DETERMINATION OF POINT-GROUP SYMMETRY *VIA* TEM EXPERIMENTS

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Abstract
Paper deals with application of electron diffraction for determination of point-group symmetry. Two electron-diffraction methods, SAED and CBED, were discussed. Determination of point-group symmetry was demonstrated on the single crystals of Si and sphalerite (ZnS). CBED opens the way for determination any of 32 point groups regardless of their centro- or non-centrosymmetric character.

1. Introduction

Information about point-group symmetry of crystalline matters is useful tool in the identification process of crystal, characterization and spatial distribution of phases and/or textures. In addition to X-ray and electron diffraction, point group determination can be performed using morphological study, by etch figures and using some of physical properties [1].

Information obtained by routine X-ray as well as electron diffraction experiments (Selected Area Electron Diffraction - SAED) leads only to one of 11 Laue groups. Using CBED (Convergent Beam Electron Diffraction) experiments, it is possible to determine point-group symmetry without any restrictions even if the crystals are smaller as are necessary for X-ray and SAED experiments.

2. Working examples

We used cubic single crystals of silicon (centrosymetric space group $Fm\bar{3}m$) and sphalerite ZnS (acentric space group $F\bar{4}3m$). Both crystals belong to the same Laue group and their types of crystal structures are frequently designated as *fcc* structures.

Corresponding point-group symmetry is $m\bar{3}m$ for silicon and $\bar{4}3m$ for sphalerite, respectively. Symmetry of special projections (defined as one of 10 plane point-groups) is:

for Si in direction [100] 4*mm*, [110] 2*mm* and [111] 6*mm* (common symmetry for both crystals as appears on the Laue and SAED photographs),

for ZnS in [100] 4*mm*, [110] *m* and [111] 3*m*.

3. Experimental

Sample preparation and apparatus
TEM samples from Si was prepared by mechanical grinding and polishing down to 0,05 mm. Final thinning was carried out by means of the sample double-side bombardment by neutral Ar^+ ions on the ION-TECH ion mill, operating at an accelerating voltage of 5 kV and 10° incidence angle.

Natural ZnS crystals were powdered in agate-mortar. Water suspension of particles was mounted on carbon-coated collodium membrane.

TEM patterns were recorded from thin parts of the crystals which were transparent for electron beam. All experiments were carried out on JEOL 2000 FX transmission electron microscope operated at 120 and 160 kV. In order to obtain the proper orientation of the crystal, double-tilt holder was employed.

Methods
Although many terms are used to describe electron diffraction in TEM, they essentially refer to one of two basic approaches:

1. Selected Area Electron Diffraction (SAED)
2. Convergent Beam Electron Diffraction (CBED).

In SAED method, spot diffraction pattern can be obtained from single crystal with optimal thickness. Every spot of the pattern corresponds to the crystal plane for which Bragg's law is fulfilled. Diffraction pattern is an almost planar section of the weighted reciprocal lattice by plane normal to primary electron beam (as an Ewald sphere of reflections with very large radius cuts it) and is created by all reciprocal lattice spots lying in this plane. These spots belong to Zero-Order Laue Zone (ZOLZ) and fulfil the condition $hu + kv + lw = 0$, where h, k, l are Miller indices of the diffracting plane and u, v, w are indices of the direction parallel to primary electron beam. Diffraction pattern comprising only ZOLZ spots is two-dimensional (2-D) pattern that provides information about projected symmetry rather than true symmetry of a zone axis. From 2-D patterns only point-group symmetry operations and the corresponding symmetry elements parallel to primary beam are possible to ascertain, i.e. only plane point group of the pattern can be determined. From symmetry of more special projections of SAED patterns only Laue group of the crystal can be identified [1,2].

Unlike SAED, CBED patterns consist of discs of variable intensity and provide more information than spot pattern. The intensity distribution within the discs is the function of inclination between the incident electron beam and particular crystal direction, thickness of the crystal and its structure [2, 3, 4]. CBED patterns can carry important information on true point 3-D crystal symmetry (not only 2-D point symmetry as in SAED patterns), if there are present deficient High-Order Laue Zone (HOLZ) lines inside the 000 disc. They originate due to elastic scattering from *hkl* planes in non-zero order layer of reciprocal space.

