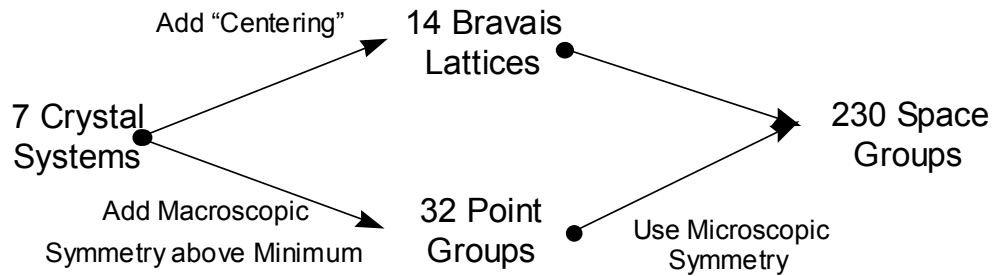


Space Groups

A space group is a representation of the ways that the macroscopic and microscopic symmetry elements (operations) can be self-consistently arranged in space. There are 230 unique manners in which this can be done and, thus, 230 space groups. Space groups add the centering information and microscopic elements to the point groups.

Schematically, the relationship between the 7 crystal systems, 14 Bravais Lattices, 32 point groups, and 230 space groups are as follows:

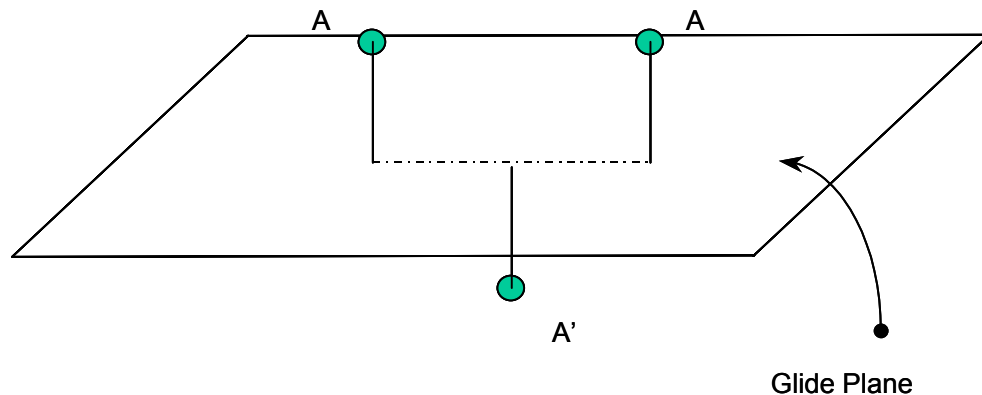


The clear starting point for this discussion is define microscopic symmetry elements: **Microscopic symmetry elements add small translations (less than a unit cell vector) to macroscopic symmetry operations.**

Microscopic Symmetry Elements

Glide planes combine reflection and translation.

Schematically:



The nomenclature for glide planes is fairly simple:

Glide Direction	Glide Magnitude	Designation
$\langle 100 \rangle$	$\frac{1}{2}$ axis length	a, b, or c
$\langle 110 \rangle$	$\frac{1}{2}$ face diagonal	n
$\langle 110 \rangle$	$\frac{1}{4}$ face diagonal	d

When one goes from a space group to the parent point group, all a's, b's, c's, n's, and d's are converted back to m's.

Screw Axes

A screw axis combines rotation and translation and adds a twist to rotation axes. Schematically:

