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The tricks of the chameleon. Unexpected Symmetry of the Diffraction Pattern

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Abstract

The first step in the structure solution process is the determination of candidate space groups on the basis of the symmetry of the diffraction pattern, in particular through the analysis of the reflection conditions. Sometimes it may happen that the diffraction pattern is indexed in an alternative setting of the space group, in which the reflection conditions appear different. The discrepancy between the observed reflection conditions and those published in the standard setting of space groups may lead the investigator to erroneously assume his sample is less symmetric than it actually is. After discussing a case from the literature where tetragonal samples were incorrectly described as orthorhombic due to an unusual indexing of the diffraction pattern, we present an example in which diffractions from a pyrite sample were indexed in the $Pb\bar{3}$ setting of the space group, instead of the standard $Pa\bar{3}$ setting, where the large set of strong violations of reflection conditions with respect to those of the standard setting could have been interpreted as a signature of symmetry lowering to $P2_13$. The structure being well-known, the real origin of the *apparent* violation

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of reflection conditions was easy to find. In a less straightforward case, in particular when dealing with a new, unknown structure, the investigator may be deceived along a wrong path.

1. Introduction

Space-group symmetry is conveniently and efficiently expressed via the Hermann-Mauguin symbols, from which both the nature and the orientation in space of symmetry elements is easily obtained. These symbols, as well as the matrix representation of the symmetry operations, depend on the basis vectors chosen by the user. The most convenient choice is called the *conventional basis*, in which the edges of the unit cell are parallel to symmetry directions of the Bravais lattice. The choice of the conventional basis is in general not unique but requires some additional conventions, like the labelling of the unique axis, when it exists, or choosing one of several possible settings for the orthorhombic groups. For example, the conventional basis of a tetragonal crystal has one basis vector along the four-fold (unique) axis and the two other in the plane perpendicular to it, at 90 degrees from each other: the choice to label **c** the basis vector along the unique axis rather than **a** or **b** is a matter convention and not a restriction due to symmetry. Similarly, choosing the basis vectors along the symmetry directions of the space-group type No. 62 leads to six different Hermann-Mauguin symbols. It has been once decided to assign the *Pnma* the status of “standard” setting, leaving its five siblings (*Pmnb*, *Pbnm*, *Pcmn*, *Pmcn* and *Pnam*) in darkness, although some occasionally do get in the spotlight. This is the case of *Pbnm*, which for historical reasons is the favourite setting in which the structure of the minerals of the olivine group is commonly reported.

The choice of a non-conventional basis is always possible and can be preferable in some cases, like in the study of phase transitions between polymorphs showing a group-subgroup relation, in the analysis of the relations between structure types, in the presence of a high degree of structural pseudo-symmetry, or in the case of twins, when the lattice

common to the twinned individuals (domains) requires a space-group description corresponding to an alternative setting 39

(a series of examples can be found in [1]). The Hermann-Mauguin symbol depends on the choice of the basis vectors 40

and reflects the setting of the space group; as a result, the number of possible settings, and therefore of the possible 41

Hermann-Mauguin symbols, even when restricting ourselves to simple and straightforward changes of basis, is much 42

larger than the number of space-group types. This variety of settings has been called a *crystallographic chameleon* [1], 43

by analogy with the skin colour change adopted by the animal as a function of the environment. 44

The metric of the unit cell adopted in an alternative setting may or may not correspond to the same crystal family; 45

accordingly, alternative settings are called *unconventional* or *non-standard* respectively. The Hermann-Mauguin 46

symbol of a space group in a non-standard setting may depart significantly from the corresponding standard symbol. 47

Also in the case of unconventional settings unusual symbols of space groups are often obtained, like $B2_1/e$ for $P2_1/c$, 48

which at first sight may puzzle the structural crystallographer. Even when the basis is conventional, the *International* 49

Tables for Crystallography present alternative settings of space groups for monoclinic and orthorhombic space groups. 50

For example, $C2/c$ becomes $I2/a$ by basis vector transformation $(\mathbf{a}, \mathbf{b}, \mathbf{c})_{I2/a} = (\mathbf{c}, \mathbf{b}, -\mathbf{a}-\mathbf{c})_{C2/c}$ (e.g. gypsum: [2]). An even 51

simpler case is that of orthorhombic groups mentioned above. The basis vector transformation from $Pnma$ to $Pbnm$ is 52