HOLZ lines have large scattering angles and therefore are not visible in a regular diffraction pattern. In CBED patterns they are detected because of complementary nature of intensity. A dark deficient HOLZ lines in a central disc correspond to an excited reflex on the HOLZ circle. Arrangement of the HOLZ lines is very sensitive to exact crystal orientation and lattice parameters [2, 4].

The determination of point groups from CBED patterns can be performed by means of two methods:

1. Approach of Buxton et al. [5] requires the knowledge of:

Bright-Field **P**attern Symmetry (BP) - symmetry of central disc

Whole **P**attern Symmetry (WP) – symmetry of ZOLZ and HOLZ

Dark-Field **P**attern Symmetry (DP) - symmetry of diffracted discs

Symmetry of pair diffracted discs, for which the diffraction indices have opposite signs (DP).

There exist flow diagrams and tables, which are necessary to employ in point group assigning process. Very often, three CBED patterns taken from the same zone axis are sufficient to identify the crystal point group.

2. Approach of Tanaka et al. [6] – represents an easier method as described above, diffraction group is deduced from symmetry of intensity distribution in diffracted discs appearing in hexagonal 6-beams, rectangular 4-beams and squared 4-beams patterns. For point-group determining there are elaborated flow diagrams and tables and may be sufficient to inspect only one CBED pattern.

4. Results and discussion

As a first step, SAED technique was used. SAED patterns served to assign the relevant zone-axis orientation. The determination of point groups by means of SAED is shown on fig. 1a, b, c. SAED spot patterns of Si single crystal in directions , , and have symmetries 6*mm*, 4*mm* and 2*mm,* respectively and so point group of Si is $m\bar{3}m$ [1]. SAED patterns of ZnS (fig. 2a, b, c) in special zone axis , and are identical with those of Si (from the view of pattern symmetry) so the determined point group of sphalerite is $m\bar{3}m$, as well. This is not consistent with its true point group.

CBED pattern symmetry and point-group studies are performed according to the method proposed by Buxton et al. [5].

The zone axis CBED pattern from Si crystal is in fig. 3**.** At first sight it exhibit a hexagonal symmetry (6*mm*), but from the distribution of fine deficient HOLZ lines in 000 disc is apparent that the BP symmetry degenerated to 3*m*. Whole pattern (WP) from Si single crystal in direction has the symmetry 3*m*, as well (fig.4). This plane point group is determined on the basis of the symmetry of First Order Laue Zone (FOLZ), which do not respect the 6-fold symmetry of ZOLZ. From fig. 5a, b is possible to assess symmetry of intensity distribution in equivalent diffracted discs with indices $2\bar{2}0$ and $\bar{2}20$ (±DP). The $\bar{2}20$ DP intensity maps has only one mirror plane *m* perpendicular to the reflection vector, which connects the central beam with relevant diffracted disc (apparent symmetry 2*mm* is

