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SCHOOL ON SYNCHROTRON RADIATION

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Rietveld Analysis Tutorials

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School on Synchrotron Radiation-ICTP 2000
Rietveld Analysis Tutorials

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1 INTRODUCTION

This tutorial will show how the Rietveld method works, it will give some practical hints to the students so that they can start working with Rietveld analysis in their laboratories. Some examples will show the typical problems that they can face. FULLPROF [1], a program that is in the public domain will be used.

1.1 Files organization

The folder **ICTP_2000** contains all the necessary files to work with these tutorials. It is divided into seven general folders:

- **xrd**,
- **nd**,
- **synchrotron**,
- **xrd+nd**,
- **fullprof**,
- **winplotr**,
- **zipfiles**

xrd ,nd,synchrotron, xrd+nd folders contain all the necessary files to work with neutron diffraction (nd) and x-ray diffraction during the guided tutorials.

fullprof \ docs contains this document and Fullprof Manual.

1.2 File Description

Fullprof needs two input files:

- raw datafile ***.DAT** containing the experimental data
- parameter file ***.PCR** containing crystallographic and instrumental information.

Fullprof writes some output files:

- ***.OUT**: main output file containing all control variables and refined parameters
- ***.PRF**: observed and calculated profile
- ***.RPA**:summary of refined parameters
- ***.SYM**: list of symmetry operators
- ***.SUM**: parameter list after last cycle, summary of the last parameters, their standard deviations and reliable factors
- ***.HKL**: complete list of reflections of each phase

1.3 Folder Content

The folders **xrd**, **nd**, **synchrotron** and **xrd+nd** are divided into different folders with compound names. In each one there are two files, the data file and a text document with the necessary crystallographic data obtained from the "Inorganic Chemical Structure Database" (ICSD) [2].

The specific *.PCR file for each compound should be made by the students, overwriting a file from any other compound.

Taking as an example the Y_2O_3 compound, the files are named in the following way:

- Y_2O_3x.dat is the data file (x stands for x-ray).

The parameter files or "PCR" files are named as follows:

- Y_2O_3xi.pcr for the initial file (before refinement, with crystallographic parameters as taken from literature) and
- Y_2O_3xf.pcr for the final file (as obtained after refinement)

The "plot" files which will be generated during the refinement

- Y_2O_3x.prf. This *.prf file is the "Profile" file that will be read by WINPLOTR, and contain the experimental, calculated and difference plots. Y_2O_3xi.prf is the plot for the initial refinement (with crystallographic data as obtained from literature) and Y_2O_3xf.prf is the plot obtained after the structure has being completely refined.

Please, after you finish the refinements, compare both plots. Please, never use the "i" files (i.e. Y_2O_3xi.pcr) and "f" files (Y_2O_3xf.pcr) for refinements, these should be kept as backups.

2 GUIDED TUTORIAL

2.1 Starting a refinement

As a general rule, to start a refinement, first copy the initial PCR file with another name to save the original file without any change. Remember that when FULLPROF runs, it will overwrite the PCR file. I would recommend renaming it as the data file. As an example, let us continue with the Y_2O_3. Using the files for this compound contained in the folder ICTP_2000\synchrotron\Y_2O_3, we copy the file Y_2O_3xi.pcr as Y_2O_3x.pcr.

Open the Y_2O_3x.pcr file and take a look. Initial crystallographic data were obtained from reference ICSD 2000/release 1 66242 [2]. See also space group number 206 [3].

The initial PCR files always have NCYCLE=1 and Number of refined parameters=0.

Change the NCY to a larger value (between 10 and 15) and start the "parameters turn on" by increasing the "Number of refined parameters".

Note that the refinable parameters are numbered according to the recommendable "turn on sequence" [4].

During refinement, periodically take a look to the refined diffractogram by reading the file Y_2O_3x.prf with the program WINPLOTR. I also recommend to take a look to the Y_2O_3x.sum file (or the more extended file Y_2O_3x.out) to see the details of the refinement.

Finish the refinement and check your results by taking a look to the file Y_2O_3xf.pcr and compare it with your final version of Y_2O_3x.pcr. Also check the final refined diffractogram with WINPLOTR and observe the R parameters that you have obtained. Your results will be discussed in the class.

2.2 Refinement of Neutron Diffraction Data

Even though this tutorial is part of a Synchrotron School, I consider that in a Rietveld Analysis tutorial some neutron diffraction must be included. The main difference in neutron diffraction lies on the scattering factors (scattering lengths (b) in this case). Since b dependence with atomic number is not monotonic, many important applications arise, i.e. neighbor elements in the periodic table might have very different b values, which is not the case for xrd. Also, light elements, like oxygen, have very high b values. These are strong advantages in certain cases like the refinement of occupation numbers in substitutional solid solutions with neighboring elements and the refinement of atomic positions of light elements. Also refinement of anysotropic

temperature factors with powder diffraction must be performed with nd. To work with nd, please use the files in the folder: ICTP_2000\nd\$PbSO_4$.

Please, note the following differences in the PCR file compared with xrd:

- JOBTYP (Job in line 2) is now 1.
- INSTRM (Ins in line 3) is now 6 (This is for D1A/D2B instrumentation at ILL).
- Atoms and not ions should be used I.e., Pb and not Pb+4. This is because the nucleus is the scatterer and not the electron cloud.

After finishing the refinement we will try to refine anysotropic temperature factors, please save the file PbSO4n.pcr as PbSO4na.pcr. Put N_Type, at the end of line 11-4-1, equals 2 and add two lines for each atom with the anisotropic temperature factors and their codes. Usually an initial value of the order of 0.001 for β_{ij} should be OK. Important: These codes must be set according to the symmetry restrictions on the β_{ij}. See the additional notes.

2.3 Combined Neutron and X-ray Diffraction Refinement

There are many advantages in combining X-ray and neutron diffraction: X-rays are more sensitive to high atomic number atoms, while neutron can "see" very well some elements like Oxygen, or can distinguish Hydrogen from deuterium, furthermore neutron are well suited for the determination of thermal parameters. So if there is the possibility of having both data, why do not try to use simultaneously the information coming from these different sources? You will find in the folder ICTP_2000\nd+xrd the data of $PbSO_4$ obtained with x-ray and neutron diffraction. Take a look at the *.pcr file, to see how to use both the patterns, and then try to do a refinement. Compare the results you obtained with those obtained using only x-ray and only neutron. The results will be discussed in the class.

2.4 Intensities extraction

FULLPROF can be also used as a Profile Matching tool, without the knowledge of the structure. When this is the case the following general changes must be made in the PCR files:

- All atoms with their atomic positions and the rest of their parameters should be erased.

- The number of atoms (Nat) should be set equal to zero.
- JBT in line 11-2 should be set equal to 2. (Note that after running for the first time, IRF in line 11-2 is automatically set equal to 2)
- Scale, in line 11-5 should be 1.0.
- Set JLKH (line 3) to 1. This flag will make the program to write the output file Codfil.hkl that contains the information about the integrated intensities.

Please, note that in this case, except for the cell parameters (a, b, c, α, β, γ), there is no crystallographic model so, only profile shape parameters are being refined. Do not refine Bov, for example.

Also, you will note that, if the cell parameters are appropriate, the refinement will converge very fast. Also you'll get very low values of the R parameters. To work with the profile matching mod, you have to use the files in the folder: ICTP_2000\xrd\Al_2O_3\extract. Follow the same procedures as in the other sections.

After finishing your refinement, take a look to the HKL file. There you will find the results of the intensities extraction.

2.5 Multiphase refinement, Quantitative analysis

You will find the necessary files in the folder

ICTP_2000\synchrotron\quantitative.

First of all read the Y2O3Al2O3.prf file using WINPLOTR. This was obtained with only one single phase. You will see that there are some reflections which can not be refined. They correspond to the second crystalline phase Al_2O_3. Copy Y2O3Al2O3xi.pcr as Y2O3Al2O3x.pcr and open it .

Note that NPHASE=2 (Line 2) and that there are two sets of atom parameters, one for the first phase (Y_2O_3) and another for the second one (Al_2O_3). Also in this case ATZ$\neq$0.

ATZ = Z·Mw·f^2/t

This parameter is used to calculate the weight percentage of the phase.

- Z: Number of formula units per cell,
- Mw:molecular weight.
- f: Used to transform the site multiplicities to their true values. For a stoichiometric phase f=1 if these multiplicities are calculated by dividing the Wyckoff multiplicity m of the site by the general multiplicity

M. Otherwise f=Occ.M/m, where Occ. is the occupation number given in line 11-41 of the FULLPROF manual.

- t: Is the Brindley coefficient that accounts for microabsorption effects. It is required for quantitative phase analysis only. When phases have like absorption, this factor is nearly 1.

So, if microabsorption is neglected and Occ. is the multiplicity true values, then:

ATZ= Z·Mw

Weight percentage of the different phases will be found in the SUM or OUT files.

For Y_2O_3 Z=16 and Mw=581.43

For Al_2O_3 Z=6 and Mw=209.9,

thus you can calculate ATZ.

Start the refinement by turning on the parameters. In this case you will notice quite a good refinement from the beginning. The reason for this is that this exercise is just to show the use of quantitative phase analysis and not how to refine this particular structure.

After you finish take a look to the end of the Y2O3Al2O3x.sum file, you will find the percentages of each phase. Also take a read the Y2O3Al2O3x.prf file with WINPLOTR.

2.6 Introducing scattering sets in the PCR file

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Sometimes the scattering factors' database of the program does not have a certain scattering factor (i.e. O^{-2}) and it is necessary to introduce it from the PCR. Do that for the O^{-2} ion in any PCR for xrd. The coefficients for the Cromer polynomial are:

3.750400 16.515100 2.842900 6.592000 1.543000 .319200 1.62100 43.348600 .242100

Introduce them into line 8-2 (See FULLPROF instructions). Remember to change NSCAT (Nsc) to 1. Refine again.

2.7 Calculating a diffractogram with anomalous scattering effects

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Anomalous scattering effect for a certain element can be introduced through its scattering factor that will now take the form:

$$f = f_o + f'(E) + if''(E) \tag{1}$$

Where f_o is the "normal" scattering factor, depending only on angle and f' and f" are Energy dependents.

