Single crystal X-ray diffraction

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based on the Hungarian version of the Laue lab description which was written by
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INTRODUCTION

X-ray diffraction is a key and diverse test method used in all aspects of the modern natural sciences. Different X-ray diffraction methods exist for the investigation of crystalline and amorphous solids, liquids and gases. X-ray diffraction procedures are used in the case of crystalline materials for both polycrystalline and single crystal samples, however the methods used in these two groups are significantly different. In polycrystalline or powder diffraction, a monochromatic X-ray beam interacts with large number of crystallites with different spatial orientation. Therefore, quite a lot of crystal orientation meet with the conditions of diffraction and several diffraction maxima (reflections) become measurable. The powder diffraction techniques can be effectively used in the following cases:

- (I) Phase analysis: identification one or more crystalline phases from polycrystalline or powdered sample.
- (II) Determination of lattice parameters: very accurate lattice parameters of a known crystal structure is measured.
- (III) Microstructure examination: diffraction line shape (line profile analysis) of polycrystalline sample is determined to determine crystallite size distribution and type of crystal defects in the sample.

The powder diffraction methods maybe used for the determination of unknown crystal structures (e.g. Rietveld methods), but they are not so effective as single crystal diffraction methods.

Single crystals diffraction methods are suitable for single crystal samples in which the crystalline order of the atoms does not change in the whole tested volume of the material. For example, crystal microdiffraction is also single crystal diffraction method, if the beam size is smaller than the crystallite size and only one crystallite is illuminated simultaneously.
The single-crystal diffraction techniques can be effectively used in the following cases:

- (I) Structure determination when an unknown structure or atoms arrangement of a single crystal to be determined. Nowadays, this method is used intensively for structure determination of proteins. Whereas, the unknown structure of crystallized protein is determined very precisely from X-ray diffraction allowing the determination of atomic structure of the protein molecule itself.
- (II) Determination of lattice defects in single crystal. (Crystals often contain lattice defects due to crystal preparation or deformation.) The amount and type of the dislocations in a single crystal can be determined from the shape of the diffraction peaks.
- (III) Determination of the orientation of single crystals, i.e. the orientation of the crystallographic axes of a single crystal in the coordinate system of the lab. This method is useful when the single crystal is to be machined or cut parallel to particular crystal planes. Completion of lattice defect analysis (test II) also requires the knowledge of crystal orientation.

In the following description and also in the laboratory experiment, we will deal with the details of the orientation determination method for single crystals by the Laue method.

DESCRIPTION OF THE THEORY OF LAUE METHOD

The Laue diffraction methods was the first developed single crystals diffraction method. Additionally, it is the simplest and most famous single crystals examination procedure, which is commonly used for crystals orientation determination. The method leads to about 1 deg accuracy using relative simple measurement setups. In Laue diffraction, a thin sample is illuminated by a few tenths of a millimeter diameter continuous spectrum X-ray beam and the diffraction image is recorded onto a planar or cylindrical surface with film, imaging plate or CCD detector. In the lab tests an imaging plate detector will be used.

Mostly, the recording media has a planar surface and it is perpendicular to the primary beam. If the surface is placed in the $2\theta < 90°$ range, the detector is in front reflection position (Figure 1), and if it is in the $2\theta > 90°$ range, the detector is in rear reflexion position. Due to the continuous X-ray spectrum, all crystal plane (with adequate crystal plane distance) have a specific λ wavelength components, which meets with the conditions of the Bragg's equation [1],

$$2d_{hkl}\sin(\theta_{hkl}) = \lambda \qquad (1)$$

where hkl are the Miller indices for a given crystal plane, d_{hkl} is the corresponding distance of the crystal planes and θ is a fix Bragg angle determined by the setup. Therefore, the different hkl planes reflect sharp intensity maxima in different directions with the matchinh λ wavelengths.