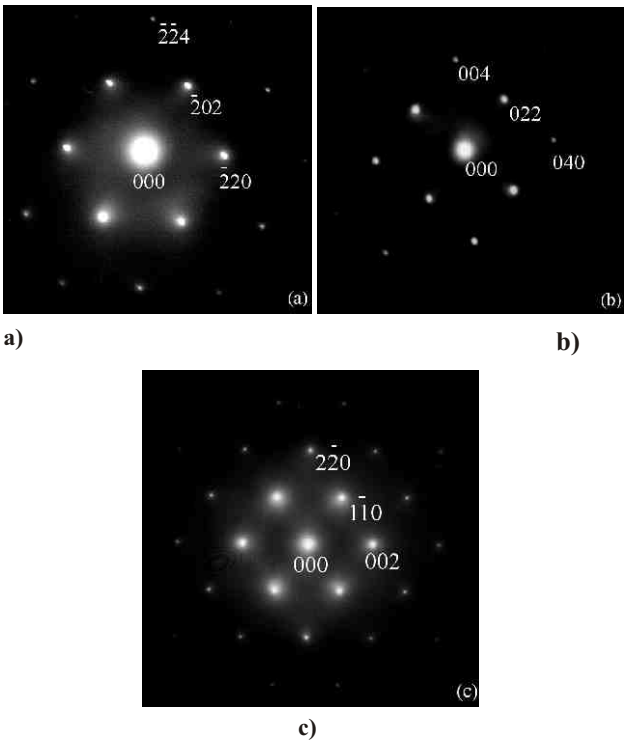


Figure 1. SAED patterns of Si crystal (2-D information only). (a) View down zone axis showing 6*mm* symmetry, (b) view down zone axis shows 4*mm* symmetry, (c) zone axis shows 2*mm* symmetry.

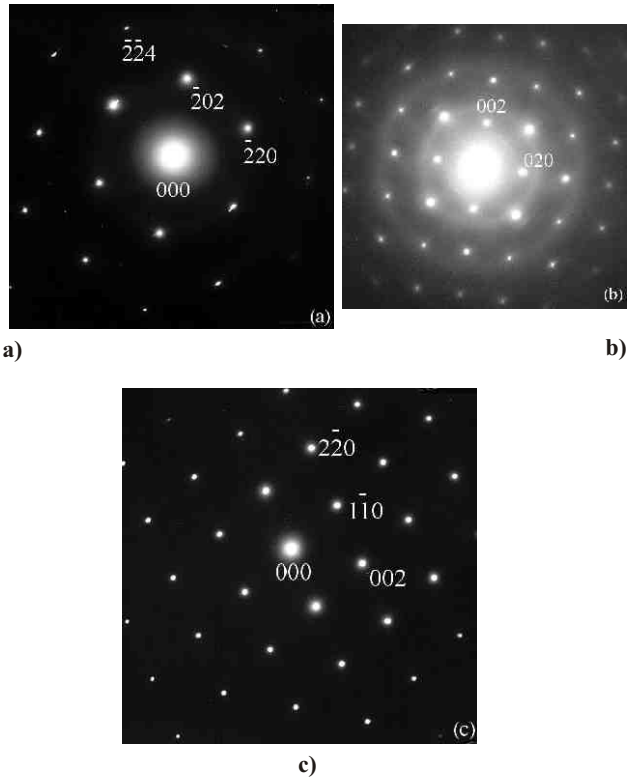


Figure 2. SAED patterns from ZnS crystal (2-D information). (a) View down zone axis showing 6*mm* symmetry, (b) view down zone axis, pattern symmetry is 4*mm,* (c) zone axis showing 2*mm* symmetry.

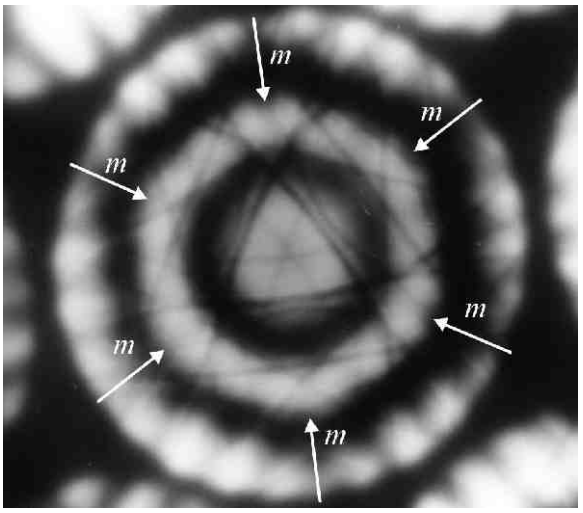


Fig. 3. zone axis CBED pattern from Si single crystal. When the symmetry of HOLZ lines is taken into consideration, plane point symmetry of 000 disc (BP) is 3*m* with three mirror planes perpendicular to the plane of the pattern (arrowed).

