

LABORATORY FOR ORIENTING SINGLE CRYSTALS

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Abstract

The study summarizes author's long experience with orienting single crystals used for optical and magnetic studies.

Introduction

For various optical and magnetic studies, single crystals in form of prisms, plates or other forms having a defined orientation with respect to the crystal axes are required. In the Institute of Physics of the Acad. Sci. of the Czech Republic, v.v.i., the Crystal orientation laboratory belongs to the Department of Structure analysis, and is located in the building Cukrovarnická 10, Prague 6. It is equipped with the Oxford Diffraction X-ray stand, which has replaced in 2001 the aged Mikrometa apparatus. The standard Chirana steel bar holder is still used for attaching film cassettes and various kinds of crystal holders.

Experimental

The back-reflection Laue method is a versatile method for aligning bulk crystals (attached on some kind of a special holder allowing rotation and/or tilting to a certain extent) in a desired position with respect to the crystallographic axes or planes. The holder together with the oriented crystal can be then mounted onto the saw and oriented specimens can be prepared by cutting. The back-reflection arrangement allows checking crystals of a theoretically unlimited size. However, the diffraction pattern represents the irradiated area only.

In the laboratory, two kinds of holders are most commonly used; one of them allows tilting and rotation around the vertical axis, both limited to less than approx. $\pm 15^\circ$

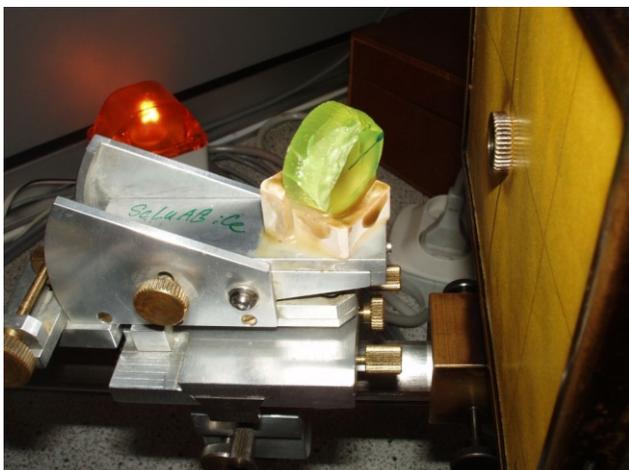


Figure 1. Crystal holder allowing rotation and tilting of the specimen.

(Figure 1). The second, with Eulerian geometry, allows full and partial rotation around the and circles, respectively (Figure 2). The former holder requires a crystal already pre-oriented by some other method, e. g. by the light extinction between crossed polarizers. The Euler holder allows rotation in a much wider range, but it can be mounted onto some kind of saw only. Crystals are glued with the aid of a certain kind of wax, usually onto a ceramic substrate. There are some other holders, used for checking of various specimens not intended to be cut. Occasionally the users bring their specimens mounted on their own holders.

The usual procedure involves checking the crystal between crossed polarizers, then pre-orienting it with the aid of the Eulerian holder, and finally setting it into an appropriate position perpendicular to some important crystallographic plane with the aid of the tilt and rotation holder. The oriented bulk crystal is then cut into smaller oriented pieces, usually plates. These are returned to the laboratory and are oriented along the second crystallographic plane. Then the cutting is repeated and oriented specimens are prepared. Some faces may be polished if needed.



Figure 2. Crystal holder with Eulerian geometry.

Interpretation

The unfiltered (polychromatic) X-ray beam singled out by a collimator passes through the hole in the film cassette and finally hits the stationary crystal. Diffracted beams are recorded on a planar film. In our laboratory, a current Mo tube, producing enough polychromatic radiation, is used. The Bragg condition is obeyed for an a priori unknown wavelength corresponding to the given d and fixed θ of the