This effect can be introduced from the PCR file in the same way as the scattering set for O^{-2} has been introduced. Change NSCAT to 1 and introduce the f' and f" in line 8-1 (See FULLPROF instructions). Remember to set JOBTYP (Job) to 2 (pattern calculation (X-ray)). Compare your results with the "normal" diffractogram.

References

[1] J. Rodriguez-Carvajal, Phisica B 192, 55 (1993).

[2] National Institute of Standards and Technology Gaithersburg, Inorganic Crystal Structure Database, ICSD Release 2000/1.

[3] T. Hann, (Editor). "International Tables for Crystallography". Second Edition. Vol. A. Kluwer Academic Pub. (1989).

[4] R. A. Young (Editor). "The Rietveld Method". Oxford University Press (1993).

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Addendum to:

Rietveld Analysis Tutorials

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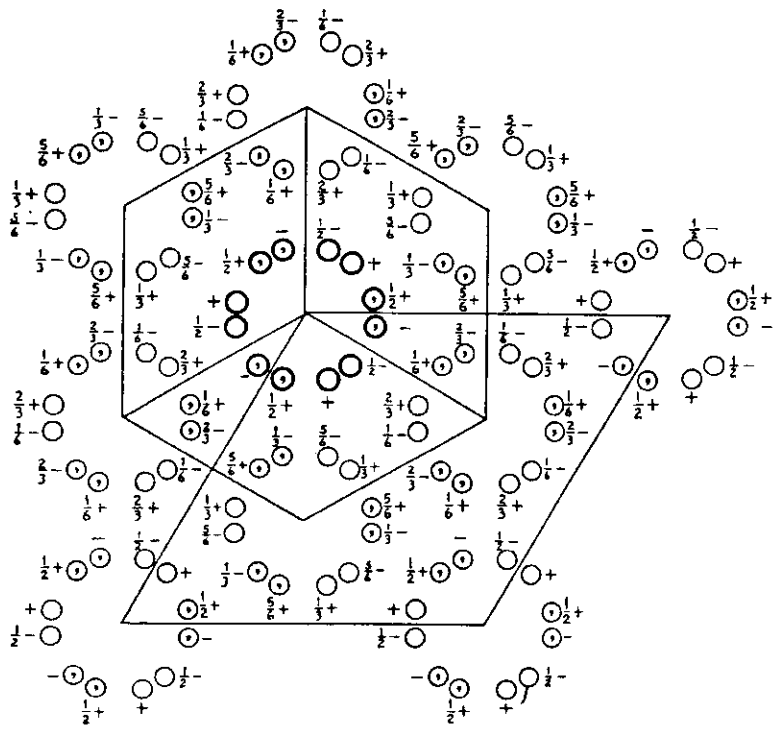
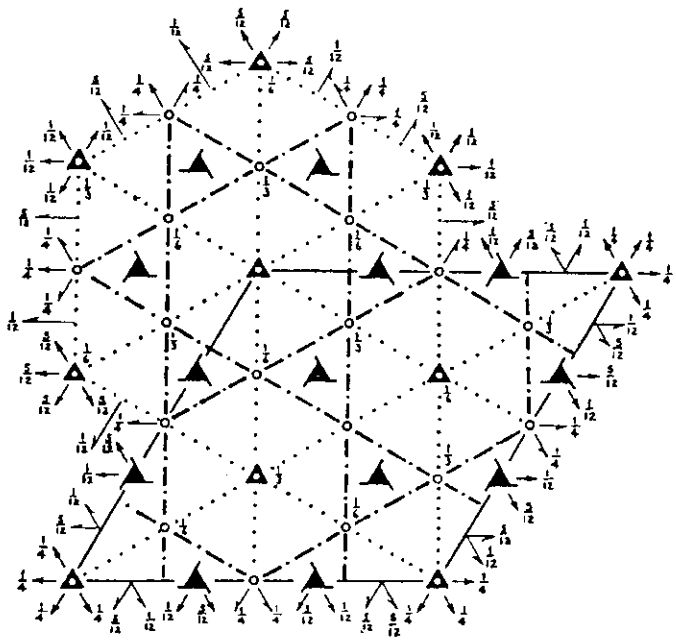
$R\,\bar{3}\,c$ D_{3d}^{6} $\bar{3}\,m$ Trigonal

No. 167 $R\,\bar{3}\,2/c$ Patterson symmetry $R\,\bar{3}\,m$

HEXAGONAL AXES





Origin at centre ($\bar{3}$) at $\bar{3}c$

Asymmetric unit $0\le x\le\frac{2}{3}$; $0\le y\le\frac{2}{3}$; $0\le z\le\frac{1}{12}$; $x\le(1+y)/2$; $y\le\min(1-x,(1+x)/2)$

Vertices $0,0,0$ $\frac{1}{2},0,0$ $\frac{2}{3},\frac{1}{3},0$ $\frac{1}{3},\frac{2}{3},0$ $0,\frac{1}{2},0$
$0,0,\frac{1}{12}$ $\frac{1}{2},0,\frac{1}{12}$ $\frac{2}{3},\frac{1}{3},\frac{1}{12}$ $\frac{1}{3},\frac{2}{3},\frac{1}{12}$ $0,\frac{1}{2},\frac{1}{12}$

Symmetry operations

For (0,0,0)+ set

(1) 1	(2) 3^+ 0,0,z	(3) 3^- 0,0,z
(4) 2 $x,x,\frac{1}{4}$	(5) 2 $x,0,\frac{1}{4}$	(6) 2 $0,y,\frac{1}{4}$
(7) $\bar{1}$ 0,0,0	(8) $\bar{3}^+$ 0,0,z; 0,0,0	(9) $\bar{3}^-$ 0,0,z; 0,0,0
(10) c $x,\bar{x},z$	(11) c $x,2x,z$	(12) c $2x,x,z$

For $(\frac{2}{3},\frac{1}{3},\frac{1}{3})+$ set

(1) $t(\frac{2}{3},\frac{1}{3},\frac{1}{3})$	(2) $3^+(0,0,\frac{1}{3})$ $\frac{1}{3},\frac{1}{3},z$	(3) $3^-(0,0,\frac{1}{3})$ $\frac{1}{3},0,z$
(4) $2(\frac{1}{3},\frac{1}{3},0)$ $x,x-\frac{1}{6},\frac{1}{12}$	(5) $2(\frac{1}{3},0,0)$ $x,\frac{1}{6},\frac{1}{12}$	(6) 2 $\frac{1}{3},y,\frac{5}{12}$
(7) $\bar{1}$ $\frac{1}{3},\frac{1}{6},\frac{1}{6}$	(8) $\bar{3}^+$ $\frac{1}{3},-\frac{1}{3},z$; $\frac{1}{3},-\frac{1}{3},\frac{1}{6}$	(9) $\bar{3}^-$ $\frac{1}{3},\frac{1}{3},z$; $\frac{1}{3},\frac{1}{3},\frac{1}{6}$
(10) $g(\frac{1}{6},-\frac{1}{6},\frac{1}{6})$ $x+\frac{1}{3},\bar{x},z$	(11) $g(\frac{1}{6},\frac{1}{3},\frac{1}{6})$ $x,2x-\frac{1}{3},z$	(12) $g(\frac{2}{3},\frac{1}{3},\frac{1}{6})$ $2x,x,z$

For $(\frac{1}{3},\frac{2}{3},\frac{2}{3})+$ set

(1) $t(\frac{1}{3},\frac{2}{3},\frac{2}{3})$	(2) $3^+(0,0,\frac{2}{3})$ $0,\frac{1}{3},z$	(3) $3^-(0,0,\frac{2}{3})$ $\frac{1}{3},\frac{1}{3},z$
(4) $2(\frac{1}{3},\frac{1}{3},0)$ $x,x+\frac{1}{6},\frac{1}{12}$	(5) 2 $x,\frac{1}{3},\frac{7}{12}$	(6) $2(0,\frac{1}{3},0)$ $\frac{1}{6},y,\frac{7}{12}$
(7) $\bar{1}$ $\frac{1}{6},\frac{1}{3},\frac{1}{3}$	(8) $\bar{3}^+$ $\frac{2}{3},\frac{1}{3},z$; $\frac{2}{3},\frac{1}{3},\frac{1}{3}$	(9) $\bar{3}^-$ $-\frac{1}{3},\frac{1}{3},z$; $-\frac{1}{3},\frac{1}{3},\frac{1}{3}$
(10) $g(-\frac{1}{6},\frac{1}{6},\frac{1}{6})$ $x+\frac{1}{3},\bar{x},z$	(11) $g(\frac{1}{3},\frac{2}{3},\frac{1}{6})$ $x,2x,z$	(12) $g(\frac{1}{3},\frac{1}{6},\frac{1}{6})$ $2x-\frac{1}{3},x,z$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{1}{3},\frac{1}{3},\frac{1}{3})$; (2); (4); (7)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates (0,0,0)+	(⅔,⅓,⅓)+	(⅓,⅔,⅔)+	Reflection conditions
36	f	1	(1) x,y,z (4) $y,x,\bar{z}+\frac{1}{2}$ (7) $\bar{x},\bar{y},\bar{z}$ (10) $\bar{y},\bar{x},z+\frac{1}{2}$	(2) $\bar{y},x-y,z$ (5) $x-y,\bar{y},\bar{z}+\frac{1}{2}$ (8) $y,\bar{x}+y,\bar{z}$ (11) $\bar{x}+y,y,z+\frac{1}{2}$	(3) $\bar{x}+y,\bar{x},z$ (6) $\bar{x},\bar{x}+y,\bar{z}+\frac{1}{2}$ (9) $x-y,x,\bar{z}$ (12) $x,x-y,z+\frac{1}{2}$	General: $hkil$: $-h+k+l=3n$ $hki0$: $-h+k=3n$ $hh2\bar{h}l$: $l=3n$ $h\bar{h}0l$: $h+l=3n$, $l=2n$ $000l$: $l=6n$ $h\bar{h}00$: $h=3n$
						Special: as above, plus
18	e	.2	$x,0,\frac{1}{4}$	$0,x,\frac{1}{4}$	$\bar{x},\bar{x},\frac{1}{4}$	$\bar{x},0,\frac{1}{4}$ $0,\bar{x},\frac{1}{4}$ $x,x,\frac{1}{4}$	no extra conditions
18	d	$\bar{1}$	$\frac{1}{2},0,0$	$0,\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$ $\frac{1}{2},0,\frac{1}{2}$ $\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$hkil$: $l=2n$
12	c	3.	$0,0,z$	$0,0,\bar{z}+\frac{1}{2}$	$0,0,\bar{z}$	$0,0,z+\frac{1}{2}$	$hkil$: $l=2n$
6	b	$\bar{3}$.	$0,0,0$	$0,0,\frac{1}{2}$			$hkil$: $l=2n$
6	a	32	$0,0,\frac{1}{4}$	$0,0,\frac{3}{4}$			$hkil$: $l=2n$