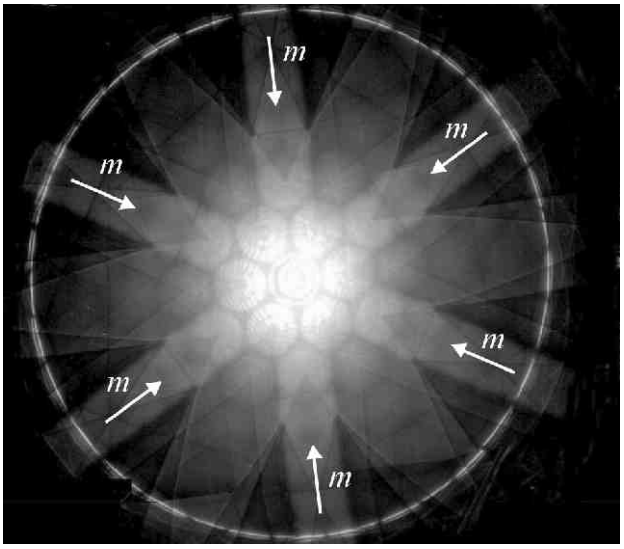
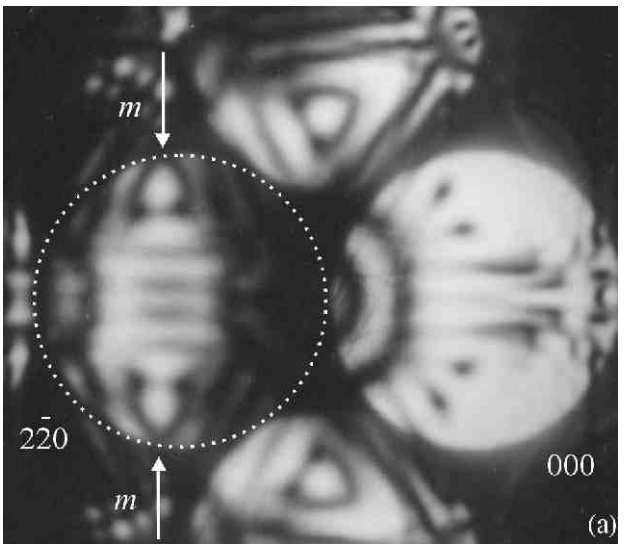
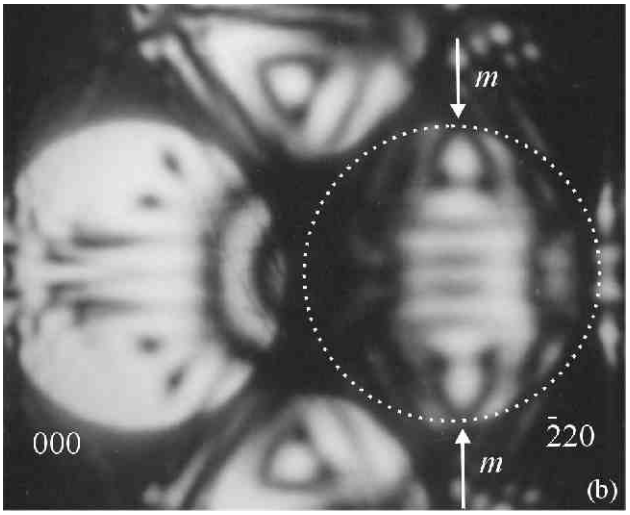


Fig. 4. Si zone axis CBED pattern. ZOLZ and FOLZ are registered (WP). The symmetry as shown by ZOLZ reflections only is 6*mm.* When FOLZ reflections are taken into consideration, the whole symmetry is reduced to 3*m*.

