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Sample Preparation

The success of an experimental investigation often depends crucially on whether suitable objects are available. Therefore, special attention must be paid to the production and preparation of the specimens. In the next two sections we will discuss established methods for the preparation and orientation of crystals. Prospective material scientists should make themselves familiar with these methods.

2.1

Crystal Preparation

Specimens for measurement purposes as well as discrete devices for various applications are mainly required in the form of thin plates, thin rods, or rectangular parallelepipeds. The production of these and also more complicated forms out of a crystal blank takes place through the following processes: cleaving, sawing, drilling, turning on a lathe, grinding, and polishing.

(a) *Cleaving* when a cleavage exists with a suitable orientation of the cleavage planes. Many crystals, such as, e.g., alkali halides of NaCl type, CaF_2 , diamond, mica, MoS_2 , and especially crystals with layered structures, possess a cleavage or a direction of preferred crack tendency. Cleavage planes are always crystallographically prominent faces parallel to net planes of large occupation density. The cleaving process must be practised with great care. Soft crystals can be cleaved with a razor blade, harder crystals with a stable blade, whereby the blade is held parallel to the cleavage plane. When cleaving soft crystals such as guanidinium iodide or gypsum, the blade is slowly pressed through the specimen, whereas cleaving harder crystals, such as, e.g., LiF or CaF_2 , requires a short and fast impact. The cleavage can be easily guided in the desired direction by making a fine notch along the cleavage plane. In any case, a massive base plate is of advantage.

(b) *Sawing with a thread saw*. When working with a thread saw, the mechanical stress on the crystal is practically negligible as opposed to cleaving. The thread saw should be used for the stress-free preparation of specimens, as well as with all specimens possessing good solubility or where chemical dissolution is possible. The thread, moistened with a suitable solution, is

moved automatically back and forth by commercial equipment and the crystal clamped in a moveable holder is pressed with an adjustable force against the thread. Cooling occurring during endothermal dissolution processes must be suppressed as far as possible when working with delicate crystals. This is done, for example, by using an almost saturated solution and by stripping off drops of liquid on the thread immediately in front of the crystal. This is especially important with highly volatile solvents such as ethyl alcohol or acetone. Difficult to dissolve crystals, such as calcite (CaCO_3) or quartz (SiO_2), can be cut using diluted hydrochloric acid or hydrofluoric acid. Suitable sawing materials are twisted natural fibers. Synthetic fibers can be used with neutral or alkaline solutions. Metal wires, e.g., made from tungsten (\varnothing 0.1–0.2 mm) are still well proven and work with a water solution, especially with crystals that are hardly dissoluble. In the case of very hard crystals, such as silicates or metals, one uses a solution consisting of a suspension of corundum or diamond powder (grain size ca. $10\text{ }\mu\text{m}$) in a highly viscous liquid such as paraffin oil or dextrin boiled in water.

(c) *Sawing with a blade saw* (normally diamond coated). The usual blade saw with outside peripheral cut and also such saws which cut with the inner periphery of a circular ring to improve the stability of the blade are only suitable for materials of low mechanical and thermal sensitivity. In any case, one must work with minimal sawing pressure and ample cooling liquid.

(d) *Spark erosion techniques*. Spark discharge methods can be used on some materials, such as alloys, to preferentially divide and separate individuals. This method also plays an important role in the smoothing of surfaces and can even achieve the quality of polishing.

(e) *Laser ablation*. Some substances allow a targeted ablation of material by laser bombardment; mainly used on very small objects in microtechnology applications.

(f) *Drilling and turning*. As in wood and metal working, crystals with different mechanical properties can also be machined with a drill or lathe. In general, sharp and fine diamond cutting tools should be used. Furthermore, when working on the lathe, one has the possibility of using grinding paste and emery paper. Hollow drills have also been found useful in the machining of cylindrical specimens of various thicknesses. Just like drilling in glass, these must operate with a plentiful supply of abrasives and cooling fluid. The drill core is then the desired specimen. Other tools such as fret saws and files are only used in special cases.

(g) *Surface grinding*. This requires flat grinding plates, which one can produce with high precision preferentially from glass or brass. Other grinding forms, e.g., with concave or convex surfaces can be produced in a similar manner. A suitable grinding plate should be provided for each grain size of the abrasive and if possible a separate working surface so that coarse grains do

not mix with the fine grains in the grinding process. Thus a high degree of cleanliness is necessary. Flat grinding plates with diamond coatings, where the danger of carrying over coarse grains is minimal, are also commercially available. For the preparation of single specimens it is still appropriate to work by hand. Only in series production it is worthwhile to work simultaneously with several objects on the grinding machine. When working by hand, the expenditure of fastening the piece in a grinding holder can be spared as long as the pieces are large enough. Small crystals and exacting work demand the use of a grinding holder, a brass ring, where the underside is machined flat. The specimen is imbedded in the ring with the aid of a suitable cement (beeswax, synthetic resins which harden or melt at low temperatures depending on the thermal stability of the crystal), so that the underside of the ring, which limits the grinding process, fixes the desired flat surface. These holders can also be fastened in automatic grinding machines.