Symmetry of special projections

Along [001] $p\,6m\,m$
$\boldsymbol{a}'=\frac{1}{3}(2\boldsymbol{a}+\boldsymbol{b})$ $\boldsymbol{b}'=\frac{1}{3}(-\boldsymbol{a}+\boldsymbol{b})$
Origin at 0,0,z

Along [100] $p\,2$
$\boldsymbol{a}'=\frac{1}{6}(2\boldsymbol{a}+4\boldsymbol{b}+\boldsymbol{c})$ $\boldsymbol{b}'=\frac{1}{6}(-\boldsymbol{a}-2\boldsymbol{b}+\boldsymbol{c})$
Origin at x,0,0

Along [210] $p\,2g\,m$
$\boldsymbol{a}'=\frac{1}{2}\boldsymbol{b}$ $\boldsymbol{b}'=\frac{1}{2}\boldsymbol{c}$
Origin at $x,\frac{1}{2}x,0$

HEXAGONAL AXES

Maximal non-isomorphic subgroups

I	[2]$R\,3\,2$	(1; 2; 3; 4; 5; 6)+
	[2]$R\,\bar{3}\,1\,(R\,\bar{3})$	(1; 2; 3; 7; 8; 9)+
	[2]$R\,3c$	(1; 2; 3; 10; 11; 12)+
	[3]$R\,1\,2/c\,(C\,2/c)$	(1; 4; 7; 10)+
	[3]$R\,1\,2/c\,(C\,2/c)$	(1; 5; 7; 11)+
	[3]$R\,1\,2/c\,(C\,2/c)$	(1; 6; 7; 12)+
IIa	[3]$P\,\bar{3}c\,1$	1; 2; 3; 4; 5; 6; 7; 8; 9; 10; 11; 12
	[3]$P\,\bar{3}c\,1$	1; 2; 3; 10; 11; 12; (4; 5; 6; 7; 8; 9)+$(\frac{2}{3},\frac{1}{3},\frac{1}{3})$
	[3]$P\,\bar{3}c\,1$	1; 2; 3; 10; 11; 12; (4; 5; 6; 7; 8; 9)+$(\frac{1}{3},\frac{2}{3},\frac{2}{3})$
IIb	none	

Maximal isomorphic subgroups of lowest index

IIc [5]$R\,\bar{3}c\,(\boldsymbol{a}'=-\boldsymbol{a},\boldsymbol{b}'=-\boldsymbol{b},\boldsymbol{c}'=5\boldsymbol{c})$; [4]$R\,\bar{3}c\,(\boldsymbol{a}'=-2\boldsymbol{a},\boldsymbol{b}'=-2\boldsymbol{b})$

Minimal non-isomorphic supergroups

I [4]$P\,n\,\bar{3}\,n$; [4]$P\,m\,\bar{3}\,n$; [4]$F\,m\,\bar{3}\,c$; [4]$F\,d\,\bar{3}\,c$; [4]$I\,a\,\bar{3}\,d$

II [2]$R\,\bar{3}\,m\,(\boldsymbol{a}'=-\boldsymbol{a},\boldsymbol{b}'=-\boldsymbol{b},2\boldsymbol{c}'=\boldsymbol{c})$; [3]$P\,\bar{3}\,1\,c\,(3\boldsymbol{a}'=2\boldsymbol{a}+\boldsymbol{b},3\boldsymbol{b}'=-\boldsymbol{a}+\boldsymbol{b},3\boldsymbol{c}'=\boldsymbol{c})$

RHOMBOHEDRAL AXES

Maximal non-isomorphic subgroups

I	[2]$R\,3\,2$	1; 2; 3; 4; 5; 6
	[2]$R\,\bar{3}\,1\,(R\,\bar{3})$	1; 2; 3; 7; 8; 9
	[2]$R\,3c$	1; 2; 3; 10; 11; 12
	[3]$R\,1\,2/c\,(C\,2/c)$	1; 4; 7; 10
	[3]$R\,1\,2/c\,(C\,2/c)$	1; 5; 7; 11
	[3]$R\,1\,2/c\,(C\,2/c)$	1; 6; 7; 12
IIa	none	
IIb	[3]$P\,\bar{3}c\,1$ $(\boldsymbol{a}'=\boldsymbol{a}-\boldsymbol{b},\boldsymbol{b}'=\boldsymbol{b}-\boldsymbol{c},\boldsymbol{c}'=\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c})$	

Maximal isomorphic subgroups of lowest index

IIc [5]$R\,\bar{3}c\,(\boldsymbol{a}'=\boldsymbol{a}+2\boldsymbol{b}+2\boldsymbol{c},\boldsymbol{b}'=2\boldsymbol{a}+\boldsymbol{b}+2\boldsymbol{c},\boldsymbol{c}'=2\boldsymbol{a}+2\boldsymbol{b}+\boldsymbol{c})$; [4]$R\,\bar{3}c\,(\boldsymbol{a}'=-\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c},\boldsymbol{b}'=\boldsymbol{a}-\boldsymbol{b}+\boldsymbol{c},\boldsymbol{c}'=\boldsymbol{a}+\boldsymbol{b}-\boldsymbol{c})$

Minimal non-isomorphic supergroups

I [4]$P\,n\,\bar{3}\,n$; [4]$P\,m\,\bar{3}\,n$; [4]$F\,m\,\bar{3}\,c$; [4]$F\,d\,\bar{3}\,c$; [4]$I\,a\,\bar{3}\,d$

II [2]$R\,\bar{3}\,m\,(2\boldsymbol{a}'=-\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c},2\boldsymbol{b}'=\boldsymbol{a}-\boldsymbol{b}+\boldsymbol{c},2\boldsymbol{c}'=\boldsymbol{a}+\boldsymbol{b}-\boldsymbol{c})$; [3]$P\,\bar{3}\,1\,c\,(3\boldsymbol{a}'=2\boldsymbol{a}-\boldsymbol{b}-\boldsymbol{c},3\boldsymbol{b}'=-\boldsymbol{a}+2\boldsymbol{b}-\boldsymbol{c},3\boldsymbol{c}'=\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c})$

Trigonal $\bar{3}\,m$ D_{3d}^6 $R\,\bar{3}\,c$

Patterson symmetry $R\,\bar{3}\,m$ $R\,\bar{3}\,2/c$ No. 167

RHOMBOHEDRAL AXES

(For drawings see hexagonal axes

Origin at centre $(\bar{3})$ at $\bar{3}c$

Asymmetric unit $\frac{1}{4} \le x \le \frac{5}{8}$; $\frac{1}{4} \le y \le \frac{5}{8}$; $\frac{1}{4} \le z \le \frac{1}{4}$; $y \le x$; $z \le \min(y, \frac{3}{2} - x)$.

Vertices $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ $\frac{5}{8},\frac{1}{4},\frac{1}{4}$ $\frac{5}{8},\frac{5}{8},\frac{1}{4}$ $\frac{3}{4},\frac{3}{4},\frac{3}{4}$

Symmetry operations

(1) 1	(2) 3^+ x,x,x	(3) 3^- x,x,x
(4) 2 $x,\bar{x}+\frac{1}{2},\frac{1}{4}$	(5) 2 $\frac{1}{4},y,\bar{y}+\frac{1}{2}$	(6) 2 $\bar{x}+\frac{1}{2},\frac{1}{4},x$
(7) $\bar{1}$ 0,0,0	(8) $\bar{3}^+$ x,x,x; 0,0,0	(9) $\bar{3}^-$ x,x,x; 0,0,0
(10) $n(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ x,x,z	(11) $n(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ x,y,y	(12) $n(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ x,y,x

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (4); (7)

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates	Reflection conditions
12 f 1	(1) x,y,z (2) z,x,y (3) y,z,x (4) $\bar{y}+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{z}+\frac{1}{2}$ (5) $\bar{x}+\frac{1}{2},\bar{z}+\frac{1}{2},\bar{y}+\frac{1}{2}$ (6) $\bar{z}+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{x}+\frac{1}{2}$ (7) $\bar{x},\bar{y},\bar{z}$ (8) $\bar{z},\bar{x},\bar{y}$ (9) $\bar{y},\bar{z},\bar{x}$ (10) $y+\frac{1}{2},x+\frac{1}{2},z+\frac{1}{2}$ (11) $x+\frac{1}{2},z+\frac{1}{2},y+\frac{1}{2}$ (12) $z+\frac{1}{2},y+\frac{1}{2},x+\frac{1}{2}$	General: hhl : $l=2n$ hhh: $h=2n$
		Special: as above, plus
6 e .2	$x,\bar{x}+\frac{1}{2},\frac{1}{4}$ $\frac{1}{4},x,\bar{x}+\frac{1}{2}$ $\bar{x}+\frac{1}{2},\frac{1}{4},x$ $\bar{x},x+\frac{1}{2},\frac{1}{4}$ $\frac{3}{4},\bar{x},x+\frac{1}{2}$ $x+\frac{1}{2},\frac{3}{4},\bar{x}$	no extra conditions
6 d $\bar{1}$	$\frac{1}{2},0,0$ $0,\frac{1}{2},0$ $0,0,\frac{1}{2}$ $\frac{1}{2},0,\frac{1}{2}$ $0,\frac{1}{2},\frac{1}{2}$ $\frac{1}{2},\frac{1}{2},0$	hkl : $h+k+l=2n$
4 c 3.	x,x,x $\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2}$ $\bar{x},\bar{x},\bar{x}$ $x+\frac{1}{2},x+\frac{1}{2},x+\frac{1}{2}$	hkl : $h+k+l=2n$
2 b $\bar{3}$.	0,0,0 $\frac{1}{2},\frac{1}{2},\frac{1}{2}$	hkl : $h+k+l=2n$
2 a 32	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$ $\frac{3}{4},\frac{3}{4},\frac{3}{4}$	hkl : $h+k+l=2n$