decreased because of presence of deficient HOLZ lines in diffracted disc). The symmetries of both diffraction discs $2\bar{2}0$ and $\bar{2}20$ are consistent. They are translated towards each other only. Therefore, ±DP symmetry is called translation symmetry (labelled 2_R,) and it indicates the presence of an inversion centre [5]. Using tab. 1, on the basis of already known plane point groups of zone axis CBED patterns (BP, WP, DP, ±DP symmetries), diffraction group of Si crystal is $6_R mm_R$. Two point groups – trigonal $\bar{3}2/m$ and cubic $m\bar{3}m$ are resulting from this diffraction group, tab. 2. To find true point group, experiment must be repeated for other zone axis. That point group, which appears in identification process for all orientations, is true crystal point-group symmetry. In our case is sufficient to tilt Si crystal to direction. Since symmetry 4*mm*, which is shown in fig.6, cannot be present in trigonal crystal system, the only convenient point group is cubic $m\bar{3}m$. $m\bar{3}m$ is



a)



b)

Figure 5. Si off-zone axis patterns. (a) $2\bar{2}0$ and (b) $\bar{2}20$ DP symmetry is *m* with mirror plane normal to diffraction vector.

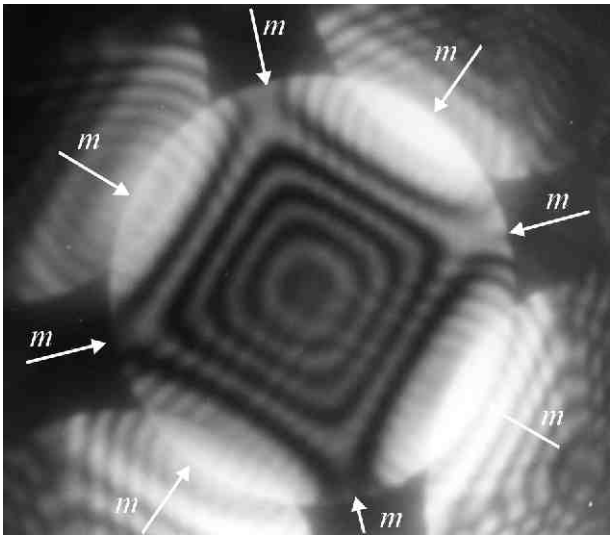
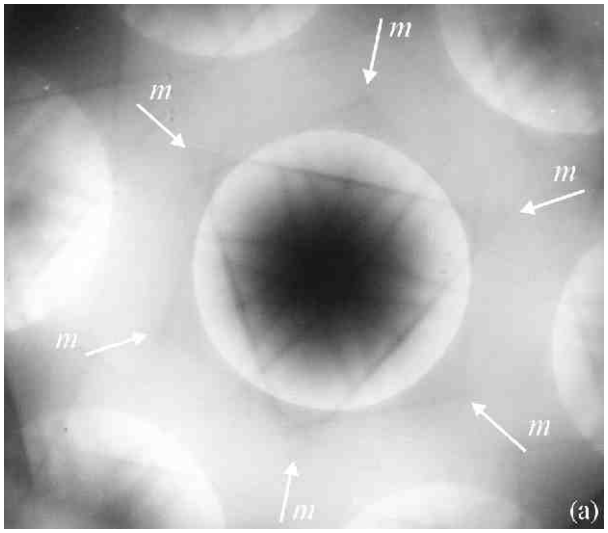
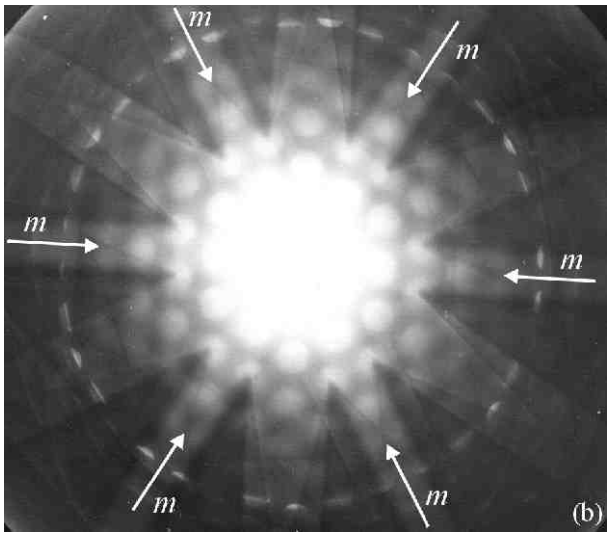


Figure 6. Si zone axis CBED pattern. BP plane point-group symmetry is 4*mm*.