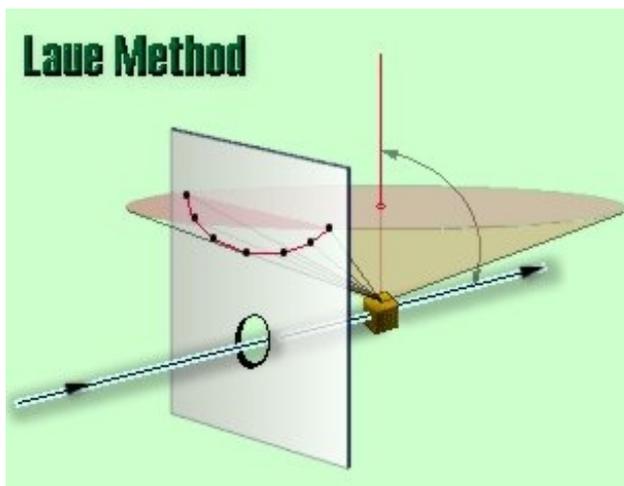


Figure 3. Geometry of the back-reflection Laue method.
www.mater.org.uk/diffraction/x-ray/laue_method.htm

respective lattice plane. The geometric scheme of the method is in Figure 3. Ordinary X-ray films are used for the recording.

The method provides a collapsed and distorted image of the reciprocal lattice [1], [2]. Diffraction spots are arranged on garlands having the form of conic sections – ellipses and hyperbolas for the front- and back-reflection arrangements, respectively. These conic sections correspond to zones in direct space and planes in the reciprocal lattice. The diffraction spots themselves correspond to reciprocal lattice points, or to more than one point placed on the same radius vector in the reciprocal space. The diffraction spots, where two or more hyperbolas cross are usually intense and they are rather isolated from their neighbors. Usually they represent reciprocal vectors corresponding to prominent crystallographic directions. For more information, see also [3, 4]. Occasionally some diffraction spot is excessively intense; in this case, the Bragg condition is accidentally obeyed for the characteristic MoK or MoK line.

In Figure 4 there is an example of a generally oriented Laue pattern with two prominent diffraction spots, (indicated by circles).

The respective angular corrections are determined with the aid of the Greninger chart (Fig. 5). The left-right hyper-

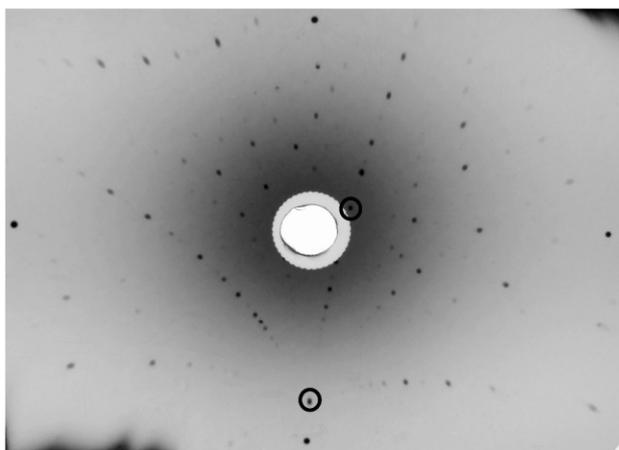


Figure 4. Generally oriented back-reflection Laue photograph with two possible prominent diffraction spots (circled).

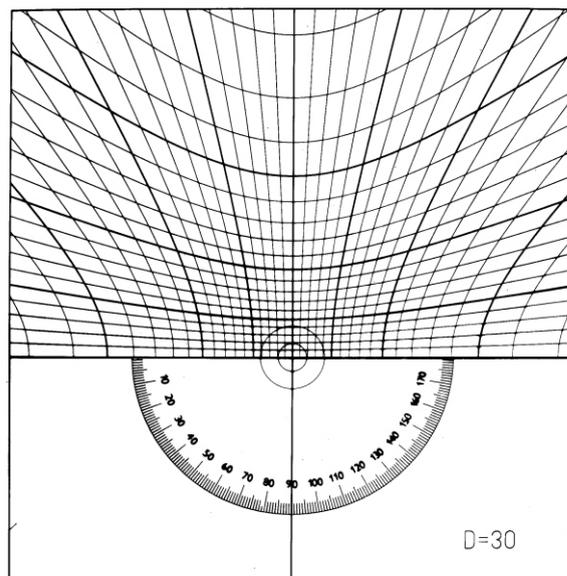


Figure 5. Greninger chart for the interpretation of back-reflection Laue photographs.

