Related topics

Crystal lattices, crystal systems, crystal classes, Bravais lattice, reciprocal lattice, Miller indices, structure amplitude, atomic form factor, Bragg equation.

Principle and task

A polycrystalline sample and a monocrystal are irradiated by an X-ray beam. The resulting diffraction patterns are recorded with an X-ray film and evaluated.

Equipment

X-ray unit. w. recorder output	09056.97	1
Diaphragm tube w. nickel foil	09056.03	1
X-ray film, 90 mm × 120 mm, 10 sheets	06696.03	2
X-ray film developer, f. 4.5 l sol.	06696.20	1
X-ray film fixing, f. 4.5 l sol.	06696.30	1
Sign holder	02066.00	1
Vernier caliper, plastic	03011.00	1
Mortar w. pestle, 70 ml, porcelain	32603.00	1
Tray (PP), 180 × 240 mm, white	47481.00	3
Microspoon, special steel	33393.00	1
Potassium bromide 100 g	30258.10	1

Problems

1. A Debye-Scherrer photograph is to be taken of a KBr sample. The Debye-Scherrer rings are to be evaluated and assigned to the corresponding lattice planes. The lattice constant of KBr must be determined.
2. The Laue diffraction pattern of a LiF monocrystal is to be recorded with an X-ray film. The Miller indices of the corresponding crystal surfaces are to be assigned to the Laue reflections.

Set-up and procedure

1) Debye-Scherrer method

To start with, the sample is crushed in a mortar until no grains can be felt when rubbing the powder between the finger tips. Coarse powder samples yield Debye-Scherrer reflections of inhomogeneous intensity distributions. The powder is spread between two strips of scotch-tape in a layer approximately 0.2 mm thick. This is fixed onto the diaphragm tube with nickel filter of thickness 1/100 mm. Samples of determined thickness can be prepared for example by perforating paper of the required thickness. Scotch-tape is stuck over the perforation on one side of the paper, then the perforation is filled with

Fig. 1: Experimental set-up for Debye-Scherrer photographs.

sample powder so that the powder surface is level with the free paper surface. The diaphragm tube is mounted, and the X-ray film enclosed in its light protection is set up vertically upon its holder, about 24 mm from the sample (see Fig. 1). (Make sure the "Tubeside" inscription is on the proper side). At maximum anode voltage, exposure time necessary for a good recognition of the interior Debye-Scherrer rings is about 5 hours. Longer exposures let the exterior low intensity rings appear more vividly. However, this has the disadvantage that the interior ring hardly can be seen, due to an overexposure of the central reflection. The film is developed in the dark room (read the notice on the package), watered, fixed during 10 minutes, watered again during 10 minutes, and then dried in air.

The distance between sample and film must be measured precisely in order to determine the diameter of the rings. It is recommended to keep well prepared samples for subsequent measurements.

2) Laue method

To start with, diaphragm tube d = 2 mm is mounted in the X-ray aperture. The counting tube mount and the crystal support are set at the 90° final position. The crystal support is then mounted into its bracket with the rounded side facing the diaphragm tube. This assures that the crystal support will not be in the path of the reflected rays. The X-ray film in its light-proof envelope stands in the corresponding holder about 2 cm from the crystal. In order to obtain undistorted Laue patterns, the crystal surface and the film must be parallel to each other, and both must be perpendicular to the primary beam. The film is exposed at maximum anode voltage. Intense reflections are obtained after 30 minutes of exposure. If weaker reflections are to be seen, too, an exposure of 90 minutes is recommended. The distance between crystal and film must be measured in order to determine the diffraction directions.