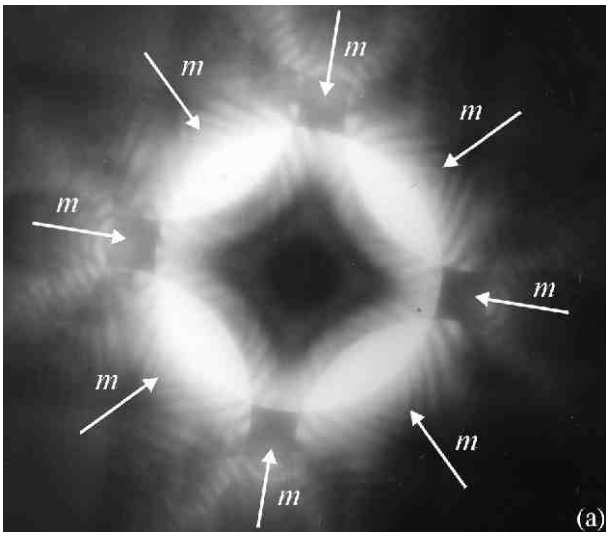


a)

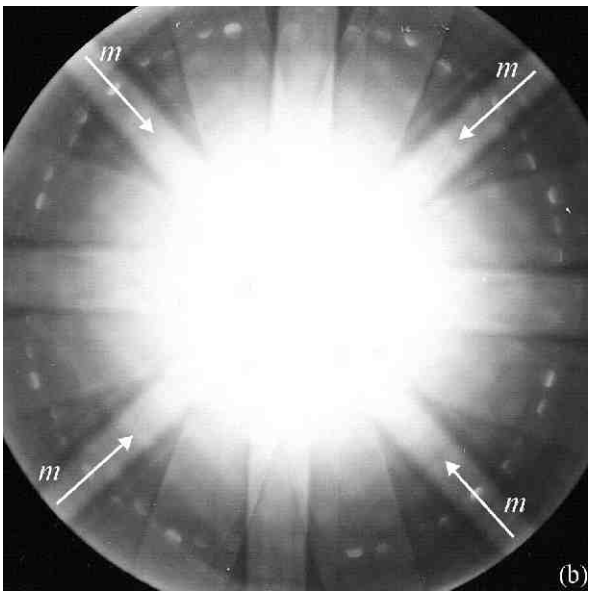


b)

Figure 7. zone axis CBED patterns from ZnS crystal. (a) Distribution of deficient HOLZ lines in 000 disc (BP) shows 3*m* symmetry (3-D information), (b) WP plane point- group symmetry is 3*m* because of FOLZ circle symmetry.



a)



b)

Figure 8. ZnS zone axis CBED patterns. (a) BP shows 4*mm* symmetry with four mirror planes perpendicular to the plane of pattern (arrowed). (b) WP plane point-group symmetry is 2*mm* with two orthogonal mirror planes normal to CBED pattern (arrowed). ZOLZ 4*mm* symmetry is decreased to 2*mm* because of FOLZ symmetry.

centrosymmetric point group, therefore this result is consistent with that one obtained by SAED method.

Point group of ZnS was determined from CBED patterns shown in fig.7a, b and 8a, b. At electron beam incidence parallel to direction, symmetries of BP and WP are 3*m* (fig.7a, b). If electron beam is perpendicular to the {100} plane, symmetries of BP and WP are 4*mm* and 2*mm*, respectively (fig.8a, b). These data with possible diffraction and point groups, which are deduced by means of tab.1 and 2, are listed in tab. 3. The $\bar{4}3m$ is the only one point group, which occurs for both crystal orientation. Consequently it is true point group of ZnS.

5. Conclusions

In this paper was shown, that by CBED method is enabled to determine not only centrosymmetric point groups of the crystals but non-centrosymmetric point groups, as well.

