear paradoxical to find that almost perfect crystals, the production of which is almost invariably fraught with difficulties, are required by industry rather than by basic research. Semiconductor device production is based on the preparation of many chips per single-crystal silicon substrate. They are cut from huge single crystal ingots, typically 300 mm in diameter in 2009 and a meter long, without any linear defect (dislocation line, see Complement 13C). This achievement in crystal growth technology was the result of large efforts toward a thorough understanding of crystal defects. These efforts were undertaken because it was vital to keep at a very low level the number of defective chips grown on a wafer. One side-effect of the mastery achieved in the preparation and processing of silicon crystals was that elaborately shaped parts like inkjet printer nozzles were made out of silicon single crystals.

Crystals with intermediate sizes are grown industrially for applications in optoelectronics (for example lithium niobate $LiNbO_3$ – see Sect. 19.2). Other materials routinely produced in the form of excellent crystals, but comparable neither in quantities nor in quality with silicon, are SiO_2 (quartz) and $AlPO_4$ (berlinite) for piezoelectric oscillators (see Chap. 15), and SiC (silicon carbide) for electronic devices.

Industrial single crystals of diamond are available in a wide range of crystal quality and crystal size, with use as different as oil drill rigs and optical elements (monochromators) for synchrotron radiation X-rays. Synthetic diamond does not reach into the jewelry range yet, but other gemstones (emerald, sapphire...) are routinely produced artificially as substitutes for their natural

counterparts. Again in a very different area, turbine blades for jet planes are made of single crystals of an aluminum-base alloy in view of their mechanical strength at the high temperatures involved.

1C.4. Growth of single-crystal thin films

Films with very small thickness, down to the nanometre range, are important for nanotechnology and basic science, e.g. for the investigation of semiconductor quantum well or quantum dot devices, or of magnetic recording and readout heads for hard disk drives. Their manufacture involves a range of approaches, based on vapor-phase or liquid-phase epitaxy (the growth of single crystal films on single-crystal substrates, with a close relation between their orientations), or molecular-beam epitaxy (MBE). The latter is a highly sophisticated technique involving extreme vacuum and requiring stringent purity controls. Multilayers, consisting of several stacked thin films exhibiting structural coherence at the interfaces, are industrially manufactured by sputtering techniques. They make up the tunnel magnetoresistance (TMR) read heads[4] used in 2011 in the hard disk drive of all recent computers. Mastering epitaxic growth processes implies a very good knowledge of the surfaces on which the layers are to be grown. This makes the study of surface crystallography very important. The description of crystal surfaces is dealt with in Section 3.8 of this book.

Further reading

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G. Dhanaraj, K. Byrappa, V. Prasad, M. Dudley, *Springer Handbook of Crystal Growth* (Springer, 2010)

4. Wikipedia, *Tunnel magnetoresistance*, http://en.wikipedia.org/wiki/Tunnel_magnetoresistance (as of Nov. 7, 2013)

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