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Graphic Representation and Nomenclature of the Four-Dimensional Crystal Classes. V. Enantiomorphic Classes

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Abstract

Distinct symbols are introduced for the members of the 44 pairs of enantiomorphic crystal classes in four dimensions. Minimal changes are made in the conventions regarding the symbols in order to make this possible.

Introduction

In three-dimensional space groups there are 219 different combinations of symmetry elements, but 11 of these are enantiomorphic and exist in two forms of opposite hand, thus generating the usually quoted total of 230 space groups. The Hermann–Mauguin notation provides symbols which distinguish explicitly the members of the enantiomorphic pairs. This problem does not exist in the three-dimensional point groups, but it does occur in the four-dimensional point groups. Although Brown, Bülow, Neubüser, Wondratschek & Zassenhaus (1978) indicated the 44 cases in which enantiomorphy occurs they did not number them separately, and the usually quoted figure of 227 for the number of four-dimensional point groups does not distinguish between the members of enantiomorphic pairs, of which there are 44. Thus if one counts these point groups in the same way as one usually counts three-dimensional space groups the total number is in fact 271, and Wilson (1990) has pointed out the need for any notation system to distinguish between the enantiomorphs. This was not done in paper III of the present series (Whittaker, 1984*b*), although the effect of the enantiomorphy on the relevant hyperstereograms has been discussed, and in two atypical cases a corresponding distinction arising in the notation has been indicated (Whittaker, 1985). In these two atypical cases the enantiomorphy arises only from the relative arrangement of twofold rotation planes. In the other 42 cases it involves handed double rotations, and the purpose of the present paper is to extend the notation to deal with this.

The double rotations 3.3 and 4.4

The double rotation **4.4** has crypto-rotation planes whose orientations are incompletely determinate (Whittaker, 1985), but a particular range of them is compatible with their lying on the *wx* and *yz* planes. The operation can then be regarded as equivalent to one or other of the two matrices

$$\begin{pmatrix} 0 & \bar{1} & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \bar{1} \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad \text{or} \quad \begin{pmatrix} 0 & \bar{1} & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & \bar{1} & 0 \end{pmatrix}.$$

These two distinct symmetry operations can obviously be represented as the double rotations $\mathbf{4^1.4^1}$ and $\mathbf{4^1.4^3}$, respectively, and they are enantiomorphic with respect to one another. For reasons discussed elsewhere it is preferable in a symbolic notation to use the unitary symbol **IV** for the fourfold double rotation, and in order to distinguish between its two enantiomorphic forms we add a subscript sign. Thus $\mathbf{IV_+ = 4^1.4^1}$ and $\mathbf{IV_- = 4^1.4^3}$. The graphical symbol adopted for use in the hyperstereograms of the crystal classes (Whittaker, 1984*a*) already contains an arrow which specifies the hand of the operation; an inward-pointing arrow corresponds to the above definition of $\mathbf{IV_+}$ and an outward-pointing arrow corresponds to $\mathbf{IV_-}$.

Exactly the same considerations apply to the double rotation **3.3**, whose two enantiomorphic forms are $\mathbf{3^1.3^1}$ denoted as $\mathbf{III_+}$ and $\mathbf{3^1.3^2}$ denoted as $\mathbf{III_-}$. Again the graphical symbol has an inward-pointing arrow for $\mathbf{III_+}$ and an outward-pointing one for $\mathbf{III_-}$.

The double rotation **6.6** can always be factorized as $\mathbf{3.3.\bar{\bar{1}}}$ and only requires a separate symbol in class 11/02 where $\mathbf{III_+.\bar{\bar{1}}}$ and $\mathbf{III_-.\bar{\bar{1}}}$ are indicated as $\mathbf{\bar{\bar{I}}II_+}$ and $\mathbf{\bar{\bar{I}}II_-}$.

The double rotations 8.8 and 12.12

The double rotations $\mathbf{8^1.8^1}$ and $\mathbf{12^1.12^1}$ (and their enantiomorphic forms $\mathbf{8^1.8^7}$ and $\mathbf{12^1.12^{11}}$) are non-crystallographic operations. This may be inferred from the the fact that the traces of the corresponding matrices referred to rectangular axes lying in their crypto-rotation planes clearly have the non-integral values 4 cos $2\pi/8$ and 4 cos $2\pi/12$ respectively. We therefore only have to consider the cases $\mathbf{8^1.8^3}$ and $\mathbf{12^1.12^5}$ (and their enantiomorphs $\mathbf{8^1.8^5}$ and $\mathbf{12^1.12^7}$),

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whose traces are respectively

$$2\cos 2\pi/8 + 2\cos 6\pi/8 = 0$$

and

$$2\cos 2\pi/12 + 2\cos 10\pi/12 = 0.$$

However, because their component crypto-rotation components are non-crystallographic in two dimensions they have to lie in uniquely defined crystallographically irrational planes (Whittaker & Whittaker, 1986), which are not useful in developing a point-group notation.