Symmetry of special projections

Along [111] $p\,6m\,m$
$\boldsymbol{a}' = \frac{1}{3}(2\boldsymbol{a}-\boldsymbol{b}-\boldsymbol{c})$ $\boldsymbol{b}' = \frac{1}{3}(-\boldsymbol{a}+2\boldsymbol{b}-\boldsymbol{c})$
Origin at x,x,x

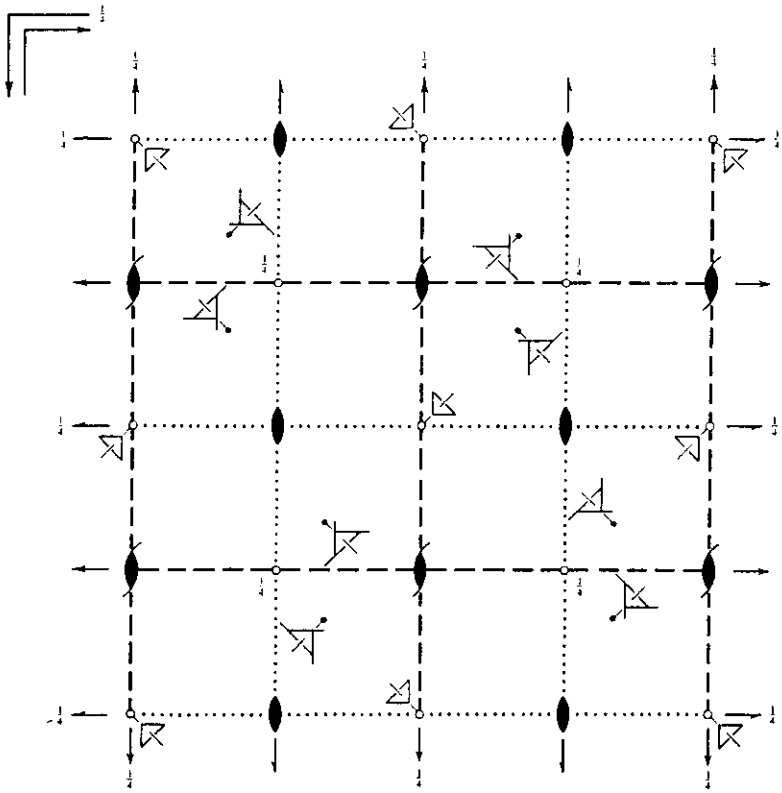
Along [1$\bar{1}$0] $p\,2$
$\boldsymbol{a}' = \frac{1}{2}(\boldsymbol{a}+\boldsymbol{b}-2\boldsymbol{c})$ $\boldsymbol{b}' = \frac{1}{2}\boldsymbol{c}$
Origin at $x,\bar{x},0$

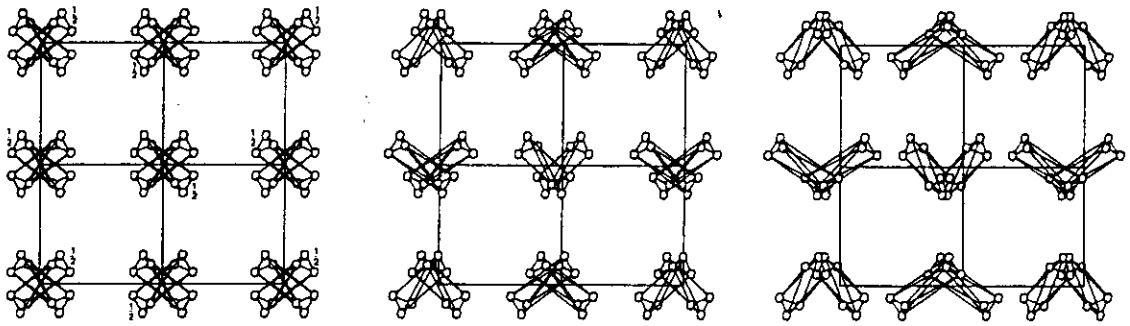
Along [2$\bar{1}\bar{1}$] $p\,2g\,m$
$\boldsymbol{a}' = \frac{1}{3}(\boldsymbol{b}-\boldsymbol{c})$ $\boldsymbol{b}' = \frac{1}{3}(\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c})$
Origin at $2x,\bar{x},\bar{x}$

(*Continued on preceding page*)

$Ia\bar{3}$ T_h^7 $m\bar{3}$ Cubic

No. 206 $I2_1/a\bar{3}$ Patterson symmetry $Im\bar{3}$





Origin at centre ($\bar{3}$)

Asymmetric unit $0\le x\le\frac{1}{2}$; $0\le y\le\frac{1}{2}$; $0\le z\le\frac{1}{4}$; $z\le\min(x,\frac{1}{2}-x,y,\frac{1}{2}-y)$

Vertices 0,0,0 $\frac{1}{2}$,0,0 $\frac{1}{2},\frac{1}{2},0$ 0,$\frac{1}{2}$,0 $\frac{1}{4},\frac{1}{4},\frac{1}{4}$

Symmetry operations

For (0,0,0)+ set

(1) 1
(2) 2(0,0,$\frac{1}{2}$) $\frac{1}{4}$,0,z
(3) 2(0,$\frac{1}{2}$,0) 0,y,$\frac{1}{4}$
(4) 2($\frac{1}{2}$,0,0) x,$\frac{1}{4}$,0
(5) 3^+ x,x,x
(6) 3^+ $\bar{x}+\frac{1}{2},x,\bar{x}$
(7) 3^+ $x+\frac{1}{2},\bar{x}-\frac{1}{2},\bar{x}$
(8) 3^+ $\bar{x},\bar{x}+\frac{1}{2},x$
(9) 3^- x,x,x
(10) $3^-(-\frac{1}{6},\frac{1}{3},\frac{1}{6})$ $x+\frac{1}{6},\bar{x}+\frac{1}{6},\bar{x}$
(11) $3^-(\frac{1}{3},\frac{1}{6},-\frac{1}{6})$ $\bar{x}+\frac{1}{3},\bar{x}+\frac{1}{6},x$
(12) $3^-(\frac{1}{3},-\frac{1}{6},\frac{1}{6})$ $\bar{x}-\frac{1}{6},x+\frac{1}{3},\bar{x}$
(13) $\bar{1}$ 0,0,0
(14) a $x,y,\frac{1}{4}$
(15) c $x,\frac{1}{4},z$
(16) b $\frac{1}{4},y,z$
(17) $\bar{3}^+$ x,x,x; 0,0,0
(18) $\bar{3}^+$ $\bar{x}-\frac{1}{2},x+1,\bar{x}$; 0,$\frac{1}{2}$,$\frac{1}{4}$
(19) $\bar{3}^+$ $x+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{x}$; $\frac{1}{2},\frac{1}{2}$,0
(20) $\bar{3}^+$ $\bar{x}+1,\bar{x}+\frac{1}{2},x$; $\frac{1}{2}$,0,$\frac{1}{4}$
(21) $\bar{3}^-$ x,x,x; 0,0,0
(22) $\bar{3}^-$ $x+\frac{1}{2},\bar{x}-\frac{1}{2},\bar{x}$; 0,0,$\frac{1}{4}$
(23) $\bar{3}^-$ $\bar{x},\bar{x}+\frac{1}{2},x$; 0,$\frac{1}{2}$,0
(24) $\bar{3}^-$ $\bar{x}+\frac{1}{2},x,\bar{x}$; $\frac{1}{2}$,0,0

For ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$)+ set

(1) $t(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
(2) 2 0,$\frac{1}{4}$,z
(3) 2 $\frac{1}{4}$,y,0
(4) 2 x,0,$\frac{1}{4}$
(5) $3^+(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ x,x,x
(6) $3^+(\frac{1}{6},-\frac{1}{6},\frac{1}{6})$ $\bar{x}-\frac{1}{6},x+\frac{1}{3},\bar{x}$
(7) $3^+(-\frac{1}{6},\frac{1}{6},\frac{1}{6})$ $x+\frac{1}{6},\bar{x}+\frac{1}{6},\bar{x}$
(8) $3^+(\frac{1}{6},\frac{1}{6},-\frac{1}{6})$ $\bar{x}+\frac{1}{3},\bar{x}+\frac{1}{6},x$
(9) $3^-(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ x,x,x
(10) $3^-(\frac{1}{6},-\frac{1}{6},-\frac{1}{6})$ $x+\frac{1}{6},\bar{x}+\frac{1}{6},\bar{x}$
(11) $3^-(-\frac{1}{6},-\frac{1}{6},\frac{1}{6})$ $\bar{x}+\frac{1}{3},\bar{x}+\frac{1}{6},x$
(12) $3^-(-\frac{1}{6},\frac{1}{6},-\frac{1}{6})$ $\bar{x}-\frac{1}{6},x+\frac{1}{3},\bar{x}$
(13) $\bar{1}$ $\frac{1}{4},\frac{1}{4},\frac{1}{4}$
(14) b $x,y,0$
(15) a $x,0,z$
(16) c 0,y,z
(17) $\bar{3}^+$ x,x,x; $\frac{1}{4},\frac{1}{4},\frac{1}{4}$
(18) $\bar{3}^+$ $\bar{x}-\frac{1}{2},x,\bar{x}$; $-\frac{1}{4},-\frac{1}{4},\frac{1}{4}$
(19) $\bar{3}^+$ $x-\frac{1}{4},\bar{x}+\frac{1}{4},\bar{x}$; $-\frac{1}{4},\frac{1}{4},-\frac{1}{4}$
(20) $\bar{3}^+$ $\bar{x},\bar{x}-\frac{1}{2},x$; $\frac{1}{4},-\frac{1}{4},-\frac{1}{4}$
(21) $\bar{3}^-$ x,x,x; $\frac{1}{4},\frac{1}{4},\frac{1}{4}$
(22) $\bar{3}^-$ $x+\frac{1}{2},\bar{x}-\frac{1}{2},\bar{x}$; $\frac{1}{4},-\frac{1}{4},\frac{1}{4}$
(23) $\bar{3}^-$ $\bar{x},\bar{x}+\frac{1}{2},x$; $-\frac{1}{4},\frac{1}{4},\frac{1}{4}$
(24) $\bar{3}^-$ $\bar{x}+\frac{1}{2},x,\bar{x}$; $\frac{1}{4},\frac{1}{4},-\frac{1}{4}$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; (2); (3); (5); (13)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
			$(0,0,0)+$	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})+$			h,k,l cyclically permutat
							General:
48	*e*	1	(1) x,y,z	(2) $\bar{x}+\frac{1}{2},\bar{y},z+\frac{1}{2}$	(3) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$	hkl : $h+k+l=2n$
			(5) z,x,y	(6) $z+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{y}$	(7) $\bar{z}+\frac{1}{2},\bar{x},y+\frac{1}{2}$	(8) $\bar{z},x+\frac{1}{2},\bar{y}+\frac{1}{2}$	$0kl$: $k,l=2n$
			(9) y,z,x	(10) $\bar{y},z+\frac{1}{2},\bar{x}+\frac{1}{2}$	(11) $y+\frac{1}{2},\bar{z}+\frac{1}{2},\bar{x}$	(12) $\bar{y}+\frac{1}{2},\bar{z},x+\frac{1}{2}$	hhl : $l=2n$
			(13) $\bar{x},\bar{y},\bar{z}$	(14) $x+\frac{1}{2},y,\bar{z}+\frac{1}{2}$	(15) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	(16) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z$	$h00$: $h=2n$
			(17) $\bar{z},\bar{x},\bar{y}$	(18) $\bar{z}+\frac{1}{2},x+\frac{1}{2},y$	(19) $z+\frac{1}{2},x,\bar{y}+\frac{1}{2}$	(20) $z,\bar{x}+\frac{1}{2},y+\frac{1}{2}$	
			(21) $\bar{y},\bar{z},\bar{x}$	(22) $y,\bar{z}+\frac{1}{2},x+\frac{1}{2}$	(23) $\bar{y}+\frac{1}{2},z+\frac{1}{2},x$	(24) $y+\frac{1}{2},z,\bar{x}+\frac{1}{2}$	
							Special: as above, plus
24	*d*	2..	$x,0,\frac{1}{4}$	$\bar{x}+\frac{1}{2},0,\frac{3}{4}$	$\frac{1}{4},x,0$	$\frac{3}{4},\bar{x}+\frac{1}{2},0$	$0,\frac{1}{4},x$ $0,\frac{3}{4},\bar{x}+\frac{1}{2}$	no extra conditions
			$\bar{x},0,\frac{3}{4}$	$x+\frac{1}{2},0,\frac{1}{4}$	$\frac{3}{4},\bar{x},0$	$\frac{1}{4},x+\frac{1}{2},0$	$0,\frac{3}{4},\bar{x}$ $0,\frac{1}{4},x+\frac{1}{2}$	
16	*c*	.3.	x,x,x	$\bar{x}+\frac{1}{2},\bar{x},x+\frac{1}{2}$	$\bar{x},x+\frac{1}{2},\bar{x}+\frac{1}{2}$	$x+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{x}$	no extra conditions
			$\bar{x},\bar{x},\bar{x}$	$x+\frac{1}{2},x,\bar{x}+\frac{1}{2}$	$x,\bar{x}+\frac{1}{2},x+\frac{1}{2}$	$\bar{x}+\frac{1}{2},x+\frac{1}{2},x$	
8	*b*	.$\bar{3}$.	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},\frac{3}{4},\frac{3}{4}$	$\frac{3}{4},\frac{3}{4},\frac{1}{4}$	$\frac{3}{4},\frac{1}{4},\frac{3}{4}$	hkl : $k,l=2n$
8	*a*	.$\bar{3}$.	0,0,0	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	hkl : $k,l=2n$

Symmetry of special projections

Along [001] $p\,2m\,m$
$\boldsymbol{a}'=\frac{1}{2}\boldsymbol{a}$ $\boldsymbol{b}'=\frac{1}{2}\boldsymbol{b}$
Origin at 0,0,z

Along [111] $p\,6$
$\boldsymbol{a}'=\frac{1}{3}(2\boldsymbol{a}-\boldsymbol{b}-\boldsymbol{c})$ $\boldsymbol{b}'=\frac{1}{3}(-\boldsymbol{a}+2\boldsymbol{b}-\boldsymbol{c})$
Origin at x,x,x

Along [110] $p\,2m\,g$
$\boldsymbol{a}'=\frac{1}{2}(-\boldsymbol{a}+\boldsymbol{b})$ $\boldsymbol{b}'=\frac{1}{2}\boldsymbol{c}$
Origin at $x,x,0$

Maximal non-isomorphic subgroups

I	[3] $I\,a\,1$ ($I\,b\,c\,a$)	(1; 2; 3; 4; 13; 14; 15; 16)+
	[4] $I\,1\,\bar{3}$ ($R\,\bar{3}$)	(1; 5; 9; 13; 17; 21)+
	[4] $I\,1\,\bar{3}$ ($R\,\bar{3}$)	(1; 6; 12; 13; 18; 24)+
	[4] $I\,1\,\bar{3}$ ($R\,\bar{3}$)	(1; 7; 10; 13; 19; 22)+
	[4] $I\,1\,\bar{3}$ ($R\,\bar{3}$)	(1; 8; 11; 13; 20; 23)+
	[2] $I\,2_1\,3$	(1; 2; 3; 4; 5; 6; 7; 8; 9; 10; 11; 12)+
IIa	[2] $P\,a\,\bar{3}$	1; 2; 3; 4; 5; 6; 7; 8; 9; 10; 11; 12; 13; 14; 15; 16; 17; 18; 19; 20; 21; 22; 23; 24
	[2] $P\,a\,\bar{3}$	1; 2; 3; 4; 5; 6; 7; 8; 9; 10; 11; 12; (13; 14; 15; 16; 17; 18; 19; 20; 21; 22; 23; 24)+($\frac{1}{2},\frac{1}{2},\frac{1}{2}$)
IIb	none	

Maximal isomorphic subgroups of lowest index

IIc [27] $I\,a\,\bar{3}$ ($\boldsymbol{a}'=3\boldsymbol{a}, \boldsymbol{b}'=3\boldsymbol{b}, \boldsymbol{c}'=3\boldsymbol{c}$)

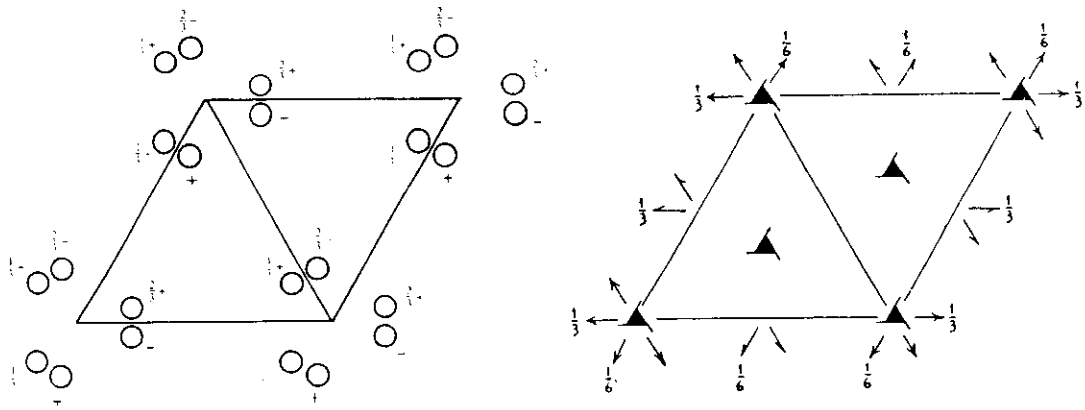
Minimal non-isomorphic supergroups

I [2] $I\,a\,\bar{3}\,d$

II [4] $P\,m\,\bar{3}$ ($2\boldsymbol{a}'=\boldsymbol{a}, 2\boldsymbol{b}'=\boldsymbol{b}, 2\boldsymbol{c}'=\boldsymbol{c}$)

$P\,3_2\,2\,1$ D_3^6 3 2 1 Trigonal

No. 154 $P\,3_2\,2\,1$ Patterson symmetry $P\,\bar{3}\,m\,1$



Origin on $2[1\,1\,0]$ at $3_2(1,1,2)\,1$

Asymmetric unit $0\le x\le 1;\quad 0\le y\le 1;\quad 0\le z\le \frac{1}{6}$

Vertices $0,0,0$ $1,0,0$ $1,1,0$ $0,1,0$
$0,0,\frac{1}{6}$ $1,0,\frac{1}{6}$ $1,1,\frac{1}{6}$ $0,1,\frac{1}{6}$

Symmetry operations

(1) 1 (2) $3^+(0,0,\frac{1}{3})$ $0,0,z$ (3) $3^-(0,0,\frac{1}{3})$ $0,0,z$
(4) 2 $x,x,0$ (5) 2 $x,0,\frac{1}{6}$ (6) 2 $0,y,\frac{1}{3}$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (4)

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates			Reflection conditions
6 c 1	(1) x,y,z	(2) $\bar{y},x-y,z+\frac{2}{3}$	(3) $\bar{x}+y,\bar{x},z+\frac{1}{3}$	General:
	(4) $y,x,\bar{z}$	(5) $x-y,\bar{y},\bar{z}+\frac{1}{3}$	(6) $\bar{x},\bar{x}+y,\bar{z}+\frac{2}{3}$	$000l$: $l=3n$
				Special: no extra conditions
3 b .2.	$x,0,\frac{1}{6}$	$0,x,\frac{5}{6}$	$\bar{x},\bar{x},\frac{1}{2}$	
3 a .2.	$x,0,\frac{1}{3}$	$0,x,\frac{1}{3}$	$\bar{x},\bar{x},0$	

Symmetry of special projections

Along [001] $p\,3\,1m$
$\boldsymbol{a}'=\boldsymbol{a}$ $\boldsymbol{b}'=\boldsymbol{b}$
Origin at $0,0,z$

Along [100] $p\,2$
$\boldsymbol{a}'=\frac{1}{2}(\boldsymbol{a}+2\boldsymbol{b})$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,0,\frac{1}{6}$