The grain size of the abrasive must be relatively homogenous to prevent deep mechanical damage to the surface. For this reason, grinding with coarse grain should be avoided as far as possible. In any case, one should use ample amount of grinding fluid. Water, propanol, and ethyl glycol have been found to be especially useful. The grinding process must be continuously controlled. For this purpose one uses precision angles made of steel, goniometers, straightedges, micrometers, and thickness gauges for the quantitative determination of thickness. These instruments can measure, or keep to specifications, angles to an accuracy of a few arcseconds and lengths to an accuracy of $0.5\ \mu\text{m}$. Employing optical interferometer devices a still better precision can be achieved.

Polishing is often required as the last step in the preparation. The methods used are mainly those proven in optics. The process can be considered as a refined form of grinding when we work with polishing plates made of plastic or pitch (for optical purposes). The only polishing fluids one can use are those which do not attack the polishing plate and have little aggressive effect on the specimen. Ethyl alcohol or higher alcohols are often used for water-soluble crystals. The recommended polishing agent is a fine wash of suspended chromium oxide, iron oxide, cerium oxide, aluminum oxide, or diamond paste. The polishing process is also carried out in several steps, from coarse- to fine-grained agents. Medium-hard crystals such as fluorite require a grain size of about $0.5\ \mu\text{m}$. The special measures needed to achieve an optic polish of the highest quality, e.g., with a flatness of $1/20$ of the wavelength in the visible spectrum, must be learned in special training courses. They, however, are only more refined methods of those discussed above.

In the technical application of crystals, the method of preparation can be considerably simplified when one succeeds in getting the desired form already during the manufacturing process.

2.2

Orientation

The term 'orientation' is used in the *passive* sense for the description of the geometrical position of a crystal referred to a crystallographic reference system, and in the *active* sense for the alignment of certain faces to the crystallographic reference system by cutting or grinding. We can, for example, search for the orientation of the basic vectors of a prominent crystallographic reference system by studying morphological details or by means of X-ray analysis (Laue method, Bragg method). The investigation of physical properties, especially with optical and piezoelectric methods, which we will come to later, can be of great help in this regard. At present, we will assume that the orientation of the crystal, in the passive sense, is known and the task is now to prepare an oriented specimen, e.g., a parallelepiped, with specified faces. We proceed as follows: first, instead of the crystallographic reference system defined by the three vectors a_i , which is normally associated with one of the seven prominent crystallographic systems due to the given minimum symmetry, we introduce a new reference system, the crystal-physical reference system. This is a Cartesian system with basic vectors e_i attached to the vectors a_i according to the following convention:

$$e_2 \parallel a_2^*, \quad e_3 \parallel a_3, \quad e_1 \parallel e_2 \times e_3$$

(a_2^* is normal to the surface (010) and is the second basic vector of the reciprocal system!)

We use, practically without exception, this Cartesian reference system for the description of physical properties as opposed to morphological properties and diffraction phenomena. If another orientation of the reference system is selected, this must be specially noted. It is often convenient to specify the faces in the crystal-physical reference system by their Miller indices. To distinguish between the crystallographic Miller indices, we use a symbol with a dash, e.g. (110)' means a face whose normal bisects the angle between e_1 and e_2 .

Now to get from an arbitrary crystal, say a melt boule, where often no morphological details are recognizable, to a defined reference base for further orientation work, it is useful to introduce another reference system which we shall call the laboratory system. This system with the Cartesian vectors e_i^L is randomly assigned to the object, however, matched as far as possible to the crystal-physical system. This is done by grinding two arbitrary surfaces F_1^L and F_2^L on the object, preferentially perpendicular to each other. Let e_1^L run parallel to the normal of the surface F_1^L and e_3^L parallel to the intercepting edge of both faces. e_2^L is thus perpendicular to both vectors in such a way that just like in the e_i system, a right-handed system is created. The situation is sketched in Fig. 2.1.