For **8.8** the unitary symbol **VIII** is therefore retained, and the hand adopted as $\mathbf{VIII}_+$ is that which makes

$$\mathbf{VIII}_+^2 = \mathbf{IV}_+.$$

This in fact equates $\mathbf{VIII}_+$ with $\mathbf{8}^1.\mathbf{8}^5$ and $\mathbf{VIII}_-$ with $\mathbf{8}^1.\mathbf{8}^3$. The graphical symbol again has the inward-pointing arrow for $\mathbf{VIII}_+$ and the outward-pointing one for $\mathbf{VIII}_-$.

The unitary symbol **XII′** for **12.12** never has to be used in describing a crystal class because it can always be factorized into explicit components **III** and **IV** of opposite hand. The combination $\mathbf{III}_+.\mathbf{IV}_-$ corresponds to (the 7th power of) $\mathbf{12}^1.\mathbf{12}^7$ and $\mathbf{III}_-.\mathbf{IV}_+$ to (the 7th power of) $\mathbf{12}^1.\mathbf{12}^5$.

Notation for the enantiomorphic classes

A distinctive notation for all the enantiomorphic classes is given in Table 1.

If only one notational position is occupied by a Roman numeral then the appropriate sign is subscripted to this symbol. If more than one position is so occupied, then the first one corresponding to a double rotation of one hand only has the appropriate sign, and any subsequent double rotations that occur in one hand only are subscripted *s* (same) or *o* (opposite) to indicate whether they are of the same or opposite hand. Operations that are present with both hands are left unsubscripted.

In most cases these rules only involve adding the appropriate sign to one symbol as compared with the previously published notation. In six cases, however, the effect is slightly more complex in that a subscript *o* is omitted from 30/02 and 30/03, the first subscript *s* is changed to a sign in 32/04 and 33/05, and the first subscript *s* is omitted and the second one changed to a sign in 33/08 and 33/09.

It has already been noted that in the only two enantiomorphic classes that do not contain a handed double rotation (29/01 and 29/02) there is a change in orientation of twofold planes which moves their symbol from position 5 to position 4 and inverts it. A similar effect also occurs in certain classes that involve a handed double rotation, namely 30/03, 30/04, 30/07, 30/08, 32/04, 32/06, 32/07, 33/05 and 33/09. A similar change affects fourfold rotation planes as well in 33/10 and 33/12.

If the enantiomorphic pairs of classes are to be listed separately it would be logical in each case to list the + one first, and it is given first in the following table. In all but seven cases the + form was the one illustrated with a hyperstereogram by Whittaker (1985), corresponding to the generating matrices given by Brown *et al.* (1978). These seven are indicated in Table 1 by an asterisk. It is not immediately obvious which of the enantiomorphs of 29/02 should be regarded as +, but it seems appropriate to regard it as the one that has its twofold planes in the same orientation as the enantiomorphic classes in system 30 within the same family.

One further point arises from a consideration of the enantiomorphy, which does not affect the