Along [210] $p\,1\,1m$
$\boldsymbol{a}'=\frac{1}{2}\boldsymbol{b}$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,\frac{1}{2}x,\frac{1}{3}$

Maximal non-isomorphic subgroups

I [2]$P3_211$ $(P3_2)$ 1; 2; 3
[3]$P121$ $(C2)$ 1; 4
[3]$P121$ $(C2)$ 1; 5
[3]$P121$ $(C2)$ 1; 6

IIa none

IIb [3]$H3_221$ $(\boldsymbol{a}'=3\boldsymbol{a},\boldsymbol{b}'=3\boldsymbol{b})$ $(P3_212)$

Maximal isomorphic subgroups of lowest index

IIc [2]$P3_221$ $(\boldsymbol{c}'=2\boldsymbol{c})$; [7]$P3_221$ $(\boldsymbol{c}'=7\boldsymbol{c})$; [4]$P3_221$ $(\boldsymbol{a}'=2\boldsymbol{a},\boldsymbol{b}'=2\boldsymbol{b})$

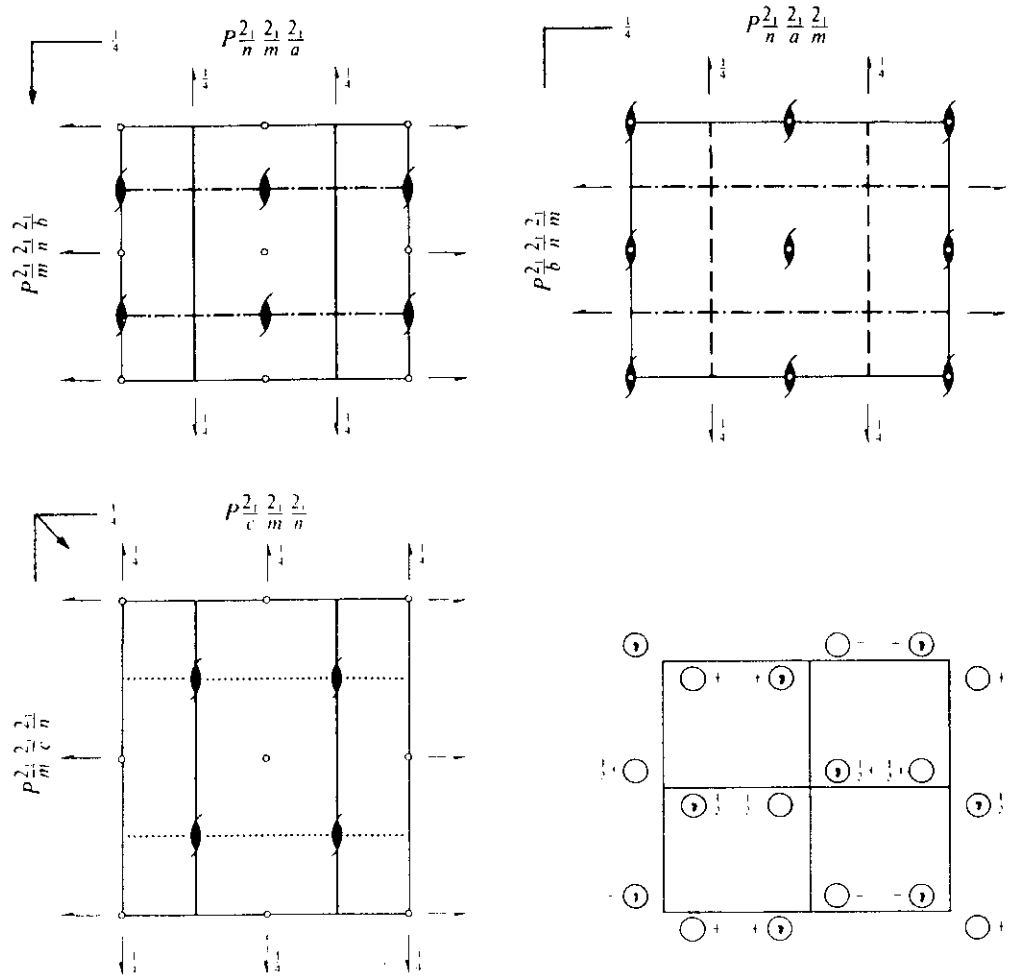
Minimal non-isomorphic supergroups

I [2]$P6_522$; [2]$P6_222$

II [3]$H3_221$ $(P3_212)$; [3]$R32$ (obverse); [3]$R32$ (reverse); [3]$P321$ $(3\boldsymbol{c}'=\boldsymbol{c})$

P n m a D_{2h}^{16} *m m m* Orthorhom

No. 62 $P\,2_1/n\,2_1/m\,2_1/a$ Patterson symmetry *P n*



Origin at $\bar{1}$ on $1\,2_1\,1$

Asymmetric unit $0 \le x \le \frac{1}{2}$; $0 \le y \le \frac{1}{4}$; $0 \le z \le 1$

Symmetry operations

(1) 1
(2) $2(0,0,\frac{1}{2})$ $\frac{1}{4},0,z$
(3) $2(0,\frac{1}{2},0)$ $0,y,0$
(4) $2(\frac{1}{2},0,0)$ $x,\frac{1}{4},\frac{1}{4}$
(5) $\bar{1}$ $0,0,0$
(6) a $x,y,\frac{1}{4}$
(7) m $x,\frac{1}{4},z$
(8) $n(0,\frac{1}{2},\frac{1}{2})$ $\frac{1}{4},y,z$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

Positions

Multiplicity, Wyckoff letter, Site symmetry		Coordinates				Reflection conditions
8 *d* 1	(1) x,y,z	(2) $\bar{x}+\frac{1}{2},\bar{y},z+\frac{1}{2}$	(3) $\bar{x},y+\frac{1}{2},\bar{z}$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}+\frac{1}{2}$		General:
	(5) $\bar{x},\bar{y},\bar{z}$	(6) $x+\frac{1}{2},y,\bar{z}+\frac{1}{2}$	(7) $x,\bar{y}+\frac{1}{2},z$	(8) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2}$		$0kl$: $k+l=2n$ $hk0$: $h=2n$ $h00$: $h=2n$ $0k0$: $k=2n$ $00l$: $l=2n$
						Special: as above, plus
4 *c* .*m*.	$x,\frac{1}{4},z$	$\bar{x}+\frac{1}{2},\frac{3}{4},z+\frac{1}{2}$	$\bar{x},\frac{3}{4},\bar{z}$	$x+\frac{1}{2},\frac{1}{4},\bar{z}+\frac{1}{2}$		no extra conditions
4 *b* $\bar{1}$	$0,0,\frac{1}{2}$	$\frac{1}{2},0,0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$		hkl : $h+l,k=2n$
4 *a* $\bar{1}$	$0,0,0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$		hkl : $h+l,k=2n$

Symmetry of special projections

Along [001] $p\,2g\,m$
$\boldsymbol{a}'=\frac{1}{2}\boldsymbol{a}$ $\boldsymbol{b}'=\boldsymbol{b}$
Origin at $0,0,z$

Along [100] $c\,2m\,m$
$\boldsymbol{a}'=\boldsymbol{b}$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,\frac{1}{4},\frac{1}{4}$

Along [010] $p\,2g\,g$
$\boldsymbol{a}'=\boldsymbol{c}$ $\boldsymbol{b}'=\boldsymbol{a}$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I
[2]$P\,2_1\,2_1\,2_1$ 1; 2; 3; 4
[2]$P\,1\,1\,2_1/a$ ($P\,2_1/c$) 1; 2; 5; 6
[2]$P\,1\,2_1/m\,1$ ($P\,2_1/m$) 1; 3; 5; 7
[2]$P\,2_1/n\,1\,1$ ($P\,2_1/c$) 1; 4; 5; 8
[2]$P\,n\,m\,2_1$ ($P\,m\,n\,2_1$) 1; 2; 7; 8
[2]$P\,n\,2_1\,a$ ($P\,n\,a\,2_1$) 1; 3; 6; 8
[2]$P\,2_1\,m\,a$ ($P\,m\,c\,2_1$) 1; 4; 6; 7

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc [3]$P\,n\,m\,a$ ($\boldsymbol{a}'=3\boldsymbol{a}$); [3]$P\,n\,m\,a$ ($\boldsymbol{b}'=3\boldsymbol{b}$); [3]$P\,n\,m\,a$ ($\boldsymbol{c}'=3\boldsymbol{c}$)

Minimal non-isomorphic supergroups

I none

II [2]$A\,m\,m\,a$($C\,m\,c\,m$); [2]$B\,b\,m\,m$($C\,m\,c\,m$); [2]$C\,c\,m\,b$($C\,m\,c\,a$); [2]$I\,m\,m\,a$; [2]$P\,n\,m\,m$($2\boldsymbol{a}'=\boldsymbol{a}$)($P\,m\,m\,n$); [2]$P\,c\,m\,a$($2\boldsymbol{b}'=\boldsymbol{b}$)($P\,b\,a\,m$); [2]$P\,b\,m\,a$($2\boldsymbol{c}'=\boldsymbol{c}$)($P\,b\,c\,m$)

deviation from isotropy is small or the anisotropic coefficients B_{ij} are physically unrealistic. A suitable parameter, which is invariant to rotation about the Cartesian axes used in defining $\mathbf{B}$, is

$$\langle u^2\rangle_{\text{all directions}} = \tfrac{1}{3}\,\text{trace}\,\mathbf{B} = \tfrac{1}{3}(B_{11}+B_{22}+B_{33}).$$

If the crystal structure refinement yields the matrix $\boldsymbol{\beta}$, but not $\mathbf{B}$, the expression

$$\langle u^2\rangle_{\text{all directions}} = \tfrac{1}{3}(2\pi^2)^{-1}\,\text{trace}\,\boldsymbol{\beta}\mathbf{g} = \tfrac{1}{3}(2\pi^2)^{-1}\sum_i\sum_j \beta_{ij}(\mathbf{a}_i\cdot\mathbf{a}_j)$$

may be employed instead, where $\mathbf{g}$ is a 3×3 matrix representing the 'metric tensor' whose elements are the scalar products $\mathbf{a}_i\cdot\mathbf{a}_j$ of the base vectors in real space.