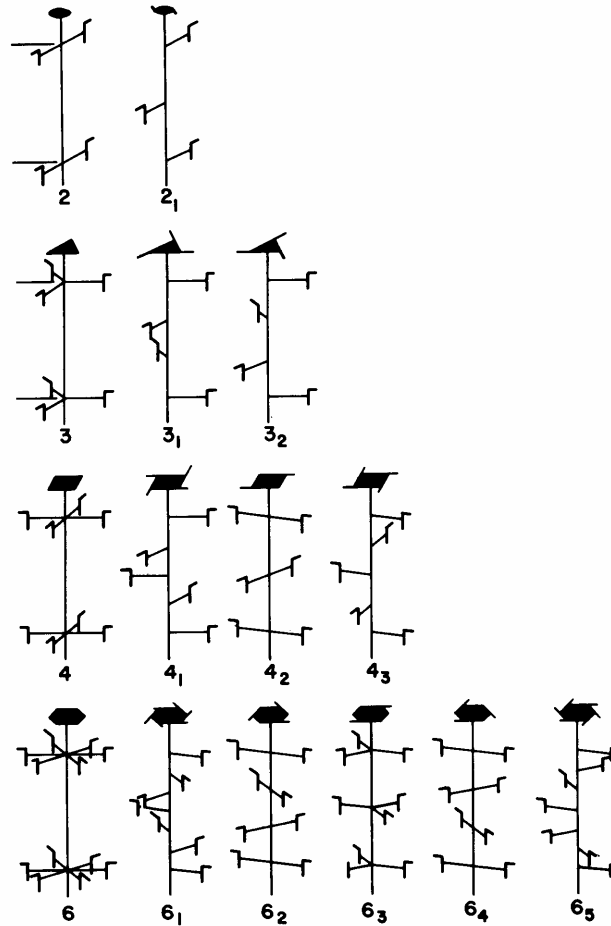


FIG. 1-23. Possible screw axes. (After Azaroff, L. V., "Introduction to Solids." McGraw-Hill, New York, 1960.)

Rules for screw axis labeling:

- Angle of rotation is $\phi = 360^\circ/n$
- After n rotations of ϕ and n translations of t , the total translation must be a multiple of the lattice translation vector T :

$$t = mT/n$$

- Since $m = 0, 1, 2, 3 \dots$ and $3/2 t = t + 1/2 t$, the only unique screw axes are:
- $2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, 6_5$ where the subscript is "m".
- If $m > n/2$, then the rotation is counter-clockwise from top view (right- and left-handedness). Right-handed is defined as clockwise from above.

When one goes from a space group to the parent point group, all n_m 's, are converted back to n 's.

Space Group Designations (International or Hermann-Maquin System)

Space group designations follow the same rules as point group designations with the added centering designations - A, B, C, F, I, and P.

Crystal System	Point Group		Space Group	
	Full	Short	Full	Short
Triclinic	1	1	P1	P1
	$\bar{1}$	$\bar{1}$	$P\bar{1}$	$P\bar{1}$

Crystal System	Point Group		Space Group	
	Full	Short	Full	Short
Monoclinic	m	m	Pm Pc Cm Cc	Pm Pc Cm Cc
	2	2	P2 P2 ₁ C2	P2 P2 ₁ C2
	$\frac{2}{m}$	$\frac{2}{m}$	P $\frac{2}{m}$ P $\frac{2_1}{m}$ P $\frac{2}{c}$ P $\frac{2_1}{c}$ C $\frac{2}{m}$ C $\frac{2}{c}$	P $\frac{2}{m}$ P $\frac{2_1}{m}$ P $\frac{2}{c}$ P $\frac{2_1}{c}$ C $\frac{2}{m}$ C $\frac{2}{c}$

Crystal System	Point Group		Space Group	
	Full	Short	Full	Short
Orthorhombic	2mm	mm	P2mm	Pmm
			P2 ₁ mc	Pmc
			P2ma	Pma
			P2 ₁ mn	Pmn
			P2cc	Pcc
			P2 ₁ ca	Pca
			P2cn	Pcn
			P2ba	Pba
			P2 ₁ bn	Pbn
			P2nn	Pnn
			C2mm	Cmm
			C2 ₁ mc	Cmc
			C2cc	Ccc
			A2mm	Amm

Crystal System	Point Group		Space Group	
	Full	Short	Full	Short
			A2ma A2bm A2ba F2mm F2dd I2mm I2ma I2ba	Ama Abm Aba Fmm Fdd Imm Ima Iba
	222	222	P222 P222 ₁ P2 ₁ 2 ₁ 2 P2 ₁ 2 ₁ 2 ₁ C222 C222 ₁ F222 I222 I2 ₁ 2 ₁ 2 ₁	P222 P222 ₁ P2 ₁ 2 ₁ 2 P2 ₁ 2 ₁ 2 ₁ C222 C222 ₁ F222 I222 I2 ₁ 2 ₁ 2 ₁
	$\frac{2}{m} \frac{2}{m} \frac{2}{m}$	mmm	P $\frac{2}{m} \frac{2}{m} \frac{2}{m}$ P $\frac{2}{n} \frac{2}{n} \frac{2}{n}$ P $\frac{2}{c} \frac{2}{c} \frac{2}{m}$ P $\frac{2}{b} \frac{2}{a} \frac{2}{n}$ P $\frac{2}{m} \frac{2}{m} \frac{2}{a}$ P $\frac{2}{n} \frac{2}{n} \frac{2}{a}$ P $\frac{2}{m} \frac{2}{n} \frac{2}{a}$ P $\frac{2}{c} \frac{2}{c} \frac{2}{a}$ P $\frac{2}{b} \frac{2}{a} \frac{2}{m}$ P $\frac{2}{c} \frac{2}{c} \frac{2}{n}$	Pmmm Pnnn Pccm Pban Pmma Pnna Pmna Pcca Pbam Pccn