Table 1. *Notation for all enantiomorphic classes*

Ordinal number	Number of Brown *et al.* (1978)	1st enantiomorph	2nd enantiomorph
36	10/01	IV_+	IV_-
37	11/01	III_+	III_-
38	11/02	$\mathrm{I\mathring{I}I}_+$	$\mathrm{I\mathring{I}I}_-$
76	16/01	$\mathrm{IV}_+\ 2/2$	$\mathrm{IV}_-\ 2/2$
77	17/01	$\mathrm{III}_+\ -/2$	$\mathrm{III}_-\ -/2$
78	17/02	$\mathrm{III}_+\ 2/2$	$\mathrm{III}_-\ 2/2$
112	21/01	$\mathrm{III}_+/-/2$	$\mathrm{III}_-/-/2$
113	21/02	$\mathrm{III}_+/2/2$	$\mathrm{III}_-/2/2$
114	21/03	$\mathrm{III}_+/-/2-/2$	$\mathrm{III}_-/-/2-/2$
115	21/04	$\mathrm{III}_+/2/2\ 2$	$\mathrm{III}_-/2/2\ 2$
154	26/01*	VIII_+	VIII_-
155	26/02*	$\mathrm{VIII}_+\ 2/2$	$\mathrm{VIII}_-\ 2/2$
160	28/01	$\mathrm{IV}_+\mathrm{III}_o$	$\mathrm{IV}_-\mathrm{III}_o$
161	28/02	$\mathrm{IV}_+\mathrm{III}_o\ 2/2$	$\mathrm{IV}_-\mathrm{III}_o\ 2/2$
162	29/01	$3/3---2$	$3/3---/2$
163	29/02	$3/3---2/2$	$3/3--2/2$
171	30/01	$\mathrm{III}_+\ \mathrm{IV}_s$	$\mathrm{III}_-\ \mathrm{IV}_s$
172	30/02*	$\mathrm{III}_+\ \mathrm{IV}/2/2$	$\mathrm{III}_-\ \mathrm{IV}/2/2$
173	30/03*	$\mathrm{III}_+/2/2\ \mathrm{IV}--2$	$\mathrm{III}_-/2/2\ \mathrm{IV}-2$
174	30/04	$\mathrm{III}_+\ \mathrm{IV}_s\ 2/2-2$	$\mathrm{III}_-\ \mathrm{IV}_s\ 2/2\ 2$
175	30/05	$3/3\ \mathrm{IV}_+$	$3/3\ \mathrm{IV}_-$
176	30/06*	$\mathrm{III}_+/2/2\ \mathrm{IV}_o/2\ 2\ 2\ 2$	$\mathrm{III}_-/2/2\ \mathrm{IV}_o/2\ 2\ 2\ 2$
177	30/07	$6/6\ \mathrm{IV}_+--2$	$6/6\ \mathrm{IV}_--2$
178	30/08*	$3/3\ \mathrm{IV}_+\ 2/2-2$	$3/3\ \mathrm{IV}_-\ 2/2\ 2$
191	32/01	$\mathrm{IV}_+\ \mathrm{IV}_s$	$\mathrm{IV}_-\ \mathrm{IV}_s$
192	32/02	$\mathrm{VIII}_+/2/2\ \mathrm{IV}_o$	$\mathrm{VIII}_-/2/2\ \mathrm{IV}_o$
193	32/03	$\mathrm{IV}_+\ \mathrm{IV}_s-2/2$	$\mathrm{IV}_-\mathrm{IV}_s-2/2$
194	32/04	$\mathrm{IV}/2/2\ \mathrm{IV}_+-----2$	$\mathrm{IV}/2/2\ \mathrm{IV}_-----2$
195	32/05	$\mathrm{IV}_+\ \mathrm{IV}_s\ 3$	$\mathrm{IV}_-\ \mathrm{IV}_s\ 3$
196	32/06	$\mathrm{VIII}_+/2/2\ \mathrm{IV}_s-2---2$	$\mathrm{VIII}_-/2/2\ \mathrm{IV}_s-2--2$
198	32/08	$\mathrm{VIII}_+/4/4\ \mathrm{IV}_o----2$	$\mathrm{VIII}_-/4/4\ \mathrm{IV}_o-----2$
201	32/11	$\mathrm{IV}_+\ \mathrm{IV}_s\ 3\ 2$	$\mathrm{IV}_-\ \mathrm{IV}_s\ 3\ 2$
212	33/01	$\mathrm{IV}_+\ \mathrm{IV}_s\ \mathrm{III}_o$	$\mathrm{IV}_-\ \mathrm{IV}_s\ \mathrm{III}_o$
213	33/02	$\mathrm{VIII}_+-\mathrm{III}_o$	$\mathrm{VIII}_--\mathrm{III}_o$
214	33/03	$\mathrm{IV}_+\ \mathrm{IV}_s\ \mathrm{III}_s$	$\mathrm{IV}_-\ \mathrm{IV}_s\mathrm{III}_s$
215	33/04	$\mathrm{IV}_+\ \mathrm{IV}_s\ \mathrm{III}_o\ 2/2$	$\mathrm{IV}_-\ \mathrm{IV}_s\ \mathrm{III}_o\ 2/2$
216	33/05	$\mathrm{IV}/2/2\ \mathrm{IV}_+\ \mathrm{III}_s----2$	$\mathrm{IV}/2/2\ \mathrm{IV}_-\ \mathrm{III}_s---2$
217	33/06	$\mathrm{IV}_+\ \mathrm{IV}_s\ \mathrm{III}_s\ 2/2$	$\mathrm{IV}_-\ \mathrm{IV}_s\ \mathrm{III}_s\ 2/2$
218	33/07	$\mathrm{IV}_+\ \mathrm{IV}_s\ 3/3$	$\mathrm{IV}_-\ \mathrm{IV}_s\ 3/3$
219	33/08	$\mathrm{IV}/2/2\ \mathrm{IV}/2\ \mathrm{III}_+---2\ 2$	$\mathrm{IV}/2/2\ \mathrm{IV}/2\ \mathrm{III}_----2\ 2$
220	33/09	$\mathrm{IV}/2/2\ \mathrm{IV}\ \mathrm{III}_+\ 2---2$	$\mathrm{IV}/2/2\ \mathrm{IV}\ \mathrm{III}_-2--2$
221	33/10	$4/4\ \mathrm{IV}_+\ \mathrm{III}_s----4/4$	$4/4\ \mathrm{IV}_-\ \mathrm{III}_s---4/4$
222	33/11	$\mathrm{IV}_+\ \mathrm{IV}_s\ 3/3\ 2/2$	$\mathrm{IV}_-\ \mathrm{IV}_s\ 3/3\ 2/2$
223	33/12	$4/4\ \mathrm{IV}_+\ \mathrm{III}_s\ 2--4/4\ 2$	$4/4\ \mathrm{IV}_-\ \mathrm{III}_s\ 2--2\ 4/4$