Single crystals Si and ZnS belong to the same $m\bar{3}m$ Laue group. It is a consequence of inspection of SAED pattern symmetry. The same non-real results can be obtained by CBED method too, if HOLZ lines will not appear in 000 disc. But in the case of their presence, the true point group can be unambiguosly determined inclusive non-centrosymmetric (i.e. non-Laue) groups, as well. By CBED method the sphalerite point-group symmetry $\bar{4}3m$ is recognized.

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Table 1. Relation between the diffraction groups and plane symmetry of CBED patterns published in [3, 5]

Diffraction group	Bright field (BP)	Whole pattern (WP)	Dark field (DP) (general)	Dark field (DP) (special)	±DP (general)	±DP (special)	Projection diffraction group
1	1	1	1	none	1	none	1_R
1_R	2	1	2	none	1	none	1_R
2	2	2	1	none	2	none	21_R
2_R	1	1	1	none	2_R	none	21_R
21_R	2	2	2	none	21_R	none	21_R
m_R	*m*	1	1	*m*	1	m_R	$m1_R$
m	*m*	*m*	1	*m*	1	*m*	$m1_R$
$m1_R$	2*mm*	*m*	2	2*mm*	1	$m1_R$	$m1_R$
$2m_Rm_R$	2*mm*	2	1	*m*	2	-	$2mm1_R$
2mm	2*mm*	2*mm*	1	*m*	2	-	$2mm1_R$
2_Rmm_R	*m*	*m*	1	*m*	2_R	-	$2mm1_R$
***2mm*1$_R$**	2*mm*	2*mm*	2	2*mm*	21_R	-	$2mm1_R$
4	4	4	1	none	2	none	41_R
4_R	4	2	1	none	2	none	41_R
41_R	4	4	2	none	21_R	none	41_R
$4m_Rm_R$	4*mm*	4	1	*m*	2	-	$4mm1_R$
4mm	4*mm*	4*mm*	1	*m*	2	-	$4mm1_R$
4_Rmm_R	4*mm*	2*mm*	1	*m*	2	-	$4mm1_R$
***4mm*1$_R$**	4*mm*	4*mm*	2	2*mm*	21_R	-	$4mm1_R$
3	3	3	1	none	1	none	31_R
31_R	6	3	2	none	1	none	31_R
$3m_R$	3*m*	3	1	*m*	1	m_R	$3m1_R$
3m	3*m*	3*m*	1	*m*	1	*m*	$3m1_R$
***3m*1$_R$**	6*mm*	3*m*	2	2*mm*	1	$m1_R$	$3m1_R$
6	6	6	1	none	2	none	61_R
6_R	3	3	1	none	2_R	none	61_R
61_R	6	6	2	none	21_R	none	61_R
$6m_Rm_R$	6*mm*	6	1	*m*	2	-	$6mm1_R$
6mm	6*mm*	6*mm*	1	*m*	2	-	$6mm1_R$
6_Rmm_R	3*m*	3*m*	1	*m*	2_R	-	$6mm1_R$
***6mm*1$_R$**	6*mm*	6*mm*	2	*2mm*	21_R	-	$6mm1_R$

Table 2. Relation between diffraction groups and point groups symmetry [3, 5]. Some of point-group nomenclatures are corrected according to [1].

	1	$\bar{1}$	2	m	$2/m$	222	$mm2$	mmm	4	$\bar{4}$	$4/m$	422	$4mm$	$\bar{4}2m$	$4/mmm$	3	$\bar{3}$	32	$3m$	$\bar{3}2/m$	6	$\bar{6}$	$6/m$	622	$6mm$	$\bar{6}m2$	$6/mmm$	23	$m\bar{3}$	432	$\bar{4}3m$	$m\bar{3}m$
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$6m_Rm_R$																																
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Table 3. Flow diagram for ZnS crystallographic point-group determination.

Zone axis	BP symmetry	WP symmetry	Possible diffraction groups	Possible point groups
<111>	$3m$	$3m$	$3m$, 6_Rmm_R	$3m$, $\bar{4}3m$, $\bar{3}m$, $m\bar{3}m$
<001>	$4mm$	$2mm$	4_Rmm_R	$\bar{4}2m$, $\bar{4}3m$