Examples:

BCC W: Space Group: Im3m Point Group: m3m

FCC Al: Space Group: Fm3m Point Group: m3m

FCC Si: Space Group: Fd3m Point Group: m3m

$d = \frac{1}{4}$ face diagonal glide

Hexagonal Mg: Space Group: $P6_3/mmc$ Point Group: $6/mmm$

$c = \frac{1}{2}$ axial glide

$6_3 =$ type 3 screw axis

Space group data allows one to look up the missing reflections for a given x-ray (or electron) diffraction pattern.

The system that we have discussed so far is the Hermann-Mauguin system or the International System. This system is the preferred method of describing crystal structures for metals and ceramics. Polymers? It is the system that is used in the JCPDS (Joint Committee on Powder Diffraction Standards) in their card file (now mainly CD-ROM) database. An example of a card:

d	2.82	1.99	1.63	3.26	NaCl						
I/I_1	100	55	15	13	Sodium Chloride (Halite)						
Rad. CuK α_1 λ	1.5405	Filter Ni	Dia.								
Cut off	I/I_1	Diffractometer	I/I cor.								
Ref. Swanson and Fuyat, NBS Circular 539, Vol. 2, 41 (1953)				d A	I/I_1	hkl	d A	I/I_1	hkl		
Sys. Cubic				S.G. Fm $\bar{3}m$ (225)	3.258	13	111				
a_0	5.6402	b_0	c_0	A	2.821	100	200				
a	β	γ	Z	4	1.994	55	220				
Ref. Ibid.				C	1.701	2	311				
$\epsilon\alpha$	$n\omega\beta$	1.542	$\epsilon\gamma$	Sign	1.628	15	222				
2V	D	mp	Color	Colorless	1.410	6	400				
Ref. Ibid.					1.294	1	331				
An ACS reagent grade sample recrystallized twice from hydrochloric acid.					1.261	11	420				
X-ray pattern at 26°C.					1.1515	7	422				
Merck Index, 8th Ed., p. 956.					1.0855	1	511				
					0.9969	2	440				
					.9533	1	531				
					.9401	3	600				
					.8917	4	620				
					.8601	1	533				
					.8503	3	622				
					.8141	2	444				

Fig. 14-1 Standard 3 × 5 in. JCPDS diffraction data card (card 628 from Set 5) for sodium chloride. Appearing on the card are 1 (file number), 2 (three strongest lines), 3 (lowest-angle line), 4 (chemical formula and name of substance), 5 (data on diffraction method used), 6 (crystallographic data), 7 (optical and other data), 8 (data on specimen), and 9 (diffraction pattern). Intensities are expressed as percentages of I_1 , the intensity of the strongest line on the pattern. Most cards have a symbol in the upper right corner indicating the quality of the data: * (high quality), i (lines indexed, intensities fairly reliable), c (calculated pattern), and o (low reliability). (Courtesy of Joint Committee on Powder Diffraction Standards.)

Space Group Designations (Pearson's)

First letter is the system:

a: triclinic

m: monoclinic

o: orthorhombic

t: tetragonal

h: hexagonal and rhombohedral

c: cubic

Second letter is centering etc.:

A: A-base centered

B: B-base centered

C: C-base centered

F: Face centered

I: Body centered

R: Rhombohedral

P: Primitive

Number: Indexing number (arbitrary), which is not unique.

To use effectively, need to know "structure type," which is the classic example of that particular structure.

