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Standardized Description of Crystal Structures

By *Dieter Schwarzenbach* (Zürich)

Abstract

A set of rules that depend only on symmetry, axial ratios and atomic coordinates is here proposed for the description of crystal structures. These rules lead to a standard description of crystal structures belonging to the same structure type. A definition of the structure type is given. The space groups isomorphous to mmm , $mm2$, 222 and $2/m$ have been analysed. An example demonstrating how the rules can be applied is discussed.

Introduction

Structures of the same "structure type" have sometimes been described so differently that neither the authors nor abstracting bodies noticed their similarity with respect to structure-type considerations. For example, the structure of Fe_3C was symbolized in *Strukturbericht* (II, p. 33, 302) as DO_{11} -type and $NiAl_3$ as DO_{20} -type (V, p. 8; 60).

This case and others were noticed by LAVES (1955) in the course of an attempt to symbolize structure types on a more geometrical basis, taking into account connection types and coordination numbers. However, it is certain that many other cases have not yet been recognized and anybody who determines a new structure may have difficulties in finding if it belongs to a new or to an already known structure type.

To remedy this situation, the American Society for Testing Materials has recently proposed (ASTM, 1961; FINK and WYMANN, 1961) new rules for structure-type symbolization which remove much of the arbitrariness of the older *Strukturbericht* symbolism.

In this context the following question arises: Is it possible to standardize structure description in such a way that those who follow such standardization will immediately recognize if structures belong to the same type or not?

Although no completely satisfactory answer to this question has been found, it will be shown, that certain rules leading into unambiguous

descriptions in most cases can be defined. In the remaining cases, the ambiguity is essentially restricted. (All monoclinic and orthorhombic types listed in SMITHELL's Reference book have been investigated.) Thus the rules are considered to be at least better than nothing. For example, as shown at the end of this paper, the Fe_3C and NiAl_3 structures are immediately recognized as belonging to the same structure type, when they are described following the rules.

If structure types were listed according to the ASTM proposal with corresponding descriptions based on the rules presented here it would be easy to check if a new structure should be considered as belonging to a new type or not.

The rules

In order to describe crystal structures of the same structure type in the same way, rules that allow one to describe structures unambiguously with regard to choice of axes and origin of coordinates are needed. Such rules should depend only on conditions of symmetry, axial ratios and atomic coordinates, since these are exactly defined properties of a structure, in contrast to the coordination around a particle or to prominent directions. A set of rules covering all space groups of the classes mmm , $\text{mm}2$, 222 and $2/m$ is presented in this paper.

Choice of axes

Only right-handed coordinate systems are considered. In the orthorhombic space groups the axes should be chosen in such a way that the space group has the same symbol as in "International Tables for X-ray Crystallography" (1952). If the choice of axes is not thus defined, then the axes should be chosen such that $a < b$, or, if that is not sufficient, $a < b < c$.

In the monoclinic systems the unique axis should be chosen as \vec{c} . For the rest the procedure is principally the same as in the orthorhombic system. The axes \vec{a} and \vec{b} have to be two of the three shortest vectors perpendicular to \vec{c} . The two-dimensional cell defined by \vec{a} and \vec{b} will be reduced, half reduced or quarter reduced¹⁾, depending on the direction marked out by the glide component or by the projection of the centred net-plane.

¹⁾ AZAROFF, L. V. and BUEGER, M. J. (1958): The Powder Method, p. 126.

Choice of the origin of coordinates

In the space groups isomorphous to mmm and $2/m$, the origin of coordinates should lie in a centre of symmetry; in centred groups, it should be one of the positions $(000, 1/2\ 0\ 0, 0\ 1/2\ 0, 0\ 0\ 1/2) + (000, 1/2\ 1/2\ 1/2)$ as in "International Tables". In the class 222 the same origin should be chosen as in "International Tables".

There are always eight such origins that may be partly translation-equivalent in multiple cells.

In the class $mm2$ the origin should lie on a twofold axis or screw axis (this applies also to group $Pmn2_1^{(2)}$), in centred groups on one of the axes $(00z), (1/2\ 0\ z), (0\ 1/2\ z), (1/2\ 1/2\ z)$. In this class, there are four such axes that may be translation-equivalent.

The "special-origin" of a set of equivalent points is defined as follows:

The "special origin" is one of the origins defined above. If the "special origin" is used as the origin of coordinates, one point of the set of equivalent points will have the coordinates $0 \leq x, y, z \leq 1/4$ so that the whole set may be defined by these coordinates, which may be called minimal positive coordinates. In class $mm2$ one point of the set will have coordinates $0 \leq x, y \leq 1/4$; if for this point z is chosen as zero, then the height of the "special origin" in the \vec{c} -direction is fixed for the set of equivalent points.