Theory and evaluation

When X-rays impinge upon the atoms of a solid, they are scattered by the electrons. The scattering power of the single atoms is represented by the atomic form factor f, which is roughly proportional to the number of electrons in the atom. We thus have:

$$f \sim Z \quad (Z = \text{atomic number}) \qquad (1)$$

If the solid has an orderly periodic structure, constructive interferences occur among the single diffraction waves. The direction of the resulting diffraction reflections is determined by Bragg's relation.

$$2d \sin \vartheta = \lambda \qquad (2)$$

d = distance between the lattice planes
ϑ = Bragg (glacing) angle
λ = wavelength

The intensity of the scattered reflections is proportional to the magnitude of the structure amplitude F. The latter is obtained by summation of the scattering amplitudes and their phases over the n atoms of the elementary lattice cell. If the co-ordinates of the n atoms are called u_n, v_n and w_n, the following relationis valid for F (h, k, l) (h, k, l = Miller indices of the reflecting lattice plane):

$$F (h, k, l) = \sum_n f_n \exp [-2\pi i (u_n h + v_n k + w_n l)] \qquad (3)$$

Fig. 2: Scattering geometry of the Debye-Scherrer method.
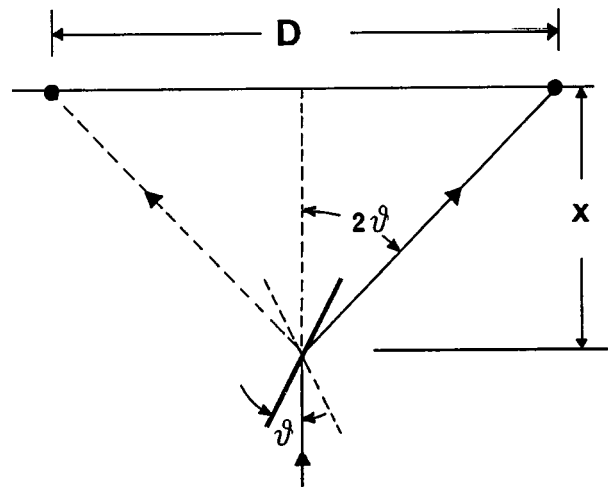
For body centred cubic (bcc) lattices, the following relation is valid:

F = 0 if the sum of the indices,
 h + k + l, is odd (4)

F = 2f if the sum of the indices,
 h + k + l, is even

For face centred cubic (fcc) lattices, the following is valid:

F = 0 if h, k and l are mixed, that is odd (5)
 and even indices are present

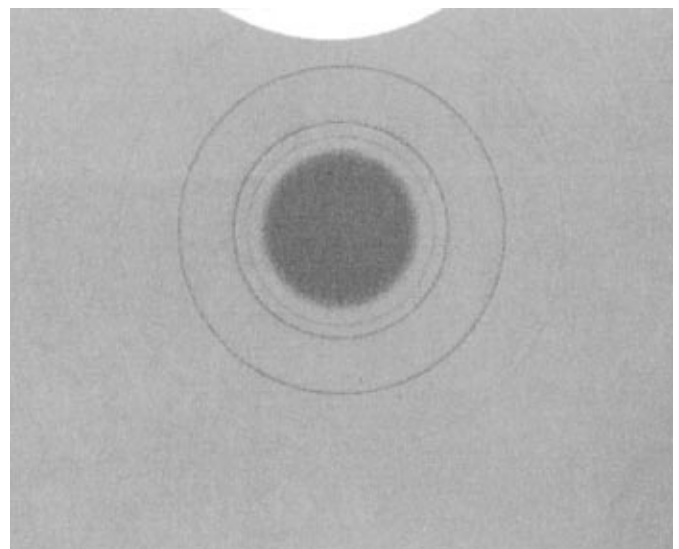F = 4f if the indices h, k and l are either
 all even or odd

Fig. 3: Debye-Scherrer rings for a KBr powder sample.

Debye-Scherrer method

If monochromatic X-rays impinge upon a polycrystalline sample with randomly distributed crystallites, among the latter there always are some which are oriented in such a way that their lattice planes and the primary beam fulfil Bragg's relation. Thus, all reflections belonging to a particular lattice plane are distributed upon the mantle of a circular cone, of which the primary beam is the axis and the aperture angle is 4ϑ. An X-ray film placed perpendcularly to the primary beam will thus record concentric circles as reflection images (Debye-Scherrer rings) (see Fig. 2 and 3). If the diameter of a diffraction ring is D, and x the distance between the sample and the film, Bragg's angle is given by the expression:

$$\vartheta = \frac{1}{2}\,\text{arc tan}\,\frac{D}{2x} \qquad (6)$$

If the sampe consists of cubic crystals with the lattice constant a, the following is valid for the distances d(hkl) between the lattice planes n(hkl):