Example:

cF8	STRUCTURE TYPE CLNa	SPACE GROUP $Fm\bar{3}m$	SPACE GROUP NUMBER 225				
	REFERENCE V.M. Goldschmidt 1926 9 Pl SKRIFTER UTGITT AV DET NORSKE VIDENSKAPS-AKADEMIT, OSLO Remarks: Space lattice given for $MgSe$						
	a = 0.5463	b =	c = [.nm]				
	ALPHA =	BETA =	GAMMA = [DEGREE]				
	ORIGIN AT $m\bar{3}m$						
	ATOMIC POSITIONS :						
	ATOMS	WYCKOFF NOTATION	SYMMETRY	x	y	z	OCCUPANCY
	Cl	4 (b)	$m\bar{3}m$	0.5	0.5	0.5	1.00
	Na	4 (a)	$m\bar{3}m$	0.0	0.0	0.0	1.00
	Ag-Bi-Ge-Te		Ag-Bi-Pb-Te			AgBiS ₂	
	Ag-Bi-S-Sb		Ag-Bi-S-Se			Ag-Bi-Sb-Se	
	Ag-Bi-Sb-Te		AgBiSe ₂			AgBiTe ₂	
	Ag-Bi-Se-Te		AgErS ₂			AgErSe ₂	
	AgHoSe ₂		AgInS ₂			Ag-In-Sb-Se	
	AgInSe ₂		AgInTe ₂			AgLuS ₂	
	Ag-Pb-S-Sb		Ag-Pb-Sb-Te			AgS ₂ Sb	
	Ag-S-Sb-Se		AgS ₂ Sn			AgS ₂ Tm	
	AgS ₂ Yb		AgSbSe ₂			Ag-Sb-Se-Te	
	AgSbTe ₂		Ag-Se-Sn			AgSe ₂ Y	
	AgSnTe ₂		AmAs			AmBi	
	AmN		AmO			AmP	
	AmS		AmSb			AmSe	

Space Group Designations (Structure Reports)

The final system is/was favored by metallurgists (an elite group) is based on "Strukturbericht" or, in English, "structure reports".

These designations start with a letter that is followed by a number. The letter signifies what type of material:

A: element

B: AB compound

- C: AB₂ compounds
- D: A_nB_m compounds
- E-K: more complex compounds
- L: "alloys"
- O: organics
- S: silicates

Note that alloys and compounds are inconsistently defined. For example, TiAl is called L1₀ despite its AB stoichiometry.

Examples:

B1 NaCl type. Face-centered cubic: *Fm*3*m*; *cF*8. Four sodium atoms at 0,0,0; 0,½,½; ½,0,½ and ½,½,0; four chlorine atoms at ½,½,½; ½,0,0; 0,½,0 and 0,0,½. For NaCl, *a* = 5.64 Å. See Fig. 1. **Examples:** BaS, CdO, CdS, CrN, HfC, HfN, NaCl, NiO (HT), PbS, PbSe, TiO, UC, UO, UP, US, VO, ZrO.

B2 CsCl or β' Cu-Zn type. Cubic: *Pm*3*m*; *cP*2. One cesium atom at 0,0,0; and one chlorine atom at ½,½,½. For CsCl, *a* = 4.11 Å. See Fig. 1. **Examples:** AgCd, CoTi, CsCl, FeAl, FeCo, FeTi, FeV, β NiAl, β NiGa, δ NiIn, NiTi, β' Cu-Zn.