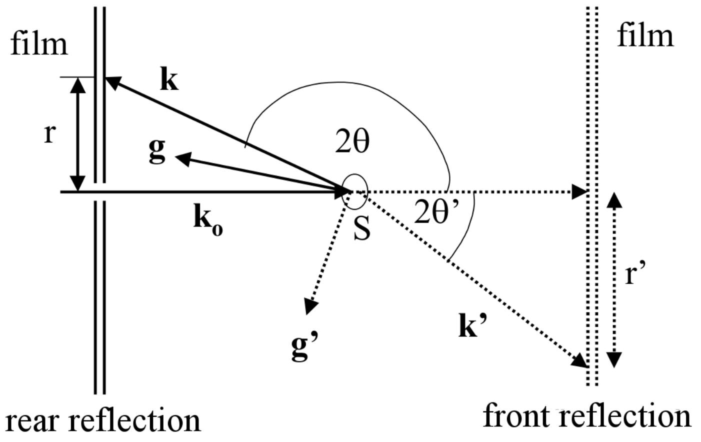


Figure 1: The Laue-geometry. S - indicates the sample. (arrows indicate only the direction of the different vectors).

The normal direction of the reflecting planes (this is the g diffraction vector) can be determined from the directions of reflections and that of the the primary beam as shown in Figure 1. The Bragg equation can be reformulated to reflect the relationship between the g diffraction vector and the primary beams and the scattered k0 and k wave vectors,

$$k - k_0 = g \quad . \tag{2}$$

Based on Eq 2., the vector g is in the plane which is spanned by k and k0 vectors. A characteristic feature of Laue image is that if the crystal along an axis of symmetry is illuminated the Laue pattern of the diffraction image will show this symmetry, as shown in Figure 2.

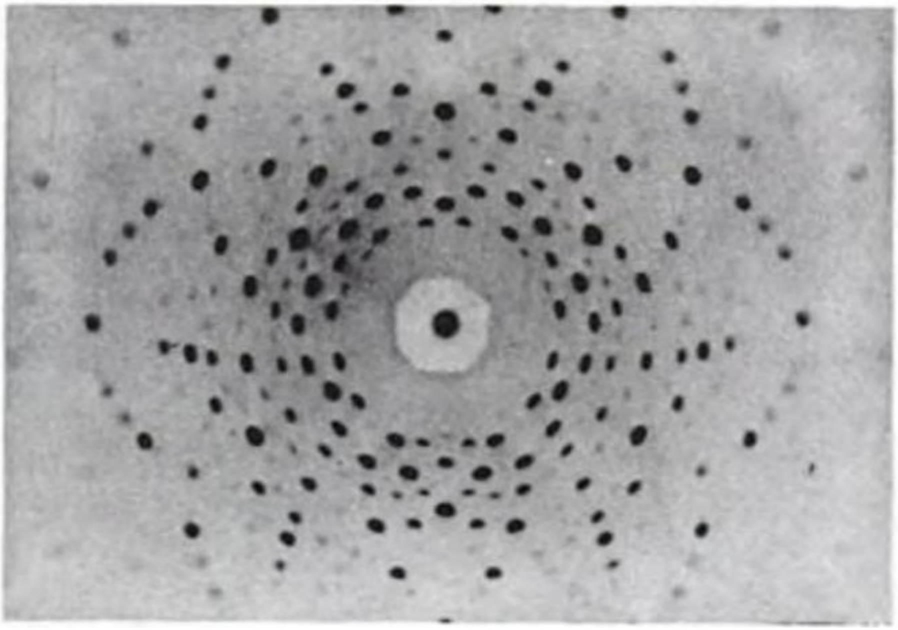


Figure 2: Laue image of a quartz single crystal. The incident beam is parallel to the c axis of the hexagonal crystal, so that diffraction image has a three fold symmetry.

Therefore, directions of the symmetry axis can be recognized without further investigation, even without the knowledge of parameters of the crystal unit cell.

The crystal planes, which are parallel to a common direction form a zone. The common direction of the planes is called zone axis (see Figure 3a). The vector of the zone axis, A_{uvw}, can be expressed as a linear combination of the vectors of the unit cell,

$$A_{uvw} = ua_1 + va_2 + wa_3 \quad , \tag{3}$$

where u, v and w are integers and a_1, a_2 and a_3 are the vectors of the unit cell. An hkl plane is parallel to the axis if A_{uvw} vector of the zone axis is normal to the H_{hkl} vector of the plane, so that scalar product of the zone axis and the vector of the plane is zero,

$$A_{uvw} H_{hkl} = 0 \quad , \tag{4}$$

From the theory of diffraction we know that the g_{hkl} diffraction vector of a hkl plane is parallel to the normal vector of the reflecting plane. Thus, these reflections belongs to a zone,