Alternatively, we may require the $\boldsymbol{\beta}$-matrix corresponding to the single parameter $\langle u^2\rangle_{\text{all directions}}$. Such a matrix may serve, for instance, as a starting point for an anisotropic structure refinement. It is given by

$$\boldsymbol{\beta} = 2\pi^2\mathbf{g}^{-1}\langle u^2\rangle_{\text{all directions}}.$$

For orthogonal crystal-axis systems, $\mathbf{a}_i\cdot\mathbf{a}_j$ is zero for $i \neq j$ and the matrix representing the metric tensor is of diagonal form

$$\mathbf{g} = \begin{pmatrix} a_1^2 & 0 & 0 \\ 0 & a_2^2 & 0 \\ 0 & 0 & a_3^2 \end{pmatrix}.$$

The reciprocal matrix is then

$$\mathbf{g}^{-1} = \begin{pmatrix} 1/a_1^2 & 0 & 0 \\ 0 & 1/a_2^2 & 0 \\ 0 & 0 & 1/a_3^2 \end{pmatrix} = \begin{pmatrix} b_1^2 & 0 & 0 \\ 0 & b_2^2 & 0 \\ 0 & 0 & b_3^2 \end{pmatrix}.$$

Thus the elements of $\mathbf{g}^{-1}$ are given by the scalar products $\mathbf{b}_i\cdot\mathbf{b}_j$ of the base vectors in reciprocal space. For oblique-axis systems $\mathbf{g}$ and $\mathbf{g}^{-1}$ have off-diagonal elements, but it is still true that these elements are $\mathbf{a}_i\cdot\mathbf{a}_j$ for the $\mathbf{g}$ matrix and $\mathbf{b}_i\cdot\mathbf{b}_j$ for $\mathbf{g}^{-1}$.

4.4.5. *Symmetry restrictions on the anisotropic temperature factor*

In the general case, there are six anisotropic temperature-factor coefficients β_{ij} per atom and these define the major axes and the orientation of the thermal vibration ellipsoid. For an atom in a site of special symmetry, the

number of independent coefficients can fall from 6 to 4, 3, 2 or 1. To investigate the effect of symmetry it is necessary to formulate mathematically the requirement that the $\boldsymbol{\beta}$-matrix is invariant under all relevant symmetry operations. Translations and inversions are without effect on the general form of $\boldsymbol{\beta}$ because they do not alter the orientation of the thermal ellipsoid. Mirror planes and glide planes, therefore, have the same effect as a two-fold axis lying along the normals to the planes; screw axes and inversion axes of higher order than two produce an effect equivalent to the corresponding rotation axes. Thus it is only necessary to examine the influence of the rotation axes 2, 3, 4 and 6.

The discussion now follows the same lines as for the symmetry restrictions on the force-constant matrices (see section 3.2). We represent the symmetry operation by an orthogonal 3×3 matrix $\mathbf{P}$ and apply the equation

$$\mathbf{P}^{\mathrm{T}}\boldsymbol{\beta}\mathbf{P} = \boldsymbol{\beta}, \tag{4.75}$$

which expresses the invariance of the matrix $\boldsymbol{\beta}$ to the symmetry operation $\mathbf{P}$ (p. 251). Equation (4.75) assumes that the $\boldsymbol{\beta}$-matrix is referred to a Cartesian axis system; for oblique crystal-axis systems the $\mathbf{B}$-matrix must be used in place of $\boldsymbol{\beta}$. Thus the general form of (4.75) for any axis system becomes, with the aid of the relation (4.68),

$$\mathbf{P}^{\mathrm{T}}\mathbf{F}^{\mathrm{T}}\boldsymbol{\beta}\mathbf{F}\mathbf{P} = \boldsymbol{\beta}, \tag{4.76}$$

where $\mathbf{F}$ is the Cartesian transformation matrix defined in (4.69).

As a simple example, consider the matrix

$$\mathbf{P} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

representing a two-fold axis of symmetry along the y direction. Assuming an orthogonal crystal-axis system, (4.75) gives $\beta_{12} = -\beta_{12}$ and $\beta_{23} = -\beta_{23}$; i.e. $\beta_{12} = \beta_{23} = 0$ and so only four independent β_{ij} coefficients remain.

In this way it is possible to build up systematically the β_{ij} restrictions for atomic sites representing all the thirty-two point groups. It is found (Peterse and Palm 1966) that eighteen cases of β_{ij} restrictions occur. These are listed in table 4.1 in which the six entries on one line represent β_{11}, β_{22}, β_{33}, $2\beta_{12}$, $2\beta_{13}$, $2\beta_{23}$. A blank entry indicates an unrestricted coefficient; identical coefficients are represented by symbols A or B occurring more than once on the same line. Thus case number 4 gives three unrestricted coefficients β_{11}, β_{22}, β_{33}, and three zero off-diagonal coefficients β_{12}, β_{13}, β_{23}; this corresponds to the point group 222 for which the directions of the principal axes of the thermal ellipsoid are fixed by the three two-fold axes. The thermal ellipsoid degenerates into a sphere for the cubic point groups represented by case number 17 in table 4.1.

Table 4.1 *The eighteen β_{ij} restrictions for the first atom of an equivalent set given in Volume* 1 *of International Tables* (After Peterse and Palm 1966)

Case number	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
1				0		0
2					0	0
3				0	0	
4				0	0	0
5	A	A			0	0
6	A	A			B	B
7	A	A			B	$-B$
8	A	A		0	0	0
9		A	A	0	0	
10		A	A	B	B	
11		A	A	$-B$	B	
12		A	A	0	0	0
13		A		A		0
14		A		A	0	0
15		A		A	B	$2B$
16	A	A		A	0	0
17	A	A	A	0	0	0
18	A	A	A	B	B	B

Peterse and Palm have compiled a second table, table 4.2, which is used in conjunction with table 4.1 to yield the β_{ij} restrictions for all the special positions listed in the *International Tables of X-ray Crystallography*, Volume 1 (1952). The columns in table 4.2 refer to the 230 space groups, and the rows to the symbols *a*, *b*, *c*, ... used in the *International Tables* to denote special positions of any space group. All monoclinic space groups are entered twice: the first entry is for a unique *c*-axis, and the second entry for a unique *b*-axis. Rhombohedral space groups also occur twice: first with a rhombohedral unit cell and then with the alternative choice of a hexagonal cell. For the tetragonal and cubic space groups the centre of symmetry, if present, coincides with the origin of the unit cell. The nature of the β_{ij} restrictions for the *first* atomic coordinates in an equivalent set in the *International Tables* is given by the appropriate numerical index in table 4.2 which refers to one of the eighteen cases listed in table 4.1.

For each space group the *International Tables* give the symmetry restrictions on the fractional coordinates *xyz* of all atoms in special positions. If used in conjunction with tables 4.1 and 4.2 of Peterse and Palm, the *International Tables* also give the symmetry restrictions on the β_{ij} coefficients. This information is required for many structure-factor refinement programs.

Peterse and Palm consider only the *first* atom of each equivalent set of special positions listed under each space group of the *International Tables*.

Table 4.2 *The β_{ij} restrictions for all space groups and for every special position: to be used in conjunction with table* 4.1 (After Peterse and Palm 1966)

Space group	Special position														
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	*m*	*n*	*o*
1															
2															
3	2	2	2	2											
3	1	1	1	1											
4															
4															
5	2	2													
5	1	1													
6	2	2													
6	1	1													
7															
7															
8	2														
8	1														
9															
9															
10	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
10	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
11					2										
11					1										
12	2	2	2	2			2	2	2						
12	1	1	1	1			1	1	1						
13					2	2									
13					1	1									
14															
14															
15					2										
15					1										
16	4	4	4	4	4	4	4	4	3	3	3	3	1	1	1
	p	*q*	*r*	*s*	*t*										
	1	2	2	2	2										
17	3	3	1	1											
18	2	2													
19															
20	3	1													
21	4	4	4	4	3	3	1	1	2	2	2				
22	4	4	4	4	3	1	2	2	1	3					
23	4	4	4	4	3	3	1	1	2	2					
24	3	1	2												
25	4	4	4	4	1	1	3	3							
26	3	3													
27	2	2	2	2											
28	2	2	3												
29															
30	2	2													
31	3														
32	2	2													

Table 4.2 (*cont.*)

Space group	Special position														
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	*m*	*n*	*o*
33															
34	2	2													
35	4	4	2	1	3										
36	3														
37	2	2	2												
38	4	4	1	3	3										
39	2	2	1												
40	2	3													
41	2														
42	4	2	3	1											
43	2														
44	4	4	1	3											
45	2	2													
46	2	3													
47	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
	p	*q*	*r*	*s*	*t*	*u*	*v*	*w*	*x*	*y*	*z*				
	4	4	4	4	4	3	3	1	1	2	2				
48	4	4	4	4			3	3	1	1	2	2			
49	2	2	2	2	4	4	4	4	3	3	1	1	2	2	2
	p	*q*													
	2	2													
50	4	4	4	4			3	3	1	1	2	2			
51	1	1	1	1	4	4	1	1	1	1	3				
52			2	3											
53	3	3	3	3	3	3	1	3							
54			1	2	2										
55	2	2	2	2	2	2	2	2							
56			2	2											
57			3	2											
58	2	2	2	2	2	2	2								
59	4	4			3	1									
60			1												
61															
62			1												
63	3	3	4		3	3	2								
64	3	3		3	1	3									
65	4	4	4	4	2	2	4	4	4	4	4	4	2	3	1
	p	*q*													
	2	2													
66	4	4	2	2	2	2	3	1	2	2	2	2			
67	4	4	3	3	1	1	4	3	3	1	1	2	3	1	
68	4	4			3	1	2	2							
69	4	4	3	1	2	4	4	4	4	2	1	3	3	1	2
70	4	4			3	1	2								
71	4	4	4	4	4	4	4	4	4	4		3	1	2	
72	4	4	2	2		3	1	2	2	2					
73			3	1	2										
74	3	3	1	1	4	3	1	3	1						
75	8	8	2												
76															

Table 4.2 (*cont.*)