$(\mathbf{a}, \mathbf{b}, \mathbf{c})_{Pbnm} = (\mathbf{c}, \mathbf{a}, \mathbf{b})_{Pnma}$, the inverse transformation $(\mathbf{a}, \mathbf{b}, \mathbf{c})_{Pnma} = (\mathbf{b}, \mathbf{c}, \mathbf{a})_{Pbnm}$. Quite obviously, if the data collection is 53

obtained in the alternative setting, the structure cannot be solved in standard setting: either the Laue indices of the 54

reflections are transformed - i.e. $(hkl)_{Pnma} = (klh)_{Pbnm}$ - or the structure is solved in the alternative setting. 55

Higher-symmetry cases can be more tricky. A permutation of the basis vectors in a tetragonal crystal brings the unique 56

(fourfold axis) along the \mathbf{a} or \mathbf{b} basis vector, and this may be misleading for the less careful investigator. In the case of 57

cubic crystals, one may intuitively conclude that the permutation of basis vectors does not lead to any change of setting, 58
because by definitions the three directions corresponding to the cubic basis vectors are made equivalent by the three- 59
fold rotations along the body diagonals. However, the threefold rotation results in a cyclic permutation of the three axes, 60
whereas permutations of two axes only does not necessarily leave the setting of the space group invariant. In particular, 61
space groups of type No. 205 occur in two different settings, $Pa\bar{3}$ and $Pb\bar{3}$, something that is probably less commonly 62
known and may result in some confusion in the daily work of the structural crystallographer [3]. After a brief 63
explanation, we present two concrete examples, one from the literature and one from our own data collection, of how 64
overlooking the possibility of alternative settings may lead to unexpected problems. 65

2. Alternative descriptions of crystal structures in different space-group settings 66

The symmetry of a crystal structure is described by its space group, *i.e.* a group of isometries (distance-preserving 67
transformations) in the three-dimensional Euclidean space (E^3). A change of coordinate system from $Oabc$ to $O'a'b'c'$ 68
(O and O' being the origins in the two coordinate systems) leads to an alternative description of the crystal structure, in 69
which the fractional atomic coordinates are different from those of the original setting. If the matrix representation of 70
the symmetry operations in the two coordinate systems is the same, then the two alternative descriptions are *equivalent*. 71
The group formed by all the isometries of E^3 is known as the Euclidean group $\mathcal{E}(3)$; every space group is a subgroup of 72
 $\mathcal{E}(3)$. The Euclidean group is itself a subgroup of the affine group $\mathcal{A}(3)$, which is the group of all invertible affine 73
transformations, *i.e.* invertible transformations which preserve points, straight lines and planes, ratios of distances 74
between points lying on a straight line, as well as parallelism of lines, although not necessarily angles between lines or 75
distances between points. In crystallography, the affine group plays a role in case of metric specialisation, *i.e.* in case of 76
crystals whose cell parameters take special value or ratios beyond those imposed by the symmetry itself. 77

Let \mathcal{K} be a space group and \mathcal{G} a subgroup of it which is still a space group. \mathcal{K} can be decomposed in i cosets with respect 78

to \mathcal{G} , where i is the index of \mathcal{G} in \mathcal{K} , *i.e.* the ratio of the orders of \mathcal{K} and \mathcal{G} : 79

$$i = |\mathcal{K}| / |\mathcal{G}| \quad [4] \quad (1) \quad 80$$

The right coset decomposition is written as follows: 81

$$\mathcal{K} = \cup_{j=1, i} \mathcal{G} k_j, \quad k_1 = 1, \quad k_k \notin \mathcal{G} k_j, \quad \forall k < j \quad (2) \quad 82$$

which simply means that the first coset is the subgroup itself ($k_1 = 1$, thus $\mathcal{G} k_1 = \mathcal{G}$) and the operation k_k does not occur in 83

any of the previous cosets ($k < j$). The decomposition can also be obtained in terms of left cosets: 84

$$\mathcal{K} = \cup_{j=1, i} k_j \mathcal{G}, \quad k_1 = 1, \quad k_k \notin k_j \mathcal{G}, \quad \forall k < j. \quad (3) \quad 85$$

Depending on whether the two decompositions (2) and (3) are identical or not, the relation between \mathcal{K} and \mathcal{G} is different. 86