The chart can be downloaded from the page
<http://www-xray.fzu.cz/xraygroup/www/grchart.html>.

bolae correspond to the shape and position of garlands depending on the angle made with the primary beam. The vertical hyperbolas allow a determination of angles between the diffraction spots on hyperbolas. When printed appropriately scaled, correct values can be read corresponding to the sample-to-film distance of 30 mm. Note that the garlands (and respective hyperbolas) closer to the origin are progressively flatter. In the extreme case of the reciprocal lattice plane just parallel to the initial beam (and perpendicular to the film), the hyperbola degenerates into a straight line.

The angular corrections of the crystal mounted on the tilt and rotation holder are read as two perpendicular coordinates of a selected diffraction spot with aid of the Greninger chart. For the Euler holder, the crystal must first be set by rotation of the circle to the equatorial plane, and then rotated by circle into the appropriate position. After the corrections are done, the selected reciprocal vector is just parallel to the primary beam and perpendicular to the film. The corresponding crystallographic plane is parallel to the film and perpendicular to the primary beam.

An aligned crystal provides a diffraction pattern, where the distribution of diffraction spots and of hyperbolas reflects the Laue symmetry around the axis parallel to the primary beam. This arrangement is usually characteristic for the given crystalline substance, orientation, and experimental conditions.

The final Laue photographs are compared visually with a standard photograph of the same compound from the author's archive. If these standard lauegrams are not available (for crystals not studied before) the following procedure is performed: First, a small fragment is mounted on the Buerger precession camera [5], aligned with the aid of the standard procedure for this method, then a precession pho-

tograph is recorded, lattice parameters calculated and respective reciprocal lattice vectors identified. Then the special back reflection cassette is mounted on the precession camera, the motion is switched off, and precession angle is set to 0. Under such conditions, a back reflection lauegram is recorded. This photograph serves then as a standard for orientation of bulk crystals. The procedure is then repeated for all necessary crystallographic directions.

Examples of crystals studied

In the past decades numerous oriented specimens of various crystalline compounds were prepared. Some of them are listed here: PbCl_2 , PbBr_2 , PbWO_4 (PWO), PbMoO_4 (PMO), YAlO_3 (YAP, Yttrium-aluminum perovskite), LuAlO_3 , LiBaF_3 , LiCaAlF_6 , garnets (YIG, LuAG, GGG), magnetite, LiYF_4 , LiLuF_4 , Lu_2SiO_5 (LSO), Y_2SiO_5 (YSO), $(\text{Lu}, \text{Y})_2\text{SiO}_5$ (LYSO), CdWO_4 and many others. In a small gallery, some characteristic back-reflection Laue photographs are presented, with important crystallographic planes (perpendicular to the primary beam) indicated (Figs. 6-9).

Problems

Surfaces of crystals studied

Most of crystals studied are artificially grown in the laboratory. Therefore they only rarely exhibit natural crystallographic planes. Their shapes rather depend on the growth method and/or previous cuttings. Most of crystals are Czochralski- or Bridgmann-grown cylinders. While the former provides smooth surfaces well suitable for X-ray diffraction, the surface of the latter is defined by the shape of the ampoule and usually is matt, often with bubbles and is thus inappropriate for diffraction in most instances. The currently used remedy is grinding and polishing of a small plane in the appropriate area of the crystal prior the diffraction experiment. In some instances (PbCl_2) polishing provides an excellent surface while in other materials it damages the near-surface zone, affecting thus the quality of diffraction pattern.

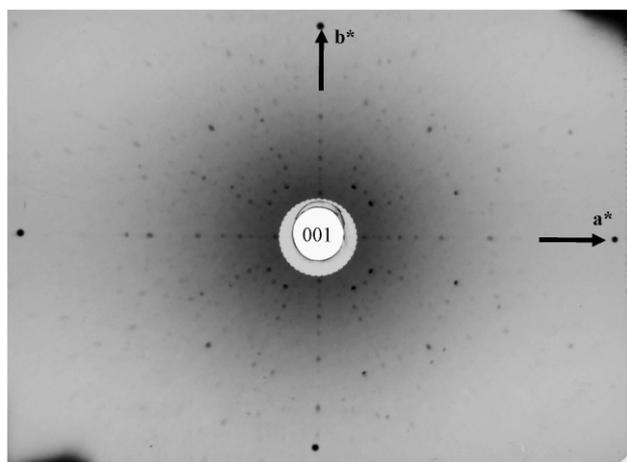


Figure 6. Lutetium-aluminum garnet, $\text{Al}_5\text{Lu}_3\text{O}_{12}$, cubic, (001), (fourfold axis), a^* and b^* vectors indicated.

