

2 The Crystalline State

The outward appearance of a crystal is exceptionally variable, but all the variations which occur can be explained in terms of a single fundamental principle. To grasp this, we must first come to terms with the nature of the crystalline state. The following are a few properties that are characteristic of crystals:

- Many crystals not only have smooth faces, but, given ideal growth conditions, have regular geometric shapes. Fig. 2.1 shows a crystal of garnet with the form called a rhomb-dodecahedron. This is a polyhedron whose faces are 12 rhombi. Turn to Fig. 15.3, a pattern which you can (and should!) use to make a model of a rhomb-dodecahedron.
- If some crystals (e.g. NaCl) are split, the resulting fragments have similar shapes with smooth faces – in the case of NaCl, small cubes. This phenomenon is known as *cleavage*, and is typical only of crystals.
- Figure 2.2 shows a cordierite crystal and the colors that an observer would see when the crystal is viewed from the given directions. The colors that appear depend on the optical absorption of the crystal in that particular direction. For example, if it absorbs all spectral colors from white light except blue, the crystal will appear blue to the observer. When, as in this case, the absorption differs in the three directions, the crystal is said to exhibit *pleochroism*.

Fig. 2.1

A garnet crystal with the shape of a rhomb-dodecahedron

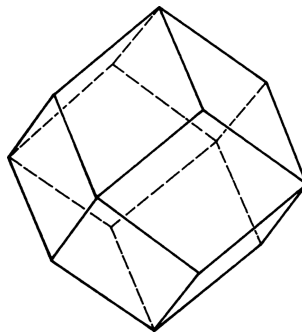
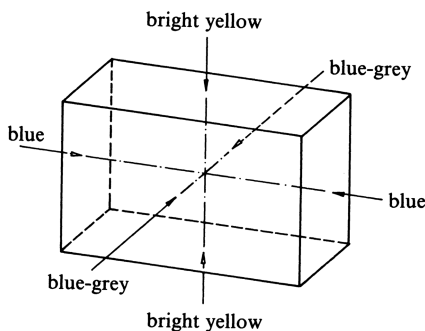


Fig. 2.2

Pleochroism as shown by a crystal of cordierite



- When a crystal of kyanite (Al_2OSiO_4) is scratched parallel to its length with a steel needle, a deep indentation will be made in it, while a scratch perpendicular to the crystal length will leave no mark (see Fig. 2.3). The *hardness* of this crystal is thus different in the two directions.
- If one face of a gypsum crystal is covered with a thin layer of wax and a heated metal tip is then applied to that face, the melting front in the wax layer will be ellipsoidal rather than circular (Fig. 2.4), showing that the thermal conductivity is greater in direction III than in direction I. *Such behavior – different values of a physical property in different directions – is called anisotropy*, (see also Fig. 2.5c). If the melting front had been circular, as it is, for example, on a piece of glass, it would imply that the thermal conductivity is the same in all directions. *Such behavior – the same value of a physical property in all directions – is called isotropy* (see Fig. 2.5a, b).

Anisotropy of physical properties is normal for crystals. It is, however, not universal, as there are some crystals whose properties are isotropic. If, for example, the above

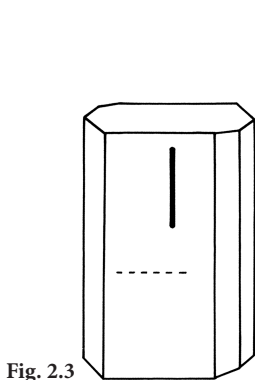
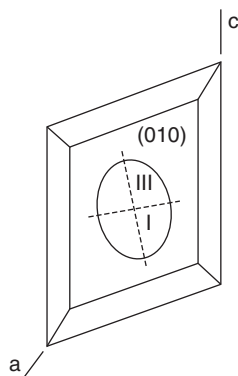
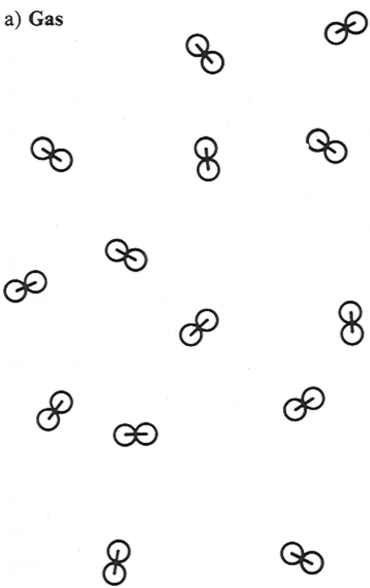
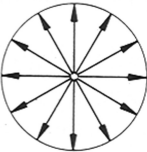