If the two decompositions (2) and (3) do not give the same result, then, in general, $k_k \mathcal{G} k_k^{-1} = \mathcal{G}'$. By taking all the i 87

operations k_k , $j = [1, i]$, where i is the index in Eq. (1), one gets a set of n subgroups ($2 \leq n \leq i$) $\mathcal{G}, \mathcal{G}', \mathcal{G}'' \dots$ which are 88

conjugated subgroups of \mathcal{K} . Conjugation is a similarity transformation and groups $\mathcal{G}, \mathcal{G}', \mathcal{G}'' \dots$ are all of the same type, 89

i.e. they have the same Hermann-Mauguin symbol when expressed in their conventional basis; at least some of their 90

symmetry elements, however, are differently oriented or located in space. 91

If the two decompositions (2) and (3) give the same result, then $k_k \mathcal{G} = \mathcal{G} k_k$ for any k_k . This result can be rewritten as $k_k \mathcal{G} k_k^{-1}$ 92

$= \mathcal{G}, \forall k_k$. \mathcal{G} is a normal (invariant, self-conjugate) subgroup of \mathcal{K} ; in symbols, $\mathcal{G} \triangleleft \mathcal{K}$. 93

If \mathcal{G} is not a normal subgroup of \mathcal{K} , then one can always find an intermediate group \mathcal{M} such that \mathcal{G} is a normal subgroup 94

of \mathcal{M} . \mathcal{M} is called the normalizer of \mathcal{G} with respect to \mathcal{K} and indicated as $\mathcal{N}_{\mathcal{K}}(\mathcal{G})$. It follows that $\mathcal{G} \triangleleft \mathcal{N}_{\mathcal{K}}(\mathcal{G}) \triangleleft \mathcal{K}$. We 95

consider the two cases $\mathcal{K} = \mathcal{A}(3)$ and $\mathcal{K} = \mathcal{E}(3)$. The normalizers $\mathcal{N}_{\mathcal{A}}(\mathcal{G})$ and $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$ are known as the *affine normalizer* 96

and the *Euclidean normalizer* of \mathcal{G} , respectively [5],[6]. The cosets of $\mathcal{N}_{\mathcal{E}}(\mathcal{G})$ with respect to \mathcal{G} give the alternative 97

descriptions of a crystal structure: alternative sets of fractional atomic coordinates in the same unit cell. The matrix 98

representation of the symmetry operations is unchanged under the action of $\mathcal{N}_E(\mathcal{G})$ or $\mathcal{N}_A(\mathcal{G})$ so that the Hermann- 99

Mauguin symbol of \mathcal{G} is not affected when the crystal structure description is modified by an operation of these 100

normalizers. 101

The structure of rock salt, space-group type $Fm\bar{3}m$, can be described with Na in position $4a$ (0,0,0) and Cl in position 102

$4b$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) or with Cl in position $4a$ and Na in position $4b$. The normalizer of the space group is $\mathcal{N}_E(Fm\bar{3}m) = Pm\bar{3}m$ 103

with basis vectors $\mathbf{a}/2$, $\mathbf{b}/2$, $\mathbf{c}/2$ with respect to those of $Fm\bar{3}m$; the coset decomposition gives two cosets, the group 104

$Fm\bar{3}m$ itself and a second coset $Fm\bar{3}m \cdot t(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Any of the operations in this coset, obviously including the additional 105

generator $t(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, map the Wyckoff position $4a$ of $Fm\bar{3}m$ onto the Wyckoff position $4b$ and vice versa. The only 106

degree of freedom in a cubic space group being the value of the single independent cell parameter, $\mathcal{N}_A(\mathcal{G}) = \mathcal{N}_E(\mathcal{G})$ for 107

cubic crystals. This explains why there are two alternative but equivalent descriptions of rock salt: they are related by 108

the operations of $\mathcal{N}_E(Fm\bar{3}m)$ which are not in $Fm\bar{3}m$. Because $Fm\bar{3}m$ is normal in $\mathcal{N}_E(Fm\bar{3}m)$, the two descriptions of the 109

structure correspond to the same Hermann-Mauguin symbol. 110

In case of metric specialisation, the Euclidean normalizer is a supergroup of that corresponding to the general (non- 111

specialized) metric: it is called an enhanced Euclidean normalizer (the enhanced Euclidean normalizer corresponding to 112

the highest possible metric specialization coincides with the affine normalizer). As a consequence, the number of 113