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad (7)$$

using (6) and (7), one obtains from (2):

$$\sin^2\vartheta = \sin^2\left(\frac{1}{2}\,\text{arc tan}\,\frac{D}{2x}\right) \qquad (8)$$

$$= \frac{\lambda^2}{4a^2}\,(h^2 + k^2 + l^2)$$

The interference rings are assigned to the indices of the reflecting lattice plane as follows: the ratios are obtained from the sums of the squares of the h, k, l triples: one then searches for coincidence between these ratios and the ratios of the observed $\sin^2\vartheta$ values related to the innermost interference ring. To begin with, it is endeavoured to obtain a coincidence by surmising that the innermost ring must be assigned to the (100) plane. If this yields no satisfactory result, one tries with the (110) plane, and so forth, until a satisfactory coincidence of ratios is found (see Tab. 2).

Table 1 gives the ring diameters D obtained from the Debye-Scherrer photographs, as well as the correcsponding glancing angles.

ring	D/mm	ϑ	h k l	a/pm
1	20.2	11.6°	1 1 1	665.4
2	23.9	13.5°	2 0 0	661.8
3	38.2	19.6°	2 2 0	651.3
4	52.0	23.9°	2 2 2	660.5
5	72.0	28.4°	4 0 0	649.7

Table 1: Evaluation of Debye-Scherrer rings
Distance between sample and film: x = 23.5 mm

Table 2 gives the assignment schema for cubic crystals.

h k l	$\frac{h^2 + k^2 + l^2}{1^2 + 0^2 + 0^2}$	$\frac{h^2 + k^2 + l^2}{1^2 + 1^2 + 0^2}$	$\frac{h^2 + k^2 + l^2}{1^2 + 1^2 + 1^2}$	$\frac{\sin^2\vartheta}{\sin^2\vartheta_1}$
1 0 0	1	–	–	
1 1 0	2	1	–	
1 1 1	3	1.5	1	1
2 0 0	4	2	1.33	1.33
2 1 0	5	2.5	1.67	
2 1 1	6	3	2	
2 2 0	8	4	2.67	2.78
2 2 1	9	4.5	3	
3 0 0	9	4.5	3	
3 1 0	10	5	3.33	
3 1 1	11	5.5	3.67	
2 2 2	12	6	4	4.10
3 2 0	13	6.5	4.33	
3 2 1	14	7	4.67	
4 0 0	16	8	5.33	5.60

Table 2: Indexing of Debye-Scherrer rings.

The results of table 2 show that in the KBr lattice, reflections are obtained only from the (111), (200), (220), (222) and (400) planes; this means that only even or odd h, k, l triplets appear. According to (5), the KBr crystal is thus a face centred cubic (fcc) crystal.

The wavelenght of the Cu-K_α X-rays is λ = 154.5 pm. This value allows to calculated the KBr lattice constant a, using equation (8) (see Tab. 1)

$$a = \frac{\lambda}{2\sin\vartheta}\,\sqrt{h^2 + k^2 + l^2} = (658 \pm 7)\,\text{pm};\ \frac{\Delta a}{a} = 1\,\%$$

(Literature value: a = 659 pm)