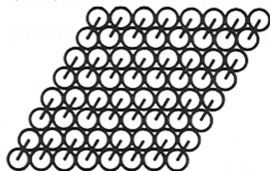
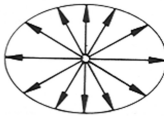
**Fig. 2.3****Fig. 2.4**

Fig. 2.3 A crystal of kyanite, with a scratch illustrating the anisotropy of its hardness

Fig. 2.4 A crystal of gypsum covered with wax showing the melting front. The ellipse is an isotherm, and shows the anisotropy of the thermal conductivity

Representation of the state	Retention of shape	Retention of volume	Distribution of molecules	Physical properties
a) Gas 	No	No	Statistically homogeneous ¹	 Isotropic ²
b) Liquid Boiling point 	No	Yes		
c) Crystal Melting point 	Yes	Yes		
			Periodically homogeneous ¹	 Anisotropic ³

¹ Equal physical properties in parallel directions \Rightarrow

² Equal physical properties in all directions

³ Different physical properties in different directions

Fig. 2.5a–c Schematic representation of the states of matter. (a) gas, (b) liquid, (c) crystal

experiment with wax had been carried out on a face of a cubic crystal of galena, the melting front would have been circular. Similarly, if a sphere is cut from a crystal of copper, and heated, it will remain spherical as its radius increases. The thermal conductivity in these cases is the same in all directions, and thus isotropic.

The origin of all of the phenomena listed above lies in the internal structure of crystals. In order to understand this better, let us now consider the various states of aggregation of matter.

All matter, be it gas, liquid or crystal, is composed of atoms, ions or molecules. Matter is thus *discontinuous*. Since, however, the size of the atoms, ions and molecules lies in the Å region ($1 \text{ Å} = 10^{-8} \text{ cm} = 0.1 \text{ nm}$) matter appears to us to be *continuous*. The states of matter may be distinguished in terms of their tendency to retain a characteristic volume and shape. A gas adopts both the volume and the shape of its container, a liquid has constant volume, but adopts the shape of its container, while a crystal retains both its shape and its volume, independent of its container (see Fig. 2.5).

Gases. Figure 2.5a illustrates the arrangement of molecules in a gas at a particular instant in time. The molecules move rapidly through space, and thus have a high kinetic energy. The attractive forces between molecules are comparatively weak, and the corresponding energy of attraction is negligible in comparison to the kinetic energy.

What can be said about the distribution of the molecules at that particular instant? There is certainly no accumulation of molecules in particular locations; there is, in fact, a random distribution. A. Johnsen has illustrated this by a simple analogy (Fig. 2.6a): we scatter 128 lentils over the 64 squares of a chessboard, and observe that in this particular case some squares will have no lentils, some 1, 2, or even 3 – but on average 2. If, instead of single squares we considered blocks of four squares, the number of lentils in the area chosen would fall between 7 and 9, while any similar block of 16 squares would have exactly 32 lentils. Thus, two distinct areas of the same size will tend to contain the same number of lentils, and this tendency will increase as the areas considered become larger. This kind of distribution is considered to be *statistically homogeneous*, i.e. it shows the same behavior

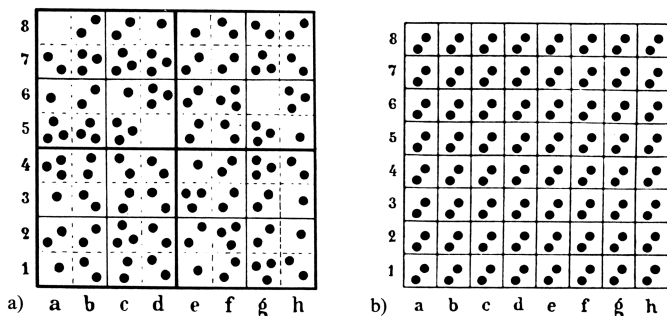


Fig. 2.6a, b Statistical (a) and periodic (b) homogeneity after Johnsen

in parallel directions, and it may easily be seen that the physical properties of the distribution are isotropic, i.e. are equal in all directions.