equivalent descriptions of the crystal structure increases. For example, a compound crystallising in a space group of 114

type $Pccn$ (No. 49) has $\mathcal{N}_E(\mathcal{G}) = Pmmm$ with basis vectors $\mathbf{a}/2$, $\mathbf{b}/2$, $\mathbf{c}/2$. The additional generators of $\mathcal{N}_E(\mathcal{G})$ with respect 115

to \mathcal{G} are the three translations $a/2$, $b/2$ and $c/2$. The same crystal structure can therefore be described in the same axial 116

setting of the same space group in the eight ways related by $t(\frac{1}{2},0,0)$, $t(0,\frac{1}{2},0)$, $t(0,0,\frac{1}{2})$ (as well as all their combinations 117
and the operations in the corresponding cosets). Moreover, $\mathcal{N}_A(\mathcal{G}) = P4/mmm$, which corresponds to the enhanced 118
Euclidean normalizer for $a = b$, with basis vectors $\mathbf{a}/2$, $\mathbf{b}/2$, $\mathbf{c}/2$, with additional generator the reflection $m_{x,x,z}$ with 119
respect to $\mathcal{N}_E(\mathcal{G})$. This means that if $a = b$, then the same structure can also be described in the same axial setting of the 120
same space group in eight more ways (thus sixteen in total), related to the other eight descriptions by a reflection about 121
a $(1\bar{1}0)$ plane passing through the origin (as well as all the operations in the corresponding cosets). The two other 122
tetragonal metric specialisation, *i.e.* $b = c$ or $a = c$, do not lead to enhanced Euclidean normalizers, so that the number of 123
equivalent descriptions does not increase: in fact, the symmetry elements along the two directions of specialisation are 124
not of the same type (c and n respectively). Similarly, a cubic metric specialisation, *i.e.* $a = b = c$, does not increase the 125
number of equivalent descriptions with respect to $\mathcal{N}_A(\mathcal{G})$. Now, operations that do *not* belong to the affine normaliser 126
result in alternative but non-equivalent descriptions of the crystal structure and also modify the Hermann-Mauguin 127
symbol of the space group. For example, three-fold rotations about the $[111]$ direction (as well as any operation in the 128
corresponding coset) change the space-group symbol from $Pccm$ to $Pmaa$ - basis vector change $(\mathbf{a},\mathbf{b},\mathbf{c})_{Pmaa} = (\mathbf{c},\mathbf{a},\mathbf{b})_{Pccm}$ - 129
or $Pbmb$ - basis vector change $(\mathbf{a},\mathbf{b},\mathbf{c})_{Pbmb} = (\mathbf{b},\mathbf{c},\mathbf{a})_{Pccm}$. 130

3. Data collection in alternative settings of the space-group 131

Data collection from diffractometers equipped with point detectors required the user to choose the unit cell on the basis 132
of a limited number of diffractions, before the data collection actually started. The introduction of area detectors have 133
made this step no longer necessary: the unit cell can be chosen *a posteriori* and often in a rather automatic way, 134
following the suggestions by the software. When the basis vectors obtained following this procedure are differently 135

oriented with respect to the standard setting of the space group, the reflection file has to be re-indexed in the standard 136
 setting, or an alternative setting of the space group has to be used for the structure solution and refinement. Modern 137
 software packages are usually able to recognize the choice of an alternative setting, and to operate the transformation to 138
 a standard setting. This is however not always the case and the investigator should be aware that the automatic indexing 139
 may sometimes result in an unusual setting. This may induce mistakes in subsequent structure analysis, as we are going 140
 to show with a couple of concrete examples. 141

3.1 Overlooked symmetry in analcime 142

A textbook example was reported recently on analcime, a mineral belonging to the family of feldspathoids which 143
 crystallizes in a cubic space group of type $Ia\bar{3}d$ or in its translationengleiche subgroup of type $I4_1/acd$. Sugano & Kyono 144
 [7] investigated two tetragonal synthetic samples that had been reheated for 24 and 48 hours respectively. As reminded 145
 in the Introduction, the choice of labelling c the basis vector along the unique axis of a tetragonal crystal is a matter of 146
 convention and not imposed by any symmetry consideration. For reasons that are unclear (no CIF file was provided) the 147
 diffraction data [7] were indexed in one case in an a -unique setting, and in the other case in a b -unique setting. These 148
 unusual settings misled to authors to think their samples were orthorhombic, because no systematic absences from the 149
 fourfold screw axis were observed along the $00l$ row (they were along the $h00$ and $0k0$ rows respectively) and to draw 150
 conclusions about cation ordering that turned out to be contradictory with respect to the experimental data, once the 151
 latter were re-indexing in the conventional c -unique setting [8]. The incorrect interpretation was likely the result of no 152
 warning being issued from the automatic data treatment. This could have been avoided had the investigators been aware 153
 of the possibility that their data were expressed in an alternative setting of the space group. 154