Some crystalline materials are covered by a nearly X-ray amorphous layer, well known examples are gold and some intermetallic compounds.

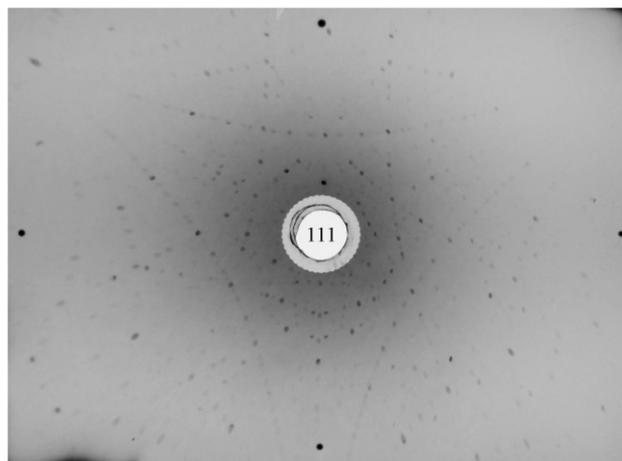


Figure 7. Lutetium-aluminum garnet, $\text{Al}_5\text{Lu}_3\text{O}_{12}$, cubic, (111), (threefold axis, slightly misoriented).

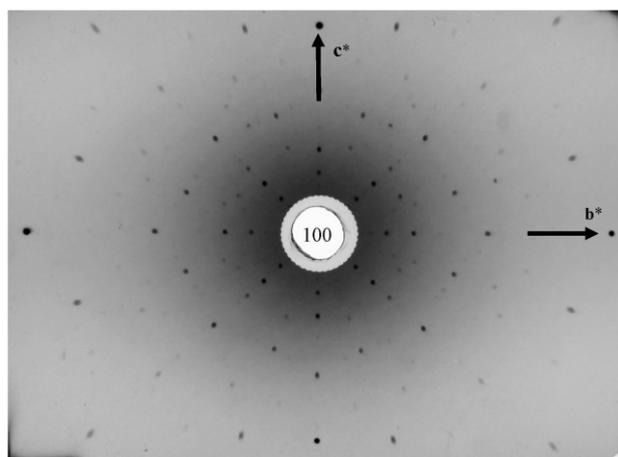


Figure 8. Lead tungstate PbWO_4 (PWO, stolzite), tetragonal, scheelite structure, (100), (twofold axis).

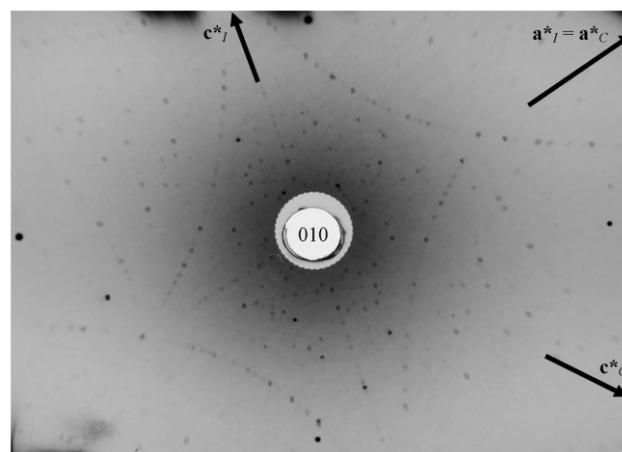


Figure 9. Lutetium silicate oxide Lu_2SiO_5 , (LSO), monoclinic, (010), (monoclinic twofold axis), a^* and c^* vectors of two optional unit cells (C and I centered) are indicated.



Pseudosymmetry

Many structures are formally derived by deforming some “ideal” type structure. Typical examples are perovskites or closest-packed structures. Due to structural deformation, like coordination polyhedra tilting (in perovskites) or unequal occupancy of holes (in closest-packed structures) some symmetry elements are “lost”. As the real atomic positions are still close to these of the “ideal” type structure, a strong pseudosymmetry often persists. The diffraction images taken along the “lost” and true axes are often very similar, so that they can be mismatched. The Laue pattern must be very carefully checked in order to determine the true symmetry.