The number of translation-nonequivalent "special origins" of a set of equivalent points is shown in table 1.

Table 1. Number of translation-nonequivalent "special origins" of a set of equivalent points

mmm and 222	$mm2$ and $2/m$
$N = \frac{z}{2^{3-n}}$	$N = \frac{z}{2^{2-n}}$
P-lattices	P-lattices
$N = \frac{z}{2^{4-n}}$	$N = \frac{z}{2^{3-n}}$
C- and I-lattices	C-, I-, A-, and (for $2/m$) B-lattices
$N = \frac{z}{2^{5-n}}$	$N = \frac{z}{2^{4-n}}$
F mmm and F 222	F $mm2$
N = number of "special origins"	n = number of special atomic coordinates $0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$
z = multiplicity of the set	

²⁾ "International Tables" adopts the origin at mm for this space group.

The formulas of table 1 do not apply to the groups $Fddd$ and $Fdd2$, which cannot be dealt with in the same way as the other groups isomorphous to mmm and $mm2$. In $Fddd$ it does not even seem desirable to put the origin of coordinates at a centre of symmetry. Instead, the origin of the first setting of "International Tables" is preferred, i.e. origin at 222. There result rather complicated rules that in certain cases allow the two possible translation-nonequivalent origins to be distinguished. They will not be discussed here (a more extensive paper is in preparation to be published in *Z. Kristallogr.*).

In groups isomorphous to $2/m$ one may choose the monoclinic angle γ greater or smaller than 90° , corresponding to a choice of axes $(\vec{a} \vec{b} \vec{c})$ or $(-\vec{a} \vec{b} -\vec{c})$. Only in one of these coordinate systems can a given set of equivalent points be described in the above way by minimal parameters $0 \leq x, y, z \leq 1/4$, i.e. the "special origin" require and selects one of them.

In 222, the sets of highest multiplicity are not bound to have a "special origin" ($N=1/2$). Nevertheless there is always one origin that allows a set to be defined with coordinates $0 \leq x, y \leq 1/4, 0 \leq z < 1/2$ and this is the one to be chosen.

The origin of coordinates for the description of a crystal structure should be a "special origin" of at least one set of equivalent points. But as two sets in a structure seldom have the same "special origin", the sets have to be distinguished in the following manner:

a) By the point symmetry of the sets. Table 2 shows what sets in a structure may define the origin.

b) Sets with the same point symmetry should be distinguished by the value of their minimal positive coordinates, i.e. the coordinates they receive when they are described with their "special origin".

The "special origin" of that set of points that possesses the largest x -coordinate should be used as origin. In the case that x is invariant, the rule applies to y , and so on. Sets with the same point symmetry but different coordinates fixed by this symmetry (invariant coordinates) can be distinguished by these.

For sets in 222 and $2/m$ there exist special possibilities of discrimination.

Special rule for $mm2$: if one transforms an axial cross $(\vec{a} \vec{b} \vec{c})$ to $(-\vec{a} \vec{b} -\vec{c})$, a different description results: the coordinates $x y z$ are transformed to $x y \bar{z}$. The description having more sets with $0 \leq z \leq 1/2$ should be chosen.

Table 2. *Sequence of the sets of equivalent points, whose "special origins" may define the origin for the description of a crystal structure*

Class mmm

mmm > mm > m > 1 > two mm > two m > two 1 > three mm >
> three m > three 1 > 2/m > 222 > 2 > two mmm > four mm > etc.
After "2" the sequence begins anew. $\bar{1}$ will never define an origin.

Class mm2

mm > m > 1 > two m > two 1 > three m > three 1 >
> 2 > two mm > four m > etc.

Class 222

222 > 2 > 1 > two 2 > two 1 > three 2 > three 1 >
> two 222 > etc.

Sets with symmetry 1 defining the origin shall get coordinates $0 \leq x, y \leq 1/4, 0 \leq z < 1/2$.

Class 2/m

m > 1 > 2/m > 2 > two m > two 1 > two 2/m > two 2 >
> > four 2 > $\bar{1}$ > five m > etc.

After the choice of axes and the origin have been fixed, it is necessary to define the one point that will symbolize a set of equivalent points:

The coordinates of all sets should be given as positive. Generally a set should be defined in the same way as in "International Tables", i.e. with the combination of coordinates of the first point of a set in the Tables. If this rule does not define a single point, then the point with the minimal x or, if there are several ones, the point with the minimal x and y, etc. shall symbolize the set. In case that x is invariant, the same sequence begins with y.

The aim of the standardized description is that the similarity of structures of the same structure type may be clear directly from their description. The concept of a structure type is poorly defined, and in order to reach a standardized description by the above rules, a rather narrow definition is necessary. Structures of the same type have to fulfil the following conditions:

1. the same space group;
2. the same number of sets of equivalent points with the same point symmetry;
3. the same relative position of the "special origins" of the sets of equivalent points.