3.2 The $Pb\bar{3}$ setting of pyrite 155

16

Pyrite, FeS_2 , crystallizes in a space group of type $Pa\bar{3}$, whose Euclidean normalizer is hemihedral, namely $Ia\bar{3}$ with 156
basis vectors in common with those the space group. The operations of $Pa\bar{3}$, but also those of $\mathcal{N}_E(Pa\bar{3}) = \mathcal{N}_A(Pa\bar{3}) = Ia\bar{3}$, 157
leave the Hermann-Mauguin symbol of the space group unchanged. However, any of the operations of a cubic 158
holohedral supergroup of $Ia\bar{3}$ do produce an alternative, unconventional setting. In particular, their effect on the glide 159
planes is the following: 160

$a\ x,y,\frac{1}{4}$ is transformed to $b\ x,y,\frac{1}{4}$ 161

$c\ x,\frac{1}{4},z$ is transformed to $c\ \frac{1}{4},y,z$ 162

$b\ \frac{1}{4},y,z$ is transformed to $a\ x,\frac{1}{4},z$ 163

The Hermann-Mauguin symbol of the space group in this setting is $Pb\bar{3}$. The Wyckoff positions are transformed as in 164
Table 1, where as coset representative a twofold rotation about $[1\bar{1}0]$ has been chosen. If the data collection – the hkl,l,σ 165
file - is indexed in $Pb\bar{3}$ but the structure refinement is attempted in $Pa\bar{3}$, a large number of violations of reflection 166
conditions occur and the refinement obviously fails. The unaware investigator may be trapped in thinking he is dealing 167
with a crystal of lower symmetry, possibly twinned, whereas he is simply using an unsuitable setting of the space group. 168
This is precisely the situation we had to deal with, as described in the following section. 169

3.2 Experimental and results 170

A sample of natural pyrite, FeS_2 , in the shape of a pentagonal-dodecahedron, was obtained from Hechi, Guangxi, China. 171
Data collection was performed on a Rigaku SuperNova single source at offset/far, HyPix3000 diffractometer under the 172
program CrysAlisPro (Version 1.171.39.27b). The intensity of reflections was measured using graphite-monochromated 173
 $\text{MoK}\alpha$ radiation (0.71069 Å). CrysAlisPro program was used to refine the cell dimensions and for data reduction. The 174
data were corrected for Lorentz and polarization factors and the absorption correction coefficient, which was 175

determined using the integration method based on the observed arbitrary shape of the specimens (Table 2). Independent reflections with $F_o > 3\sigma(F_o)$ (195 in number) were used to refine the crystal structure by the full matrix-least-square method, which was performed using Jana 2006 [9].

The structure of pyrite being well-known, we assumed at first a space group of type $Pa\bar{3}$. The set of reflections indexed in $Pa\bar{3}$ included 65 violations of the reflection conditions. The average I/σ ratio of these reflections was 10.78, with the strongest reflections showing a ratio above 80. These violations cannot therefore be considered outliers. Not surprisingly, using the coordinates of Fe and S in $Pa\bar{3}$ resulted in very poor quality refinement: $R(\text{obs}) = 32.4\%$, $R(\text{all}) = 44.3\%$, $\text{GoF} = 22.4$.

