Space group determination

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2.1 Introduction

Which space group?   Choice of 230

When to decide?

Preliminary decisions based on unit cell determination (restricts the choice, at least)

More confident assignment based on a complete data set

Confirmation by successful structure refinement

Occasionally, some ambiguity remains, even then

How to decide?

No universal procedure

Automatic computer programs — beware of assumptions!

Assess reliability of all available information

Explain discrepancies and inconsistent indications

Watch for effects of systematic errors such as absorption

Problems arising from pseudo-symmetry, twinning, etc.

During data collection: assume the lowest possible symmetry consistent with the evidence

During structure determination: assume the highest possible symmetry consistent with the evidence

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Information for space group determination

Prior knowledge and other properties
      An optically pure chiral compound
      Crystal morphology
      Physical properties
      Optical properties

Unit cell geometry: metric symmetry

Laue class (symmetry of the diffraction pattern)

Systematic absences
      Unit cell centring
      Glide planes
      Screw axes

Statistical distribution of intensities
      Centrosymmetric?
      Mirror planes and two-fold rotation axes

2.2 Prior knowledge and information other than from diffraction

Known(?) chirality
      from synthetic method, compound source, or physical measurement

Chiral structures have no improper rotations (including reflection and inversion).
This reduces the possible point groups from 32 to 11 (marked E in Table 5).

Crystal morphology

Physical properties
      piezoelectricity
      pyroelectricity
      non-linear optical behaviour

Optical examination with a polarising microscope (crossed polars)
Look for sharp optical extinction every 90° of rotation
      Biaxial crystals: triclinic, monoclinic, orthorhombic
      Uniaxial crystals: tetragonal, trigonal, hexagonal
      Isotropic crystals: cubic
      Amorphous materials, e.g. glass

2.3 Metric symmetry and Laue symmetry

Metric symmetry can be higher than Laue symmetry (possibly leading to twinning); e.g. monoclinic with β close to 90°, or orthorhombic with two almost equal axes.

Metric symmetry is the symmetry of the unit cell shape.

Laue symmetry is the symmetry of the diffraction pattern (including intensities).

Tetragonal, trigonal, hexagonal and cubic crystals have two possible Laue groups each; only one possible Laue group for each of triclinic, monoclinic, orthorhombic. Primitive trigonal and hexagonal structures have the same metric symmetry, but different Laue symmetry.

Initial indications of Laue symmetry may come from the initial small set of data from which the unit cell is determined; greater confidence comes from the complete data set, after correction for effects like absorption.

Many absorption corrections are based on comparison of intensities for symmetry-equivalent reflections, so there is some circular argument here, but it is not usually a problem; trial-and-error may be necessary.

Equivalent reflections for different Laue groups

A	+ + +	B	− − −	(signs of indices)	
C	+ − +	D	− + −		
E	+ − −	F	− + +		
G	− − +	H	+ + −		

Triclinic $\bar{1}$ A ≡ B   C ≡ D   E ≡ F   G ≡ H   2 equivalents

Monoclinic 2/*m*   A ≡ B ≡ C ≡ D   E ≡ F ≡ G ≡ H   4 equivalents

Orthorhombic *mmm*   A ≡ B ≡ C ≡ D ≡ E ≡ F ≡ G ≡ H   8 equivalents

Higher symmetry crystal systems have 2 Laue groups each
     e.g. tetragonal

4/*m* $+h\ +k\ +l \equiv +k\ -h\ +l \equiv -h\ -k\ +l \equiv -k\ +h\ +l \equiv$ 4 Friedel opposites of these
     8 equivalents

4/*mmm*   also $\equiv +k\ +h\ +l$ etc.
     16 equivalents

2.4 Unit cell contents: simple estimates and calculations

If density is measured
     density = mass / volume
     $D = MZ/N_oV$
         D = density
         M = molecular mass (formula mass)
         Z = number of molecules (formula units) per cell
         N_o = Avogadro's number
     Watch the units!

If density is not measured
     18 Å³ per non-H atom
         (or a different rule for other areas of chemistry)

Use these to estimate
     the number of formula units per unit cell (appropriate to the symmetry!)
     the possible presence (how much?) of solvent
     the feasibility of the proposed structure
     the possibility of starting material!
     possible indications of molecular symmetry
         (special positions, if Z is a fraction of the expected value)

2.5 Systematic absences

Specific subsets of reflections with related indices, having zero intensity as a result of complete out-of-phase cancellation of scattering effects by symmetry-related atoms

A lattice described by a primitive unit cell (*P*) gives a diffraction pattern with reflections at the points of a primitive reciprocal lattice.

