Anti-wurtzite reoriented

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Anti-wurtzite and wurtzite are shown to be the same
crystal structure despite the claims of a recent paper
describing the crystal structure of the mineral
rambergite, $Mn_{1-x}Fe_xS$, $x \simeq 0.05$. The anti-wurtzite/
wurtzite confusion is used as an illustration to help
clarify the correct general approach to take in the
treatment and presentation of achiral non-centro-
symmetric crystal structures.

1. Comment

Eriksson & Kalinowski (2001; hereafter EK)
have determined the structure of the mineral
rambergite, a hexagonal manganese sulfide of
composition $Mn_{1-x}Fe_xS$, $x \simeq 0.05$, which *is
found to crystallize in the inverse wurtzite
structure, i.e. the wurtzite-type structure but with
the opposite absolute configuration, which can
be named anti-wurtzite*. The quote (in italics)
from EK contains one of several deep mis-
understandings in their work similar to those
chastized by Rogers (1975). The space group of
wurtzite and rambergite is $P6_3mc$, which
contains roto-inversion operations (*i.e.* several
mirror and glide reflections through various
planes), clearly indicating that the crystal
structure is achiral. As a consequence, this
crystal structure does not occur as a pair of
non-superposable enantiomorphs of opposite
chirality and the crystal structures of wurtzite
and anti-wurtzite may be brought into
congruence after an appropriate pure rotation.

EK's study of rambergite provides an illus-
tration of an orientation ambiguity (Le Page *et
al.*, 1984; Koch *et al.*, 2002). This may arise
when the structure of the crystal being studied
is already known and the point symmetry of
the crystal structure is lower than that of its
lattice. To understand the nature of the orien-
tation ambiguity, compare the crystal struc-
tures of the sample and the known model. The
comparison needs to be undertaken with the
structures oriented so that each axial direction
a, **b** or **c** in the sample (determined by the
chosen indexing of the Bragg diffraction
peaks) is respectively parallel to the corre-
sponding one in the model. This orientation

ensures that the lattices of the two structures
are parallel but may not lead, as in EK's case,
to the two structures being superposable in this
fixed orientation. In fact, in EK's case the two
crystal structures may be brought into coin-
cidence by applying one of 12 equivalent
isometries either to the sample or to the model.
Of these 12 isometries it is appropriate to
mention a rotation of π about the **a** axis or
inversion through a point. Of course, each of
these 12 isometries maps the corresponding
crystal lattice onto itself. The reorientation of
the sample may be achieved by reindexing the
diffraction pattern on an alternative reciprocal
basis. A further example helps to clarify how
orientation ambiguities may arise in practical
circumstances. In the refinement of the isotypic
crystal structures of Nb_3Si and Nb_3As in space
group $P4_2/n$ (Nb_3Si: $a = 10.22$, $c = 5.19$ Å;
Nb_3As: $a = 10.29$, $c = 5.20$ Å) working from a
list of known coordinates, Waterstrat *et al.*
(1975) found that Nb_3Si refined immediately to
$R = 0.032$, whereas Nb_3As was fixed at 0.080.
The point symmetry of the crystal structure is
$4/m$, whereas that of the lattice is $4/mmm$. A
rotation of π about the [1,1,0] direction will
map the lattice onto itself but produces the
crystal structure in an alternative orientation
on this lattice. When the Nb_3As diffraction
data was reindexed on a rotated reciprocal
basis, R dropped to 0.043. It is important to
point out that the isometries that cause orien-
tation ambiguities are identical to those that
are capable of inducing twinning by mero-
hedry.

The sets of equivalent twinning or orienta-
tion-ambiguity operations are obtained from
the coset decomposition of the crystal point

group with respect to the holohedry (*i.e.* the point symmetry of the lattice; Flack, 1987). In EK's case the point group is 6*mm* and the holohedry is 6/*mmm*. The coset decomposition is as follows:

$\{6/mmm\} = \{6mm\} + r\{6mm\} = \{1, 6, 3,$ $2_{[001]}, 3^2, 6^5, m_{[100]}, m_{[210]}, m_{[110]}, m_{[120]}, m_{[010]},$ $m_{[\bar{1}10]}\} + \{2_{[100]}, 2_{[\bar{1}10]}, 2_{[010]}, 2_{[120]}, 2_{[110]},$ $2_{[210]}, \bar{1}, \bar{6}^5, \bar{3}^5, m_{[001]}, \bar{3}, \bar{6}\}$. The direction of the axis of each of the twofold rotations is indicated as a subscript given in terms of the conventional hexagonal axes. For the mirror reflections *m* it is the direction perpendicular (*i.e.* the normal) to the mirror plane that is indicated. For all the other symmetry operations (apart from the inversion through a point $\bar{1}$) the direction [0,0,1] is implicit. The superscripts (*i.e.* ^{2} and ^{5}) indicate a power of the corresponding operation. In the nomenclature of *International Tables for Crystallography* (Hahn, 2002), but omitting the coordinates of the fixed point 0,0,0, and with the symmetry operations arranged in the same order as above, the coset decomposition may be written $\{6/mmm\} = \{6mm\} + r\{6mm\} = \{1; 6^+ 0,0,z;$ $3^+ 0,0,z; 2 0,0,z; 3^- 0,0,z; 6^- 0,0,z; m x,2x,z;$ $m 0,y,z; m x,\bar{x},z; m x,0,z; m 2x,x,z; m x,x,z\} +$ $\{2 x,0,0; 2 x,\bar{x},0; 2 0,y,0; 2 x,2x,0; 2 x,x,0; 2$ $2x,x,0; \bar{1}; \bar{6}^- 0,0,z; \bar{3}^- 0,0,z; m x,y,0; \bar{3}^+ 0,0,z; \bar{6}^+$ $0,0,z\}$. The first coset contains the symmetry operators of the point group 6*mm* whilst the second coset contains all the remaining symmetry operators of 6/*mmm*. The coset representative of the second coset, *r*, may be chosen to be any member of the second coset. All of the symmetry operations of the second coset are equivalent one to another under 6*mm* and any one of them transforms 'anti-wurtzite' into 'wurtzite'. It can be seen that one half of these twin operations are pure rotations of π, whilst the remaining twin operations are roto-inversions of different angles about the hexagonal axis. In particular, amongst the roto-inversions one finds the inversion in a point, $\bar{1}$. This analysis confirms that non-centrosymmetric crystal structures for which the point-symmetry group contains roto-inversions may be inverted by rotation.

The term *absolute configuration* as used by EK is inappropriate as it should refer to the specification of the chirality sense of molecular entities, enantiomers, and not to the chirality of whole crystals. Likewise, there is a common misuse of language that attributes to a crystal structure some property of its diffraction pattern. As an example it should be clear that a chiral crystal may always be distinguished from its enantiomorph by some suitable physical observation (*e.g.* optical activity), although in the absence of resonant scattering (anomalous dispersion), their diffraction patterns are identical. However, EK state that *without the anomalous dispersion effects the wurtzite and anti-wurtzite structures are equal*, implying that it is the crystal structures themselves that are identical rather than their diffraction patterns. It is apposite to recall Wilson's (1975) criticism of the *effect of dispersion on atomic parameters* as being meaningless. He states that *atomic parameters are determined by the interatomic forces, the symmetry of the crystal, the temperature and so on. Dispersion, anomalous or otherwise, does not affect them* (Wilson, 1975).

A fuller exposé on chiral and achiral crystal structures may be found in Flack (2003), whilst other questions concerning absolute-structure and absolute-configuration determination are dealt with by Flack & Bernardinelli (1999, 2000).

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