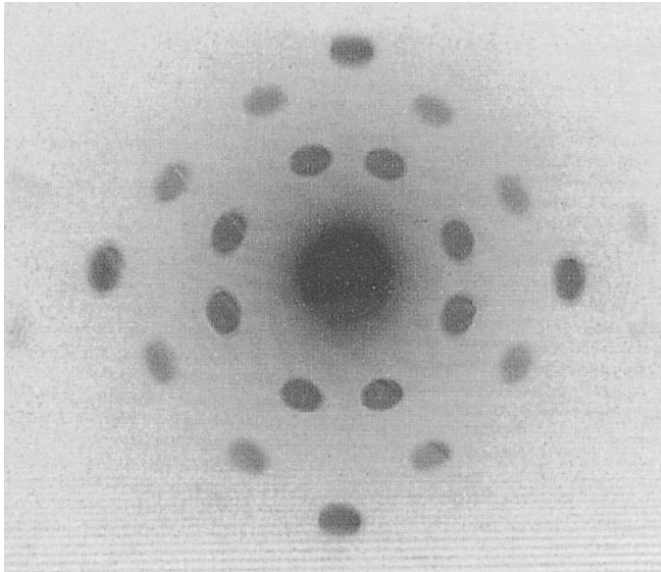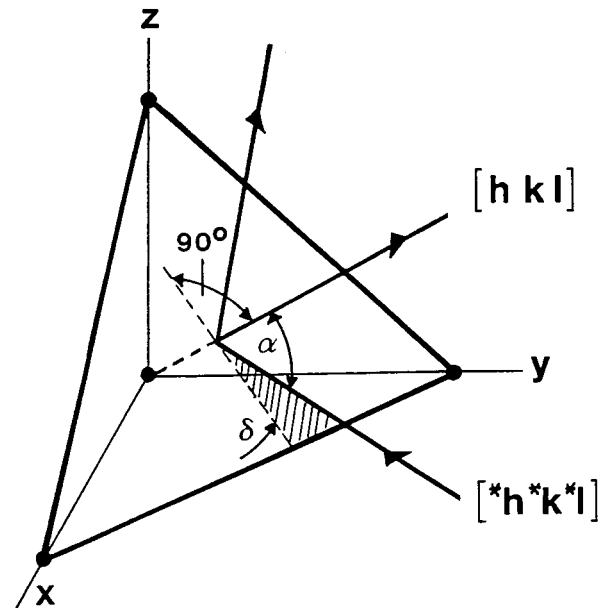Fig. 4: Laue refelctions of a LiF (100) monocrystal.

Fig. 5: Reflection from a lattice plane with random orientation.

Laue method

Laue photographs are obtained by irradiation of a monocrystal with polychrome X-rays. The method is mainly used to determine crystal symmetries and crystallographic orientations. An evaluation of Laue reflection patterns is possible for simple structures; however, it is difficult as a rule, due to the fact that the indices of the reflecting lattice planes and the wavelenghts are unknown.

Fig. 4 shows the Laue reflection pattern of the LiF monocrystal, which has a face centred cubic (fcc) lattice structure. If the pattern is rotated by 90° around the primary beam direction, it is again coherent with itself. We are thus in presence of a four-fold symmetry, with coincidence between the beam direction and the crystallographic [001] direction. The intensity of the reflections depends both upon crystallographic characteristics and the spectral intensity distribution of the X-rays.

If the X-ray beam which coincides with the crystallographic direction [*h*k*l] impinges upon a crystal plane (h k l) (see Fig. 5), the angle of incidence α is determined by the scalar product of the normal plane vector and the incidence vector. The following relation is valid for the glancing angle ϑ_{cal}:

$$\vartheta_{cal} = 90° - \alpha, \text{ with} \tag{9}$$

$$\cos \alpha = \frac{{}^*hh + {}^*kk + {}^*ll}{\sqrt{(h^2 + k^2 + l^2)\,({}^*h^2 + {}^*k^2 + {}^*l^2)}}$$

If L is the distance between a reflection and the centre of the diffraction pattern, and x as formerly the distance between sample and film, the glancing angle ϑ_{exp} obtained experimentally is:

$$\vartheta_{exp} = \frac{1}{2} \arctan \frac{L}{X} \tag{10}$$

The glancing angle ϑ_{exp} is determined from the position of the reflections according to (10), in order to assign the single reflections to the corresponding lattice planes. Then ϑ_{cal} is calculated according to (9) for all the h, k, l triplets of planes

with low indices. and for the incidence vector [001]. The sought for lattice plane is found when

$$\vartheta_{exp} = \vartheta_{cal}$$

Fig. 6 shows the reflection geometry for the particular case in which a lattice plane is parallel to the y-axis.