appearance of the notation but affects the orientational conventions for the planes corresponding to the positions within the symbols (Whittaker, 1985). In some cases a given position in the two members of an enantiomorphic pair refers to a different subset of the set of plane orientations defined for the relevant crystal family. These changes are not listed as they can easily be derived by inspection of the hyperstereogram and consideration of the effect of a reflection of it in the *xyz* plane.

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Sign distribution of two-phase structure invariants. By D. Y. GUO,* *Institute of Theoretical Chemistry, Jilin University, Changchun* 130021, *People's Republic of China*

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Abstract

An empirical investigation of the distribution of Friedel-pair two-phase structure invariants has been reported by Guo & Hauptman [*Chin. Sci. Bull.* (1989), **34**, 137-141]. In the present paper their sign distributions are calculated for some small molecules and for a protein. The statistical figures show that there exists a strong tendency towards positive values for the signs of the two-phase structure invariants. It is anticipated that Hauptman's formula [*Acta Cryst.* (1982), **A38**, 632-641] may be good enough to estimate statistically the signs of the two-phase structure invariants for these model crystals.

Introduction

It has been known for a long time that the presence of anomalous scatterers facilitates the solution of the phase problem of macromolecular structures. Hauptman (1982) used his neighbourhood principle for integrating the techniques of direct methods with anomalous dispersion for TPSI (the two-phase structure invariant), $\Psi_2=\varphi_{\mathbf{H}}+\varphi_{-\mathbf{H}}$, and concluded that the conditional probability distribution of the TPSI has a unique maximum at $\Psi_2=-\xi$. If it is statistically reasonable, the new approach of direct methods may help to solve the geometric twofold phase ambiguity of a Friedel pair for a macromolecular crystal. The concise formula is

$$\Psi_2=\varphi_{\mathbf{H}}+\varphi_{-\mathbf{H}}\approx-\xi, \qquad (1)$$

where φ is the phase of the structure factor, and ξ is defined by

$$X\cos\xi=C_{\mathbf{H}}, \qquad X\sin\xi=-S_{\mathbf{H}}, \qquad (2)$$

$$C_{\mathbf{H}}=\alpha_{\mathbf{H}}^{-1}\sum_{j=1}^{N}|f_{j\mathbf{H}}|^2\cos 2\delta_{j\mathbf{H}},$$
$$S_{\mathbf{H}}=\alpha_{\mathbf{H}}^{-1}\sum_{j=1}^{N}|f_{j\mathbf{H}}|^2\sin 2\delta_{j\mathbf{H}}, \qquad (3)$$

$$\alpha_{\mathbf{H}}=\sum_{j=1}^{N}|f_{j\mathbf{H}}|^2, \qquad (4)$$

where

$$f_{j\mathbf{H}}=|f_{j\mathbf{H}}|\exp(i\delta_{j\mathbf{H}}) \qquad (5)$$

is the atomic scattering factor for atom j. As the probabilistic TPSI is of great importance to theory, Giacovazzo (1983) later obtained a similar result and suggested its practical application (Cascarano & Giacovazzo, 1984).

Fortier, Fraser & Moore (1986) correctly pointed out that since $\delta_{j\mathbf{H}}$ is positive and generally small, both $C_{\mathbf{H}}$ and $S_{\mathbf{H}}$ are positive, and thus ξ is negative; it therefore follows that Ψ_2 as estimated by (1) has a positive value. In other words, formula (1) gives the wrong sign estimate only when the true sign of Ψ_2 is negative. The author not only agrees with Fortier *et al.*, but also decided to investigate how many wrong signs of TPSI as estimated by (1) may appear in practice and how the wrong signs are distributed with relation to the magnitudes $|E|$, and thus to go further into the question whether these wrong signs may lead to serious consequences in direct methods.

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