The Laue indices of the reflections violating the systematic absences of $Pa\bar{3}$ correspond to zonal reflection conditions. One may therefore be tempted to think one is dealing with a sample whose actual symmetry is $P2_13$, possibly twinned, in which no violation of reflection conditions appear. The refinement in $P2_13$ does converge to $R(\text{obs}) = 2.60\%$ $R(\text{all}) = 3.52\%$ with Fe in position 0.75012(15) 0.25012(15) 0.24987(15) and S split into two positions, S1 0.3652(2) 0.3652(2) 0.3652(2), S2 0.8651(2) 0.6349(2) 0.3651(2). The results is however very strongly pseudo-symmetric with respect to $Pa\bar{3}$, to which it is transformed by a change of basis vectors $(\mathbf{a}, \mathbf{b}, \mathbf{c})_{Pb\bar{3}} = (-\mathbf{b}, -\mathbf{a}, -\mathbf{c})_{Pa\bar{3}}$ with origin shift $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$, as can be verified with the routine PSEUDO at the Bilbao Crystallographic Server [10],[11]. This permutation of basis vectors corresponds to the twofold rotation $[1\bar{1}0]$ chosen to obtain the Wyckoff positions of $Pb\bar{3}$ from those of $Pa\bar{3}$ (Table 1), which shows that the origin of the apparent discrepancy with respect to the structural data already available in the literature is the fact that the reflection file has been indexed in $Pb\bar{3}$. When this setting of the space group is adopted, all

the violations of the reflection conditions disappeared and the refinement converges smoothly to $R(\text{obs}) = 2.34\%$, $R(\text{all}) = 2.64\%$, $\text{GoF} = 1.4$ (Table 3).

4. Conclusions

The use of alternative axial space-group settings has definite advantages for several problems [1]. However, when the investigator has to face experimental data expressed in such a setting he may be led to supposing his sample is less symmetric than what it actually is. We have discussed two examples: one from the literature, in which the authors did not realize they were dealing with an alternative setting of the space group, and one from our own data, which is more subtle, because the unconventional setting $Pb\bar{3}$ of the space group does not appear either in the list of space-group symbols in the *International Tables for Crystallography* - it is only mentioned in the sixth edition [12] at the end of section 1.5.4.5.3 and in Table 1.6.4.25) – or in the Bilbao Crystallographic Server [11].

Unexpected symmetry of the diffraction pattern can have several origins: twinning, stacking disorder, chemical heterogeneities, Renninger effect [13]... in some cases it can simply be a trick of the chameleon, as in the examples we have described in details. The structural investigator needs to be aware of this possibility.

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Conflict of interest

The authors declare no conflict of interest.

Keywords	212
pyrite, single crystal structure refinement, unconventional settings of space groups,	213
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Table 1. Wyckoff positions in $Pa\bar{3}$ and in $Pb\bar{3}$.