It is evident that these conditions restrict the concept of the structure type to the closest similarities between structures. On the other hand, they exclude the personal opinion of the individual scientist.

The following difficulties may arise:

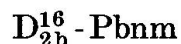
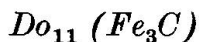
- a) Changes in the axial ratios in structures of the same type. If two axes in a structure have nearly the same length, it may be that in another structure of the same type the longer axis becomes the shorter one and vice versa, so that a different description could result. The occurrence of this case is improbable when the lengths of the two axes differ by more than approximately 5%.
- b) Variation in the value of the atomic coordinates. If two coordinates have nearly the same value, the possibility exists that in another structure of the same type the bigger coordinate becomes the smaller one and vice versa, so that the distinction of two sets of points by the value of these coordinates may be problematic. The occurrence of this case is improbable when the values of the coordinates differ by more than approximately 0.05.

In a review of all monoclinic and orthorhombic types listed in SMITHELL's Reference book only one example of such an inversion of the values of coordinates has been found. The actual occurrence of the cases a) and b) is rather rare.

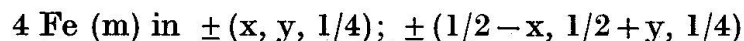
An attempt has been made to set up rules such that these difficulties can be taken into account. The sequence of sets in table 2 has been proposed with this aim in mind. In order to be on the safe side, one may have to take several descriptions into consideration, whereas the standardized description of a given structure is nearly always unique. From a consideration of the variation in axial ratios and atomic coordinates, which cover almost all structures of a given type, rules that standardize about 90% of all structures by one or two descriptions have been developed.

Application

Fe_3C has been described in the literature as Do_{11} -type, NiAl_3 as Do_{20} -type:



$$a = 4.51 \quad b = 5.08 \quad c = 6.73$$



$$\text{with } x = 0.833 \quad y = 0.040$$

8 Fe (1) in $\pm(x, y, z); \pm(x, y, 1/2 - z); \pm(1/2 - x, 1/2 + y, z);$
 $\pm(1/2 - x, 1/2 + y, 1/2 - z)$

with $x = 0.333 \quad y = 0.183 \quad z = 0.065$

4 C (m) as 4 Fe (m) with $x = 0.47 \quad y = 0.86$

Do₂₀ (NiAl₃)

D_{2h}¹⁶ - Pnma

$a = 6.60 \quad b = 7.35 \quad c = 4.80$

4 Ni (m) in $\pm(x, 1/4, z); \pm(1/2 + x, 1/4, 1/2 - z);$

with $x = -0.131 \quad z = -0.055$

4 Al (m) as 4 Ni (m) with $x = 0.011 \quad z = 0.415$

8 Al (1) in $\pm(x, y, z); \pm(1/2 + x, 1/2 - y, 1/2 - z);$

$\pm(x, 1/2 - y, z); \pm(1/2 + x, y, 1/2 - z)$

with $x = 0.174 \quad y = 0.053 \quad z = 0.856$

According to the rules discussed the axes must be chosen in such a way that *D_{2h}¹⁶* gets the symbol Pnma. This choice is unique. The "special origin" of the set of symmetry 1 defines the origin. The new description shows that the *Do₁₁*-type equals the *Do₂₀*-type:

Do₁₁ (Fe₃C)

D_{2h}¹⁶ - Pnma

$a = 5.08 \quad b = 6.73 \quad c = 4.51$

$a : b : c = 0.755 : 1 : 0.670$

4 C (m) in $\pm(x, 1/4, z); \pm(1/2 + x, 1/4, 1/2 - z)$

with $x = 0.36 \quad z = 0.47$

4 Fe (m) as 4 C (m) with $x = 0.040 \quad z = 0.667$

8 Fe (1) in $\pm(x, y, z); \pm(1/2 + x, 1/2 - y, 1/2 - z);$

$\pm(x, 1/2 - y, z); \pm(1/2 + x, y, 1/2 - z)$

with $x = 0.183 \quad y = 0.065 \quad z = 0.167$

Do₂₀ (NiAl₃)

D_{2h}¹⁶ - Pnma

$a = 6.60 \quad b = 7.35 \quad c = 4.80$

$a : b : c = 0.898 : 1 : 0.654$

4 Ni (m) as above with $x = 0.369 \quad z = 0.445$

4 Al (m) as above with $x = 0.011 \quad z = 0.585$

8 Al (1) as above with $x = 0.174 \quad y = 0.053 \quad z = 0.144$

I wish to thank Prof. F. Laves for suggesting this problem and for his valuable comments and advice. My thanks are also due to Prof. J. D. Dunitz for many helpful discussions and for reading the manuscript.

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