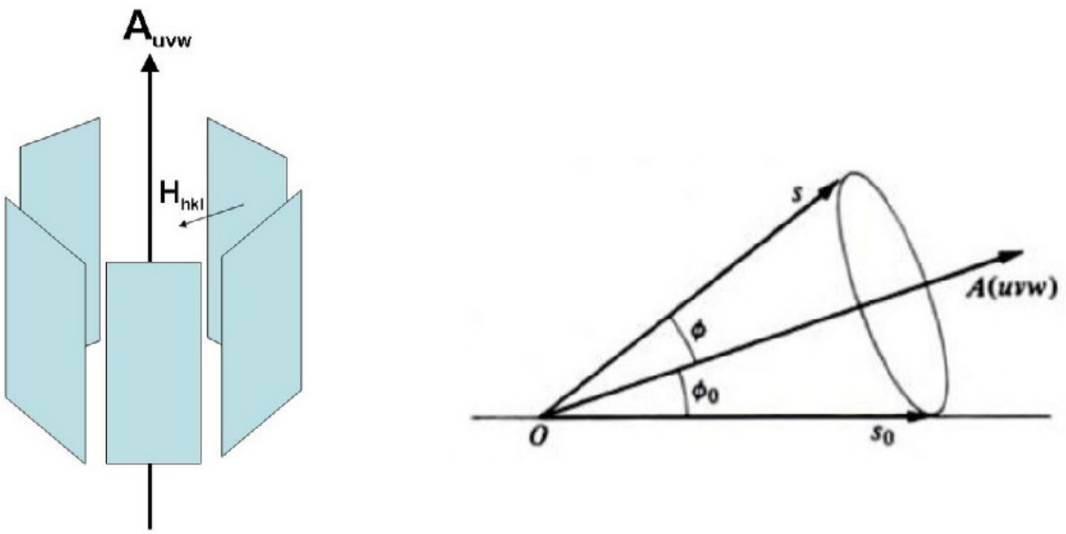
$$A_{uvw}\, g_{hkl}=0 \quad , \tag{5}$$

where

$$g_{hkl}=hb_1+kb_2+lb_3 \quad , \tag{6}$$

and b_1, b_2 and b_3 are the vectors of the reciprocal lattice. Because the vectors of the crystal's unit cell and the vectors of the reciprocal lattice are defined to meet the $a_i b_j=\delta_{ij}$ relationship, the zone law can be calculated from Eq. 3, Eq. 6 and Eq 5,

$$hu+kv+lw=0 \quad , \tag{7}$$



(a) (b)