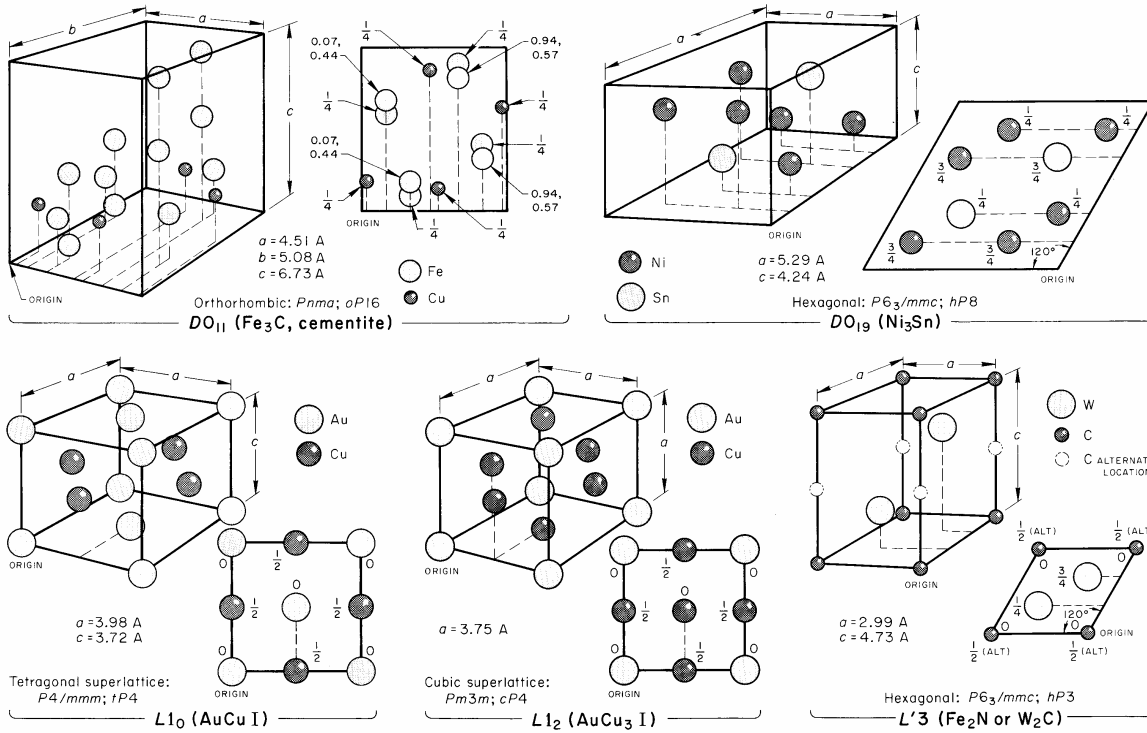
B3 ZnS (sphalerite, or zinc blende) type. Face-centered cubic: *F*43*m*; *cF*8. Four zinc atoms at 0,0,0; 0,½,½; ½,0,½ and ½,½,0; four sulfur atoms at ¼,¼,¼; ¼,¾,¾; ¾,¼,¾ and ¾,¾,¼. For ZnS (sphalerite), *a* = 5.42 Å. See Fig. 1. **Examples:** CdS, CdSe, CdTe, CuFeS₂ (HT), GaP, GaSb, InAs, InP, InSb, β MnS, β SiC, ZnO, ZnS (sphalerite), ZnSe.

B4 ZnS (wurtzite) type. Hexagonal: *P*6₃*mc*; *hP*4. Two zinc atoms at ½,¾,*z* and ¾,¼,½+*z* (with *z* = 0); two sulfur atoms at ½,¾,*z* and ¾,¼,½+*z* (with *z* = 0.371). For ZnS (wurtzite), *a* = 3.82 Å and *c* = 6.26 Å. Equivalent positions for Zn, 0,0,0 and ½,¾,½; for S, 0,0,*z* and ½,¾,½+*z* (with *z* = 0.371). See Fig. 1. **Examples:** AlN, BeO, CdS, CdSe, CuH, InN, InSb, γ MnS, ZnO, ZnS (wurtzite), ZnSe.

D0₁₁ Fe₃C (cementite) type. Orthorhombic: *Pnma*; *oP*16. Sixteen atoms per cell. See Fig. 1. **Examples:** Co₃B, Co₃C, Fe₃C, Mn₃C, Ni₃C, Pd₃P.

D0₁₉ Ni₃Sn type. Hexagonal: *P*6₃/*mmc*; *hP*8. Two tin atoms at ⅓,⅔,¼ and ⅔,⅓,¾; six nickel atoms at *x*,2*x*,¼; 2*x*,*x*,¼; *x*,*x*,¼; *x*,2*x*,¾; 2*x*,*x*,¾ and *x*,*x*,¾ (with *x* = 0.833). For Ni₃Sn, *a* = 5.29 Å and *c* = 4.24 Å. See Fig. 1. **Examples:** AlTi₁₂₋₃, Cd₃Mg, CdMg₃, Co₃Mo, Co₃W, β' Fe₃Sn, γ Ni₃In, Ni₃Sn, Ti₄Pb.