For example, LiNbO_3 represents rhombohedrally deformed perovskite [5]; only one of four triads of the “ideal” cubic perovskite persists, similarly three of the six diads, but none of the three tetrads. The $\text{-Al}_2\text{O}_3$, (corundum) is cubic closest packed structure rhombohedrally deformed due to partial occupancy of Al in tetrahedral cavities. It also exhibits a significant pseudosymmetry along “lost” axes of the non-standard F -centered rhombohedral cell.

CdWO_4 (wolframite structure) is monoclinic, derived from the ideal tetragonal structure. The \mathbf{a}^* and \mathbf{c}^* vectors correspond to tetragonal \mathbf{a}^* , \mathbf{b}^* vectors and the pseudosymmetry is so strong, that both directions cannot be distinguished on the Laue pattern along \mathbf{b}^* . However, they can be reliably distinguished on the $h0l$ precession photograph, because of the $P2/c$ space group extinction ($l=2n$).

Crystal quality

Various physical studies usually require crystals of certain degree of quality. This is not always satisfied. Instead, many crystals are composed of mosaic blocks, which are in some cases misoriented more than it is acceptable. If the crystal is carefully oriented with respect to one given block, this orientation is not valid for the rest of the crystal. In some cases such mosaicity can be revealed if the primary beam just hits the domain boundary. In such a case the diffraction spots are split, or even blurred, if there are several smaller domains in the irradiated area. The mosaicity can sometimes be observed visually on the cleavage planes.

Twinning is another complication which might appear. If the optical orientations of twin domains are different, they can be recognized optically by observing the crystal between crossed polarizers. The required oriented sample must be prepared from one domain only.

Some compounds yield Laue patterns with garlands sparsely occupied by diffraction spots. The interpretation of such patterns is difficult, as the hyperbolas are not apparent at the first glance, even if the crystal is close to the correct orientation. Magnetite, for example, belongs to such problematic materials.

Ambiguity of unit cell choice

Many crystalline compounds allow multiple unit-cell choices. For example, in the orthorhombic system, 6 permutations of unit cell vectors are possible [7], producing up to 6 possible space group symbols. In monoclinic crystals, alternative I- or C- centered unit cell choice might appear. As the researchers from other branches of physics and chemistry are usually not well trained in crystallography, they might mismatch crystal directions. A deplorable, but unfortunately very common practice is referring values of physical measurements with respect to crystallographic directions, without specifying the unit cell.

Ambiguity of modification

Some chemical compounds exist in more than one crystallographically distinct modification. In physical journals, authors sometimes forget to specify to which modification the values in the given paper refer. This fact represents another possible source of confusion. If there is any doubt about the modification of the crystal studied, a small fragment should be tested on a precession camera or a diffractometer.

References

1. Amorós, J.L., Buerger, M.J., Amorós, M.C. de: The Laue Method. New York-San Francisco-London 1975, Academic Press.
2. Barrett, Ch. S.: Structure of Metals. New York- Toronto -London 1952, McGraw Hill Book Company.
3. Ďurovič, S., Hybler, J.: Monokryštalové filmové metody. Sborník: Experimentální techniky v rentgenové a neutronové strukturní analýze, Krystalografická společnost 1994 (in Czech and Slovak).
4. Hybler, J.: Monokryštalové metody s registrací na film nebo obdobná plošná media. On the webpage: www.xray.cz/kryst/difrakce/hybler/monokrystal.htm (in Czech).
5. Buerger, M.J.: The Precession Method in X-ray Crystallography. New York-London-Sydney 1964, John Wiley & Sons.
6. Vokoun, J., Studnička, V.: Hodnocení základních materiálů elektroniky použitím rtg metod. Výzkumná zpráva č. 1620 13 712/3, TESLA VÚST A.S.Popova, Praha 1982. (In Czech)
7. Hybler, J.: The permutations of lattice parameters and space group symbols of the orthorhombic PbCl_2 . Cryst. Res. & Technol. 23, 1127-1133, 1988.

Acknowledgements

Single crystals for studies were kindly provided by M. Nikl and K. Nitsch from the Institute of Physics, Acad. Sci. of the Czech republic, v.v.i. I also thank M. Rieder for critically reading the text.