Space group	Special position														
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	*m*	*n*	*o*
77	2	2	2												
78															
79	8	2													
80															
81	8	8	8	8	2	2	2								
82	8	8	8	8	2	2									
83	8	8	8	8	2	2	8	8	2	2	2				
84	2	2	2	2	8	8	2	2	2	2					
85	8	8	8			2									
86	8	8			2	2									
87	8	8	2	8	8		2	2							
88	8	8			2										
89	8	8	8	8	4	4	8	8	2	7	7	3	3	3	3
90	5	5	8	2	7	7									
91	1	1	7												
92	7														
93	4	4	4	4	5	5	2	2	2	3	3	3	3	7	7
94	5	5	2	2	7	7									
95	1	1	7												
96	7														
97	8	8	4	5	8	2	7	3	3	7					
98	5	5	2	7	6	3									
99	8	8	4	6	1	1									
100	8	5	6												
101	5	5	2	6											
102	5	2	6												
103	8	8	2												
104	8	2													
105	4	4	4	1	1										
106	2	2													
107	8	4	6	1											
108	8	5	6												
109	4	3													
110	2														
111	8	8	8	8	4	4	5	5	3	3	3	3	2	6	
112	4	4	4	4	8	8	3	1	3	1	2	2	2		
113	8	8	5	2	6										
114	8	8	2	2											
115	8	8	8	8	4	4	4	7	7	1	1				
116	5	5	8	8	7	7	2	2	2						
117	8	8	5	5	2	2	7	7							
118	8	8	5	5	2	6	7	2							
119	8	8	8	8	4	4	7	7	1						
120	5	8	8	5	7	2	2	7							
121	8	8	4	8	5	3	3	2	6						
122	8	8	2	3											
123	8	8	8	8	4	4	8	8	4	5	5	4	4	4	4
	p	*q*	*r*	*s*	*t*										
	2	2	6	1	1										
124	8	8	8	8	2	4	8	8	2	7	3	3	2		

Table 4.2 (*cont.*)

Space group	Special position														
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	*m*	*n*	*o*
125	8	8	8	8	7	7	8	5	7	7	3	3	7		
126	8	8	4	8	8		2	7	3	3					
127	8	8	5	5	8	5	5	5	2	2	6				
128	8	8	2	5	8	2	7	2							
129	8	8	8	6	6	4	6	6	3	6					
130	5	8	8		2	6									
131	4	4	4	4	8	8	4	4	4	4	4	4	4	7	3
	p	*q*													
	3	2													
132	5	8	5	8	4	2	5	5	5	5	2	3	3	2	6
133	4	4	5	8		2	2	3	3	7					
134	8	8	4	5	7	7	5	2	3	3	7	7	7		
135	2	8	2	5	2	2	7	2							
136	5	5	2	8	5	5	5	2	2	6					
137	8	8	4	4		6	3								
138	5	8	6	6	5	2	6	6	6						
139	8	8	4	8	8	6	4	5	4	4	7	2	6	3	
140	8	8	8	5	7	8	5	5	7	3	2	6			
141	8	8	3	3	4	3	7	3							
142	8	5		2	3	7									
143	16	16	16												
144															
145															
146	18														
146	16														
147	16	16	16	16											
148	18	18	18												
148	16	16	16												
149	16	16	16	16	16	16	16	16	16	6	6				
150	16	16	16	16	15	15									
151	6	6													
152	15	15													
153	6	6													
154	15	15													
155	18	18	18	10	10										
155	16	16	16	15	15										
156	16	16	16	7											
157	16	16	13												
158	16	16	16												
159	16	16													
160	18	6													
160	16	7													
161	18														
161	16														
162	16	16	16	16	16	13	13	16	6	6	13				
163	16	16	16	16	16	16		6							
164	16	16	16	16	15	15	15	15	7						
165	16	16	16	16		15									
166	18	18	18	10	10	6	6	6							
166	16	16	16	15	15	15	15	7							

Table 4.2 (*cont.*)

Space group	Special position														
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	*m*	*n*	*o*
167	18	18	18		6										
167	16	16	16		15										
168	16	16	2												
169															
170															
171	2	2													
172	2	2													
173	16	16													
174	16	16	16	16	16	16	16	16	16	2	2				
175	16	16	16	16	16	2	2	16	2	2	2				
176	16	16	16	16	16	16		2							
177	16	16	16	16	16	14	14	16	2	15	15	6	6		
178	15	13													
179	15	13													
180	14	14	14	14	2	2	15	15	13	13					
181	14	14	14	14	2	2	15	15	13	13					
182	16	16	16	16	16	16	15	13							
183	16	16	14	13	7										
184	16	16	2												
185	16	16	13												
186	16	16	7												
187	16	16	16	16	16	16	16	16	16	5	5	2	2	7	
188	16	16	16	16	16	16	16	16	16	6	2				
189	16	16	16	16	16	14	14	16	13	2	2				
190	16	16	16	16	16	16	15	2							
191	16	16	16	16	16	14	14	16	14	14	14	14	14	13	15
	p	*q*													
	2	2													
192	16	16	16	16	16	14	2	16	2	15	13	2			
193	16	16	16	16	16	13	14	16	13	2	13				
194	16	16	16	16	16	16	15	14	15	2	15				
195	17	17	4	4	18	3	3	3	3						
196	17	17	17	17	18	3	3								
197	17	4	18	3	3										
198	18														
199	18	3													
200	17	17	4	4	4	4	4	4	18	3	3				
201	17	18	18	4	18	3	3								
202	17	17	17	3	4	18	3	3							
203	17	17	18	18	18	3									
204	17	4	18	4	4	18	3								
205	18	18	18												
206	18	18	18	3											
207	17	17	12	12	12	12	18	3	11	11					
208	17	18	18	4	9	9	18	3	3	3	10	11			
209	17	17	17	9	12	18	11	11	3						
210	17	17	18	18	18	3	10								
211	17	12	18	9	12	18	3	11	10						
212	18	18	18	10											
213	18	18	18	11											

Table 4.2 (*cont.*)

Space group	Special position													
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	*m*	*n*	*o*
214	18	18	9	9	18	3	11	10							
215	17	17	12	12	18	9	9	3	6						
216	17	17	17	17	18	9	9	6							
217	17	12	18	12	9	3	6								
218	17	4	12	12	18	3	3	3							
219	17	17	12	12	18	3	3								
220	12	12	18	3											
221	17	17	12	12	12	12	18	4	9	9	3	3	6		
222	17	12	18	12	12	18	3	11							
223	17	4	12	12	18	4	4	4	18	11	3				
224	17	18	18	12	18	9	9	3	10	11	6				
225	17	17	17	9	12	18	9	9	9	3	6				
226	17	17	12	12	4	12	18	11	3						
227	17	17	18	18	9	6	10								
228	17	18	18	12	18	3	10								
229	17	12	18	12	12	18	4	9	10	3	6				
230	18	18	9	12	18	3	10								

In using most refinement programs, it is sufficient to know the β_{ij} restrictions for one atom only of a symmetry-related set. This is because symmetry operations in the program are usually applied to the Miller indices rather than to the atomic coordinates. The determination of the symmetry relations among the β_{ij}s of a symmetry-related set are discussed by Trueblood (1956) and in the book of Lipson and Cochran (1966). They are derived in the same way as the symmetry restrictions for an individual member of the set.

4.4.6. *An example: sodium nitrate*

To illustrate the concept of the ellipsoid of thermal vibration, we refer to some recent neutron diffraction measurements on a crystal of sodium nitrate (Paul and Pryor 1972).

The structure of sodium nitrate, which is closely related to the cubic rock-salt structure, may be envisaged as follows. Suppose the cubic cell of NaCl, set up with a three-fold axis vertical, is compressed along this axis until the edges make an angle of 102° 42′ with each other, to give a face-centred rhombohedral cell. Each chlorine atom is then replaced by a nitrate group consisting of a central nitrogen atom with three oxygen atoms around it at the corners of an equilateral triangle. The three oxygens are 2.11 Å apart, and the whole group lies in a plane at right angles to the

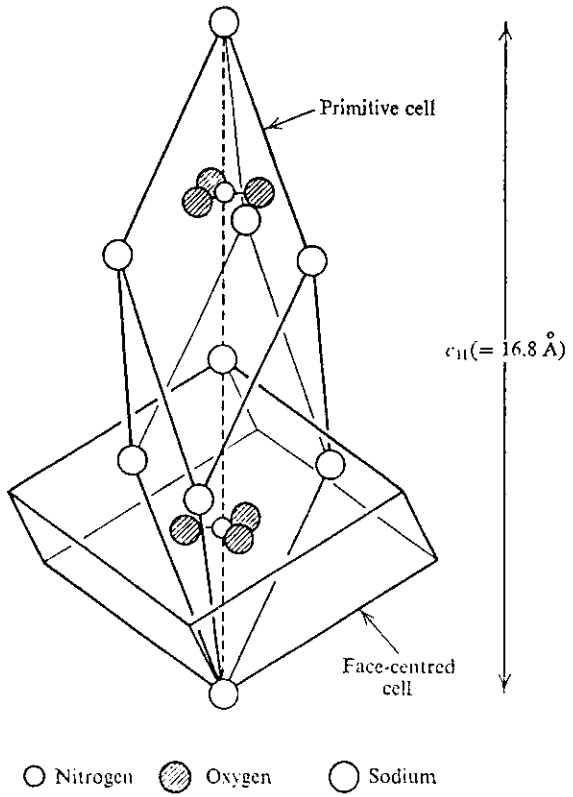


Fig. 4.5. Structure of sodium nitrate showing primitive rhombohedral cell and face-centred rhombohedral cell. Three-fold axis shown as broken line.

three-fold axis. The rhombohedral cell contains four $NaNO_3$ units, corresponding to the four NaCl units in the rock-salt structure.

However, this is not the primitive rhombohedral cell. The primitive cell (figure 4.5) contains two $NaNO_3$ units, with sodium ions at the corners and centre of the cell and two nitrate groups, inversely related to each other, on the central three-fold axis. Table 4.3 gives the cell edge and rhombohedral angle for this primitive unit cell (denoted a_R and α_R respectively) and for the face-centred cell (denoted a'_R and α'_R). a_H and c_H in table 4.3 refer to the dimensions of the hexagonal cell which corresponds to the primitive rhombohedral cell. The atomic positions in $NaNO_3$ are special positions in the space group *R3c* (number 167 of *International Tables*), and are described in the Tables in terms of either the primitive rhombohedral cell (first setting) or the corresponding hexagonal cell (second setting).