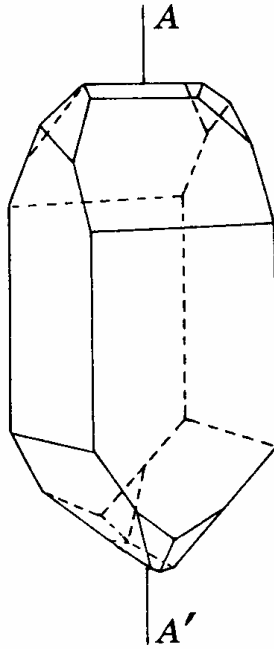
D0₂₄ Ni₃Ti type. Hexagonal: *P*6₃/*mmc*; *hP*16. Four titanium atoms at 0,0,0; 0,0,½; ⅓,⅔,¼ and ⅔,⅓,¾; 12 nickel atoms at ½,0,0; 0,½,0; ½,½,0; ½,0,½; 0,½,½; ½,½,½; *x*,2*x*,¼; 2*x*,*x*,¼; *x*,*x*,¼; *x*,2*x*,¾; 2*x*,*x*,¾ and *x*,*x*,¾ (with *x* = 0.833). For Ni₃Ti, *a* = 2.55 Å and *c* = 8.31 Å. **Examples:** Co₃Ti, Ni₃Ti, Pd₃Zr.



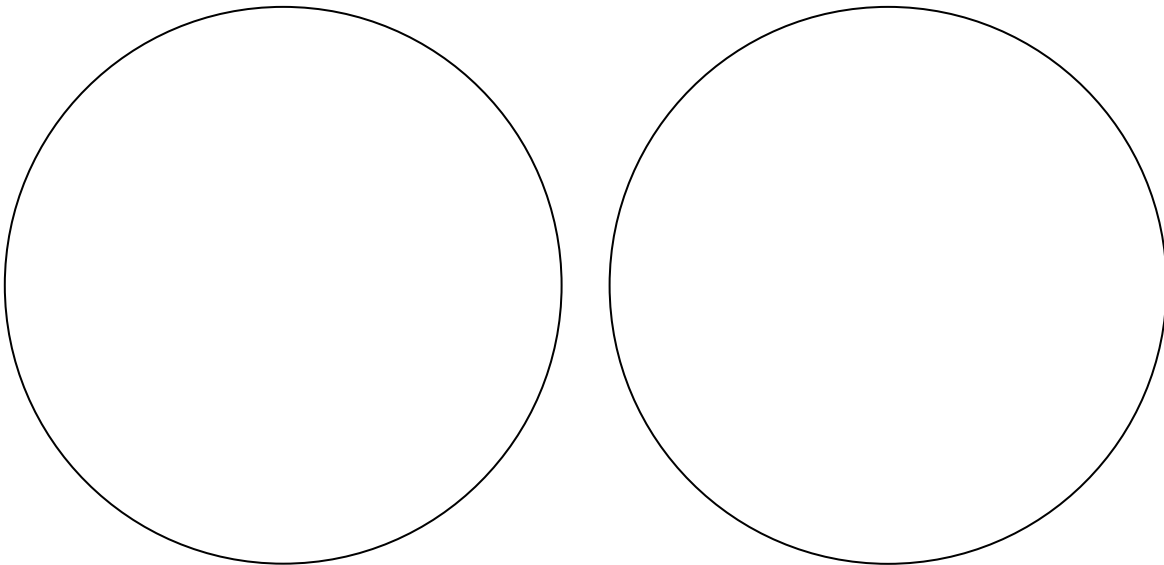
There are even more systems of classification than given here! The biggest difficulties arise due to internal and external inconsistencies, incomplete databases, and the basic complexities of three-dimensional description. Much character is built.

Example and Review

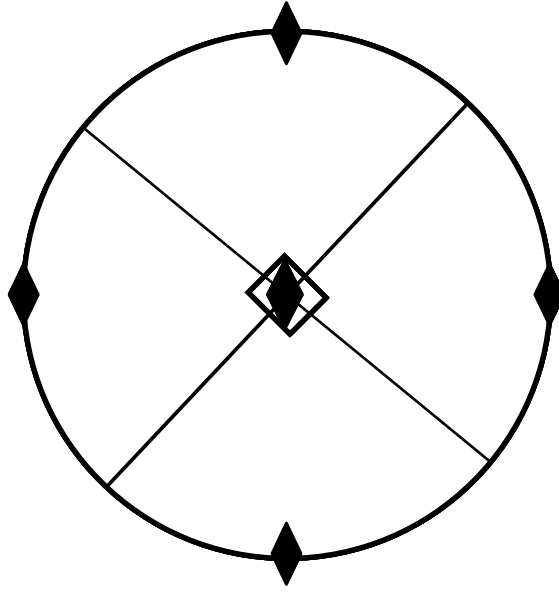
Calcopyrite (CuFeS_2), $\bar{4}2m$



Shall we draw the stereogram and find the elements?



The answer:



The mirror planes are normal to the vertical facets (a-b directions).