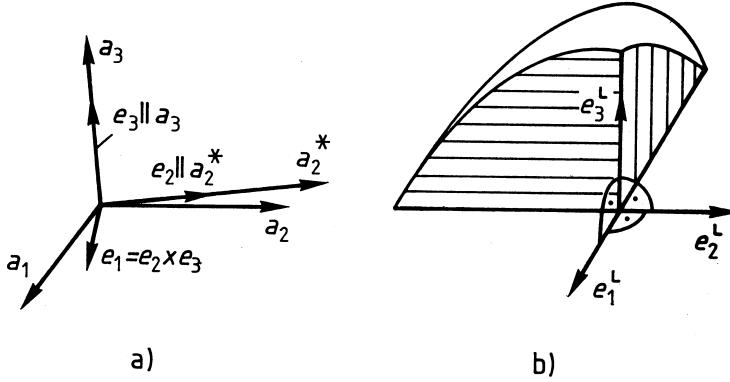


Figure 2.1 (a) Orientation of the Cartesian crystal-physical reference system in the crystallographic basic system. (b) The laboratory reference system.

To prepare the oriented specimen it is now practical to find the relationship between both Cartesian systems in order to carry out quickly and clearly all the required calculations. Thus one must set up the system $e_i = u_{ij}e_j^L$ (where $i = 1, 2, 3$) with the coefficients u_{ij} . This occurs with the help of the Laue method or the Bragg method.

The task is often to represent the unit vector of a face normal $h = h_i a_i^*$ or the unit vector of a lattice line $u = u_i a_i$ in the crystal-physical system. For this purpose we calculate the unit vectors $h/|h| = u_{1i}e_i = e_1'$ and $u/|u| = v_{1i}e_i = e_1'$, respectively. From the definition of the crystal-physical system $e_1 = e_2 \times e_3$, $e_2 = a_2^*/|a_2^*|$ and $e_3 = a_3/|a_3|$ and with the help of the known scalar products $h \cdot e_i$ and $u \cdot e_i$, we have

$$\begin{aligned} u_{11} &= \frac{1}{V a_2^* |h|} (h_1 a_3 - h_3 a_1 \cos \alpha_2), \\ u_{12} &= \frac{1}{|h|} (h_1 a_1^* \cos \alpha_3^* + h_2 a_2^* + h_3 a_3^* \cos \alpha_1^*), \\ u_{13} &= \frac{h_3}{a_3 |h|}, \\ v_{11} &= \frac{1}{V^* a_3 |u|} (u_1 a_2^* - u_2 a_1^* \cos \alpha_3^*), \\ v_{12} &= \frac{u_2}{a_2^* |u|}, \\ v_{13} &= \frac{1}{|u|} (u_1 a_1 \cos \alpha_2 + u_2 a_2 \cos \alpha_1 + u_3 a_3). \end{aligned}$$

a_i , α_i , and V and a_i^* , α_i^* , and V^* , respectively, are the values of the metric of the basic system and the reciprocal system. These relationships also allow,

without further requisites, additional measurements, referred to the selected crystallographical system, in the direction of the normals of natural crystal faces or along natural crystal edges.

All the required angle data for a special cut can now be expressed in the laboratory system and controlled by simple angle measurements during the grinding process. The practical procedure is explained below with the help of three typical examples of melt boules of cubic crystals, which often show no morphological details with respect to the determination of orientation.

(a) *Melt boule of an alkali halides of NaCl type.* These crystals possess an excellent cleavage of the cubic faces $\{100\}$. We therefore try to discover, by carefully cleaving at the edge of the boule, a cleavage face recognizable by a flat, mirror-smooth fracture. We then search for a second surface perpendicular to this face. The normal to these faces defines the crystal-physical reference system. The laboratory system, in this case, is for reasons of practicality, also fixed by the cleavage faces ($e_i = e_i^{\perp}$).

(b) *Melt boule of CsBr or CsI.* These crystals exhibit no well-developed cleavage. If one inserts the melt boule in a saturated aqueous solution of CsBr or CsI and cools the system down to several degrees, one observes after a few hours mirror-smooth surface elements of the rhombododecahedron $\{110\}$. The cubic basic vectors bisect the angles between the normals of such surface elements, which form angles of 90° . Thus the orientation of the crystal-physical system is known.

(c) *Melt boule of AgCl or AgBr.* These crystals do not possess a well-developed cleavage at room temperature nor sufficient solubility in water. In a saturated ammoniacal solution of AgCl or AgBr, they form, after a short time of evaporation, mirror-smooth surface elements of the cube faces $\{100\}$. As in (a) these allow a direct determination of crystal orientation.

The accuracy of the determination of crystal orientation can be easily checked using X-ray techniques such as the Laue method or the Bragg method.

We now imagine that the fixed crystal-physical reference system is established in space in the crystal. We thus speak of an initial reference system. During measuring processes or in technical applications, the crystal can experience certain changes which often have an effect on the quantities used to fix the orientation. Normally, we assume that the influence of such processes is so small that the orientation of the reference system, as well as the properties of the crystal, measured in this system, is only affected to a nonmeasurable extent. If this is not true, then one requires a careful analysis of the special situation, as in the case of nonlinear elasticity (see Section 4.6.3), where primary mechanical deformations are superimposed by secondary deformations.