If a centred unit cell (*A*, *B*, or *C*) is chosen instead, this is twice the size. So the corresponding reciprocal cell is halved, and it describes a reciprocal lattice with twice as many points. The actual structure and its diffraction pattern have not changed! Therefore, half the reciprocal lattice points for the new description do not correspond to observed reflections; they have zero intensity, and constitute a set of systematic absences, characteristic of the unit cell centring.

Systematic absences for centred unit cells

Centring	Points equivalent to 0,0,0	Condition for observed intensity	Fraction of observed data
P	none	none	1
A	0,½,½	$k + l = 2n$	½
B	½,0,½	$h + l = 2n$	½
C	½,½,0	$h + k = 2n$	½
I	½,½,½	$h + k + l = 2n$	½
F	0,½,½ and ½,0,½ and ½,½,0	*h*, *k*, *l* all even or all odd	¼
R	1/3, 2/3, 2/3 and 2/3, 1/3, 1/3	$-h + k + l = 3n$	1/3

n means any whole number; thus 2*n* is even and 2*n*+1 is odd.

Systematic absences for glide planes

Normal to glide plane	Reflections affected	Glide plane symbol	Translation vector	Condition for observed intensity
a axis [100]	0*kl*	b	**b**/2	$k = 2n$
		c	**c**/2	$l = 2n$
		n	(**b**+**c**)/2	$k + l = 2n$
		d	(**b**+**c**)/4	$k + l = 4n$
b axis [010]	*h*0*l*	a	**a**/2	$h = 2n$
		c	**c**/2	$l = 2n$
		n	(**a**+**c**)/2	$h + l = 2n$
		d	(**a**+**c**)/4	$h + l = 4n$
c axis [001]	*hk*0	a	**a**/2	$h = 2n$
		b	**b**/2	$k = 2n$
		n	(**a**+**b**)/2	$h + k = 2n$
		d	(**a**+**b**)/4	$h + k = 4n$
[110]	*hhl*	c	**c**/2	$l = 2n$
		d	(**a**+**b**+**c**)/4	$2h + l = 4n$

Systematic absences for screw axes:
conditions for observed intensity

Parallel to	Reflections affected	Condition for 2_1, 4_2 or 6_3	Condition for 3_1, 3_2, 6_2 or 6_4	Condition for 4_1 or 4_3	Condition for 6_1 or 6_5
a	$h00$	$h = 2n$	$h = 3n$	$h = 4n$	$h = 6n$
b	$0k0$	$k = 2n$	$k = 3n$	$k = 4n$	$k = 6n$
c	$00l$	$l = 2n$	$l = 3n$	$l = 4n$	$l = 6n$

Information from systematic absences: summary

Absences affecting general reflections
(hkl, all non-zero)
$\Rightarrow$ unit cell centring

Absences affecting layers of reflections
(one zero index, or other layers in higher systems)
$\Rightarrow$ glide planes

Absences affecting rows of reflections
(two zero indices, or other rows in higher systems)
$\Rightarrow$ screw axes

No information from systematic absences on
pure rotation and improper rotation axes
mirror planes
inversion centres

2.6 The statistical distribution of intensities

Assumptions and approximations!
Otherwise random arrangement of electron density
Equal atoms
No non-crystallographic symmetry

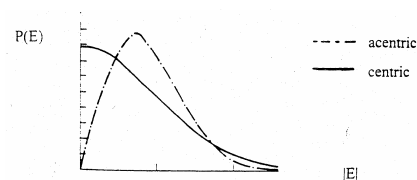Probability, not certainty

Use E values
Normalised amplitudes
Remove the effects of finite atom size and vibration (point atoms at rest)
By definition, mean of $E^2 = 1$
Symmetry elements affect the distribution of E values about their mean value
Most reliable test is for inversion symmetry, which affects all data

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Theoretical probability of a reflection having a particular value of E, for centrosymmetric structures (centric distribution of values) and for non-centrosymmetric structures (acentric distribution of values)

Mean value of $|E^2-1|$

around 0.74 for a non-centrosymmetric structure

around 0.97 for a centrosymmetric structure

Can also be used for detection of two-fold rotation axes and mirror planes by examination of appropriate subsets of data, but much less reliable.

2.7 Other points

Indistinguishable pairs of space groups from the information so far

enantiomorphous pairs, *e.g.* $P4_12_12$ and $P4_32_12$

$I222$ and $I2_12_12_1$

$I23$ and $I2_13$

Beware!

Poor quality data

Systematic absences with significant intensity

Heavy atoms and other 'non-random' distributions

Pseudo-symmetry

Twinned structures

Disorder

Successful structure solution in the wrong space group

PLATON (Ton Spek, Utrecht); available also for Windows
from Louis Farrugia, Glasgow.