Liquids. As the temperature of a gas is lowered, the kinetic energies of the molecules decrease. When the boiling point is reached, the total kinetic energy will be equal to the energy of attraction among the molecules. Further cooling thus converts the gas into a liquid. The attractive forces cause the molecules to “touch” one another. They do not, however, maintain fixed positions, and Fig. 2.5b shows only one of many possible arrangements. The molecules change position continuously. Small regions of order may indeed be found (local ordering), but if a large enough volume is considered, it will also be seen that liquids give a statistically homogeneous arrangement of molecules, and therefore also have isotropic physical properties.

Crystals. When the temperature falls below the freezing point, the kinetic energy becomes so small that the molecules become permanently attached to one another. A three-dimensional framework of attractive interactions forms among the molecules and the array becomes solid – it crystallizes. Figure 2.5c shows one possible plane of such a crystal. The movement of molecules in the crystal now consists only of vibrations about a central position. A result of these permanent interactions is that the molecules have become regularly ordered. The distribution of molecules is no longer statistical, but is *periodically homogeneous*; a periodic distribution in three dimensions has been formed (see also Fig. 3.1a).

How can this situation be demonstrated using the chessboard model? (Fig. 2.6b). On each square, there are now precisely two lentils, periodically arranged with respect to one another. The ordering of the lentils parallel to the edges and that along the diagonals are clearly different, and therefore the physical properties in these directions will no longer be the same, but distinguishable – in other words, the crystal has acquired anisotropic properties. This anisotropy is characteristic of the crystalline state.

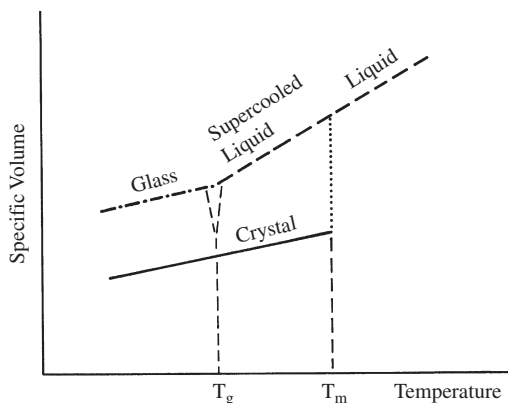
D A crystal is an anisotropic, homogeneous body consisting of a three-dimensional periodic ordering of atoms, ions or molecules.

All matter tends to crystallize, if the temperature is sufficiently low, since the ordered crystalline phase is the state of lowest energy. There exist, however, materials, such as glass, which never reach this condition. Molten glass is very viscous, and the atoms of which it is made cannot come into a three-dimensional periodic order rapidly enough as the mass cools. Glasses thus have a higher energy content than the corresponding crystals and can best be considered as a frozen, viscous liquid. They are *amorphous* or “formless” bodies. Such materials do not produce flat faces or polyhedra since an underlying order is missing. (cf. Chap. 5, “Morphology”)

What then may be said about the relationship of liquid, crystal, and glass? One possibility is to examine the change in specific volume as the temperature is raised or lowered (Fig. 2.7). As a liquid is cooled, its volume decreases smoothly. When the melting point (T_m) is reached, the liquid crystallizes, leading to a sharp change in

Fig. 2.7

Temperature dependence of the specific volume of a liquid as it forms a crystalline or a glass phase.



volume. Further cooling results in a smooth decrease in the volume of the crystalline phase.

If cooling does not cause a liquid to crystallize, the volume continues to decrease as shown by the dashed line in Fig. 2.7, corresponding to a “supercooled liquid”. When the transformation temperature, or better transformation range, T_g is reached, the curve bends and continues more or less parallel to that for the crystal. This bend corresponds to a large increase in viscosity. The liquid “freezes”, but the resulting glass is still actually a supercooled liquid.

There are many other ways in which crystals differ from amorphous material. One of these is that while a crystal has a definite melting point, a glass has a softening region. Another difference is in their different properties relative to an incident X-ray beam. The three-dimensional ordering of the atoms in crystals gives rise to sharp interference phenomena, as is further examined in Chap. 13. Amorphous bodies, as they do not have underlying order, produce no such effect.

2.1

Exercises

Exercise 2.1 Determine the volume of gas associated with each molecule at standard temperature and pressure (0°C , 101.3 kPa). What is the edge of a cube with that volume?

Exercise 2.2 Determine the packing efficiency of gaseous neon ($R_{\text{Ne}} = 1.60\text{ \AA}$) at standard conditions, where the packing efficiency is the ratio of the volume of a neon atom to the volume determined in Exercise 2.1. For comparison, a copper atom in a crystal has a packing efficiency of 74%.

Exercise 2.3 Discuss the use of the term “crystal glass”!

Crystallography

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