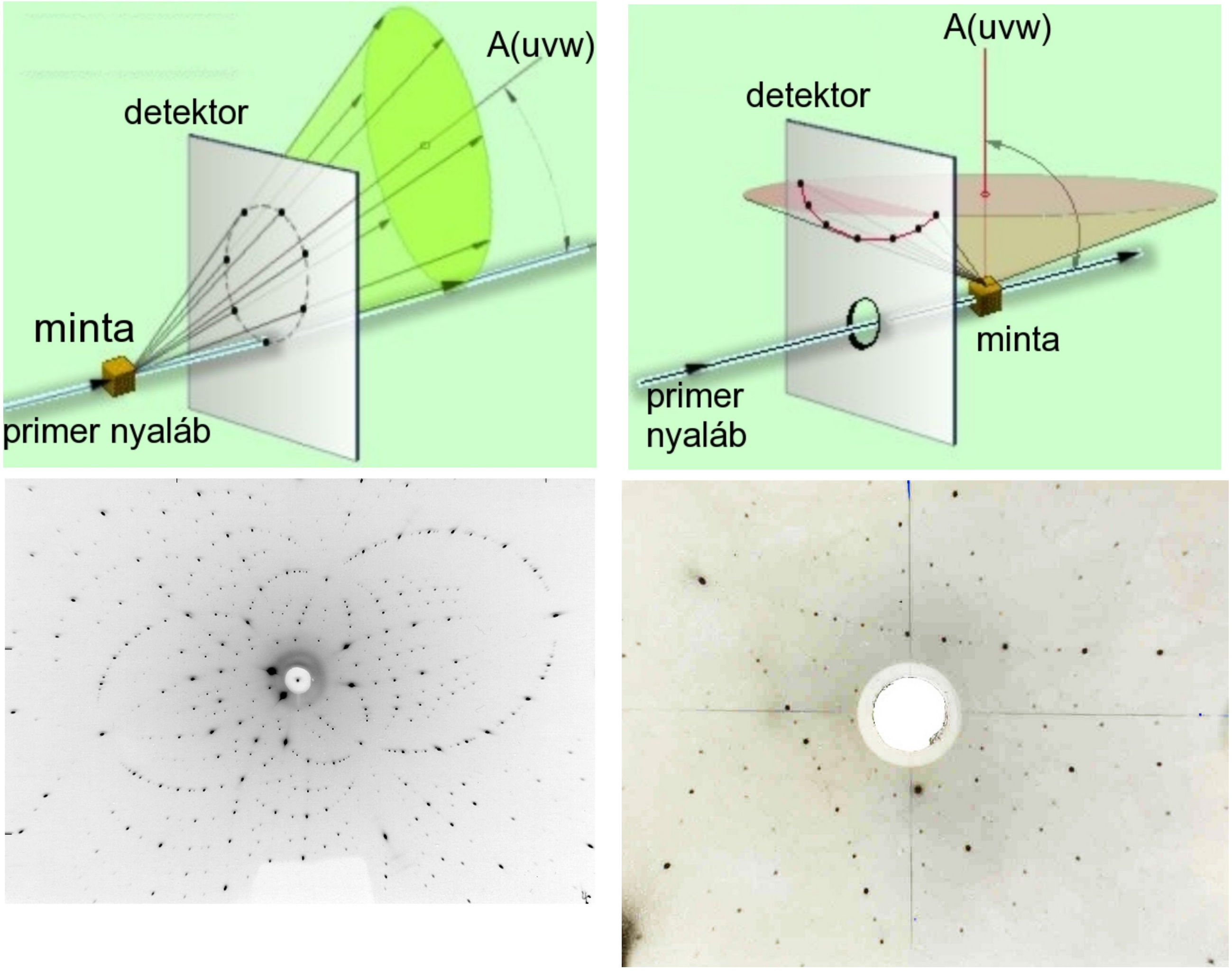
Figure 3: (a) The A_{uvw} zone axis and schematic hkl planes of the given zone. The H_{hkl} is the normal vector of the planes and it is normal to the zone axis. (b) The planes belongs to a common zone axis reflect radiation along a cone.

Let s and s_0 are the unit vectors of incident and the reflected beams on a particular hkl plane, respectively. They are λ times the k and k_0 vectors. From the Bragg's equation of Eq. 2

$$s-s_0=\lambda\, g_{hlk} \quad , \tag{8}$$

Let multiply both side of Eq. 8 by the zone axis vector, A_{uvw},

$$sA_{uvw}-s_0\, A_{uvw}=\lambda\, g_{hlk}\, A_{uvw} \quad . \tag{9}$$



(a) (b)

Figure 4: (a) Laue image of an aluminum oxide single crystal in front position. (b) Laue image of silicon single crystal rear position.

If we select hlk planes from a uvw zone, than the rhs. of Eq. 9 will be zero based on Eq. 5. This means that the angle between the direction of the incident beam and the zone axis equal to the angle between the direction of the reflected beam and the zone axis for all the hlk planes of a selected uvw zone,

$$sA_{uvw}=s_0 A_{uvw} \quad , \qquad (10)$$

Therefore, the s reflection vectors which are related to planes of a given zone axis are placed along a cone with φ_0 half angle (see Fig 3b) and the intensity maxima recorded onto a plane are placed along cone-sections. These cone-sections are ellipses in the front reflection position while they are hyperbolas in the rear reflection positions (see in Figures 4a and 4b).

SHORT DESCRIPTION OF THE EXPERIMENTAL PROCEDURE TO BE PERFORMED IN THE LAUE LAB

1. Single crystal samples will be selected for orientation determination (students can also bring their samples).
2. Sample will be attached to an adequate goniometer to position and rotate the single crystal samples in the Laue diffractometer.
3. Laue diffraction image will be captured in the diffractometer using imaging plates and it will be recorded and digitalized by an imaging plate reader.
4. Laue diffraction image will be analyzed and orientation of the crystal sample will be determined by using unit cell parameters of the crystal and the experimental parameters in a specific program.
5. Crystal orientation will be presented in an stereographic projection and rotation angles between the calculated orientation and a selected crystal orientation will be determined.

Please, know and understand, the following expressions when you participate in the Laue Lab:
Bragg-equation, unit cell and unit cell parameters, stereographic projection, zone axis, Miller-indices