The most intense reflecions in the first quadrant are represented again, and numbered, in Fig. 7.
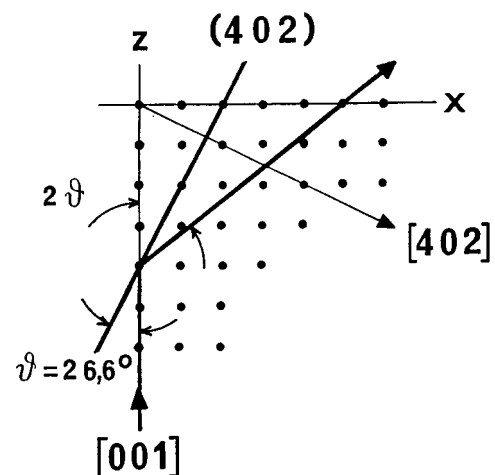

Fig. 6: Reflection from a lattice plane parallel to the y-axis.

Table 3: Indexing of Laue reflections
Distance between crystal and film: x = 22.5 mm

Reflec-tion	L/mm	ϑ_{exp}	ϑ_{cal}	h k l	d/pm	l/pm
1	30.0	26.6°	26.6°	4 0 2	90	81
2	55.0	33.9°	33.7°	6 0 4	66	73
3	64.5	35.4°	35.3°	1 1 1	232	268
4	15.5	17.3°	17.5°	1 3 1	121	73
5	25.5	24.3°	24.1°	2 4 2	82	67
6	41.5	30.8°	30.5°	1 5 3	68	69
7				0 4 2		
8				0 6 4		
9				3 1 1		
10				4 2 2		
11				5 1 3		
12				$\bar{4}$ 0 2		
13				0 $\bar{4}$ 2		

Fig. 7: Position of intense reflections.
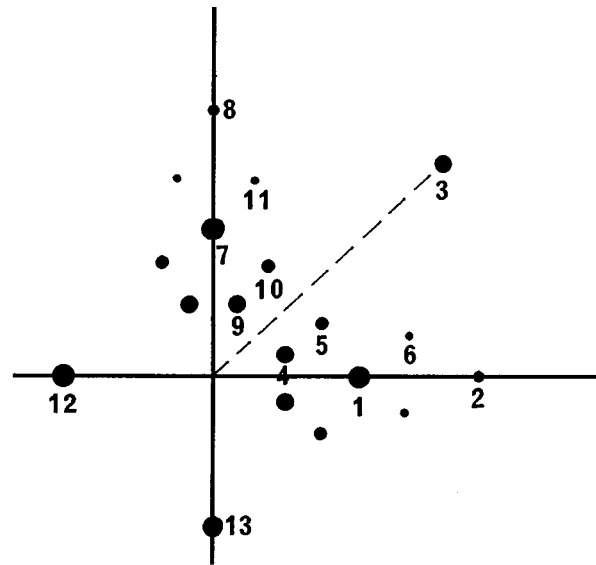
A result of table 3 is that reflections are intense only if the Miller indices are all either odd or even. According to (5), this is the case for a face centred cubic lattice. However, (5) only is valid if the atomic form factos of the lattice atoms are significantly different from each other. This is not strictly the case for LiF (Li: Z = 3; F: Z = 9). Thus, low intensity reflections can also be assigned to planes with mixed indices. Due to the symmetry of the reflection pattern, evaluation can be restricted to 1/8 of the reflections. The indices of all other reflections are obtained by permutation. Thus, for example, reflections 12 and 13 must be assigned to planes ($\bar{4}02$) and ($0\bar{4}2$).

A final control can be performed. The lattice constant of LiF is a = 403 pm. With this value and according to (7), the distances between the lattice planes can be calculated, and then the corresponding wavelengths λ according to (2). These wavelengths λ_{min} of the bremsstrahlung spectrum, as X-ray intensity is only available for $\lambda > \lambda_{min}$. The following is true for λ_{min} (Duane-Hunt, see experiment 5.4.3):

$$\lambda_{min} = 1.24 \cdot 10^{-6}\, U^{-1}\ [m] = 49.6\ pm\ (with\ U = 25\ kV)$$

In order to keep the relative error as small as possible when determining the distances between reflections, it is recommended to magnify the reflection pattern by a factor of 2. For this purpose, the pattern can be transferred to transparent paper and magnified with help of a photocopier or an overhead projector.

Literature

Charles Kittel
Introduction to Solid State Physics, John Wiley and Sons, Inc.