Position	Site-symmetry group	$Pa\bar{3}$		$Pb\bar{3}$	
		Coordinates	Reflection conditions (h,k,l cyclically permutable)	Coordinates	Reflection conditions (h,k,l cyclically permutable)
24d	1	(x,y,z) $(\bar{x}+1/2,\bar{y},z+1/2)$ $(\bar{x},y+1/2,\bar{z}+1/2)$ $(x+1/2,\bar{y}+1/2,\bar{z})$ (z,x,y) $(z+1/2,\bar{x}+1/2,\bar{y})$ $(\bar{z}+1/2,\bar{x},y+1/2)$ $(\bar{z},x+1/2,\bar{y}+1/2)$ (y,z,x) $(\bar{y},z+1/2,\bar{x}+1/2)$ $(y+1/2,\bar{z}+1/2,\bar{x})$ $(\bar{y}+1/2,\bar{z},x+1/2)$ $(\bar{x},\bar{y},\bar{z})$ $(x+1/2,y,\bar{z}+1/2)$ $(x,\bar{y}+1/2,z+1/2)$ $(\bar{x}+1/2,y+1/2,z)$ $(\bar{z},\bar{x},\bar{y})$ $(\bar{z}+1/2,x+1/2,y)$ $(z+1/2,x,\bar{y}+1/2)$ $(z,\bar{x}+1/2,y+1/2)$ $(\bar{y},\bar{z},\bar{x})$ $(\bar{y},z+1/2,x+1/2)$ $(\bar{y}+1/2,z+1/2,x)$ $(y+1/2,z,\bar{x}+1/2)$	$0kl: k = 2n$ $h00: h = 2n$	(x,y,z) $(\bar{x},\bar{y}+1/2,z+1/2)$ $(x+1/2,\bar{y},\bar{z}+1/2)$ $(\bar{x}+1/2,y+1/2,\bar{z})$ (y,z,x) $(\bar{y}+1/2,z+1/2,\bar{x})$ $(\bar{y},\bar{z}+1/2,x+1/2)$ $(y+1/2,z,\bar{x}+1/2)$ (z,x,y) $(z+1/2,\bar{x},\bar{y}+1/2)$ $(\bar{z}+1/2,x+1/2,\bar{y})$ $(\bar{z},\bar{x}+1/2,y+1/2)$ $(\bar{x},\bar{y},\bar{z})$ $(x,y+1/2,\bar{z}+1/2)$ $(\bar{x}+1/2,y,z+1/2)$ $(x+1/2,\bar{y}+1/2,z)$ $(\bar{y},\bar{z},\bar{x})$ $(y+1/2,z+1/2,x)$ $(y,z+1/2,\bar{x}+1/2)$ $(\bar{y}+1/2,z,x+1/2)$ $(\bar{z},\bar{x},\bar{y})$ $(\bar{z}+1/2,x,y+1/2)$ $(z+1/2,\bar{x}+1/2,y)$ $(z,x+1/2,\bar{y}+1/2)$	$0kl: l = 2n$ $h00: h = 2n$
8c	.3.	(x,x,x) $(\bar{x}+1/2,\bar{x},x+1/2)$ $(\bar{x},x+1/2,\bar{x}+1/2)$ $(x+1/2,\bar{x}+1/2,\bar{x})$ $(\bar{x},\bar{x},\bar{x})$ $(x+1/2,x,\bar{x}+1/2)$ $(x,\bar{x}+1/2,x+1/2)$ $(\bar{x}+1/2,x+1/2,x)$	no extra conditions	(x,x,x) $(\bar{x},\bar{x}+1/2,x+1/2)$ $(x+1/2,\bar{x},\bar{x}+1/2)$ $(\bar{x}+1/2,x+1/2,\bar{x})$ $(\bar{x},\bar{x},\bar{x})$ $(x,x+1/2,\bar{x}+1/2)$ $(\bar{x}+1/2,x,x+1/2)$ $(x+1/2,\bar{x}+1/2,x)$	no extra conditions
4b	. $\bar{3}$.	$(1/2,1/2,1/2)$ $(0,1/2,0)$ $(1/2,0,0)$ $(0,0,1/2)$	$hkl: h+k, h+l, k+l = 2n$	$(1/2,1/2,1/2)$ $(1/2,0,0)$ $(0,1/2,0)$ $(0,0,1/2)$	$hkl: h+k, h+l, k+l = 2n$
4a	. $\bar{3}$.	$(0,0,0)$ $(1/2,0,1/2)$ $(0,1/2,1/2)$ $(1/2,1/2,0)$	$hkl: h+k, h+l, k+l = 2n$	$(0,0,0)$ $(0,1/2,1/2)$ $(1/2,0,1/2)$ $(1/2,1/2,0)$	$hkl: h+k, h+l, k+l = 2n$

Table 2. Experimental details

Crystal data	
Chemical formula	FeS ₂
Mr	120
Crystal system, space group	Cubic, $Pb\bar{3}$

Temperature (K)	293
a (Å)	5.4177 (1)
V (Å ³)	159.02 (1)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	11.46
Crystal size (mm)	0.06 × 0.05 × 0.03
Data collection	
Diffractometer	Rigaku SuperNova
Absorption correction	Integration [14]
T_{\min} , T_{\max}	0.642, 0.786
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	1159, 222, 195
R_{int}	0.026
($\sin\theta/\lambda$) _{max} (Å ⁻¹)	0.994
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.028, 1.41
No. of reflections	222
No. of parameters	6
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.70 - 1.45

Table 3. Atomic coordinates and anisotropic atomic displacement parameters for pyrite in $Pb\bar{3}$

233

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	$\frac{1}{2}$	0	0	0.00253(10)	0.00253(10)	0.00253(10)	0.00006(7)	-0.00006(7)	-0.00006(7)
S	0.11511(5)	0.11511(5)	0.11511(5)	0.00302(11)	0.00302(11)	0.00302(11)	-0.00002(8)	-0.00002(8)	-0.00002(8)

Table 4. Interatomic bond distances (Å) and angles (°) for pyrite in $Pb\bar{3}$

234

Atom 1	Atom 2	Atom 3	
Fe	S	---	2.2641(3)×6
S	S	---	2.1604(4)
S	Fe	S	94.352(10)×3

28

29

S	Fe	S	85.648(10)×3
Fe	S	Fe	115.564(13)×3
Fe	S	S	102.337(14)×3