Acta Cryst. (1974). A**30**, 168

Order–Disorder in Sapphirine, Aenigmatite and Aenigmatite-like Minerals

By K. Dornberger-Schiff

Zentralinstitut für Physikalische Chemie der Akademie der Wissenschaften der Deutschen Demokratischen Republik, 1199 *Berlin-Adlershof, Germany* (*DDR*)

and S. Merlino

Istituto di Mineralogia e Petrografia dell'Università di Pisa, Pisa, Italy

(*Received* 25 *June* 1973; *accepted* 8 *August* 1973)

The chemically very different minerals aenigmatite and sapphirine are crystallographically closely related, being ordered members of isomorphous families of OD structures consisting of equivalent layers. The symbol of the OD-groupoid family characterizing their symmetry is

$$P1(2/n)1\ \{1(2_2/c_{1/2})1\}\,.$$

Formulae for the structure factor are deduced for the general member of the family and then specialized to explain the diffraction pattern of some members of interest. The twinned structures of aenigmatite, rhönite and krinovite are explained as OD twins; the constituting twin individuals are structures of maximum degree of order corresponding to the OD-groupoid family quoted above.

Introduction

Sapphirine from Mautia Hill (Tanganyika) was studied by McKie (1963), who pointed out its peculiar features. In fact, although its chemical composition $Mg_{3\cdot67}Mn_{0\cdot04}Fe^{+2}_{0.17}Ti_{0\cdot01}Fe^{+3}_{0.33}Al_{8\cdot07}Si_{1\cdot75}O_{20\cdot00}$ is normal, its diffraction pattern is unusual. The X-ray diffraction pattern was described (McKie, 1963) on the basis of a monoclinic unit cell with dimensions: $a=9{\cdot}85$, $b=28{\cdot}6$, $c=9{\cdot}96$ Å, $\beta=110°30'$. The salient feature of the pattern is the presence of diffuse streaks parallel to $\mathbf{b}^*$ for $l=2n+1$, besides sharp spots for $l=2n$.

The structure of sapphirine was not known at the time, but Patterson syntheses calculated by Fleet (1967) showed that the oxygen ions were approximately cubic close-packed with Si^{+4} and Al^{+3} in tetrahedral sites and Al^{+3} and Mg^{+2} in octahedral sites. McKie (1963) put forward the hypothesis that the special features of Mautia Hill sapphirine were linked to a partial ordering of Al^{+3} and Mg^{+2} among the octahedral sites. According to this interpretation, two extreme structural states would exist: a disordered state corresponding to normal sapphirine and a highly ordered state corresponding to a hypothetical structure with doubled **b** translation. Mautia sapphirine, with its characteristic diffuse streaks, would have a partially ordered structure.

The solution of the crystal structures of sapphirine $Mg_{3\cdot5}Al_{9\cdot0}Si_{1\cdot5}O_{20}$ (Moore, 1968, 1969) and aenigmatite $Na_2Fe_5TiSi_6O_{20}$ (Merlino, 1970; Cannillo, Mazzi, Fang, Robinson & Ohya, 1971) by showing the close crystallochemical similarities between these chemically very different minerals opened the way to explain the nature of Mautia sapphirine.

The aim of this paper is to deal with the structural nature of Mautia sapphirine, together with the related questions of the relations between sapphirine and aenigmatite, and the twinning in aenigmatite and aenigmatite-like minerals, on the basis of OD theory (Dornberger-Schiff, 1956, 1964, 1966).

Deduction of the OD-groupoid family of sapphirine and aenigmatite from X-ray data

The distribution of intensities in reciprocal space can most easily be visualized by looking at Fig. 1, which presents a unified scheme projected along the $\mathbf{b}^*$ axis. The meaning of the full and empty circles is the same for aenigmatite, sapphirine and sapphirine from Mautia Hill. The meaning of the crosses is, however, different for the different substances. We propose to discuss first the diffraction pattern of sapphirine of Mautia Hill, but wish to emphasize here that the close relation between the diffraction patterns of these substances suggests a close relation between the structures (see below).

The systematic presence or absence of intensity in the diffraction pattern of sapphirine of Mautia Hill may be summarized as follows:

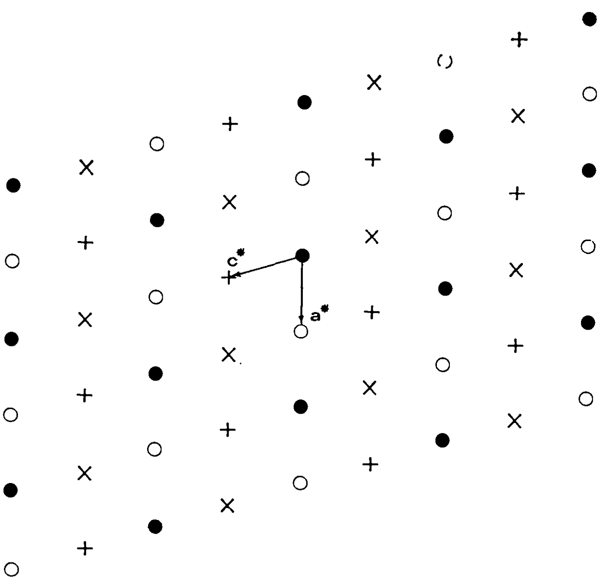
(*a*) For $l=2n$ there are sharp reflexions; for $l=2n+1$ there are diffuse streaks parallel to $\mathbf{b}^*$;

(*b*) There are maxima on the diffuse streaks, and it is possible to assign integral indices *hkl* to these maxima as well as to the sharp reflexions. This is purely formal, because the diffuse streaks prove that there is no periodicity perpendicular to $\mathbf{a}^*$ and $\mathbf{c}^*$ and thus no basic translational vector **b**.

(*c*) Sharp reflexions ($l=2n$) are present only for $2h+k+l=4n$. This rule is equivalent to two rules:

(c_1) *hkl* reflexions with $l=2n$ are present only for $k=2n$. The sharp reflexions taken by themselves may thus be indexed (indices *hKL*) with respect to a larger reciprocal cell with $\mathbf{B}^*=2\mathbf{b}^*$ and $\mathbf{C}^*=2\mathbf{c}^*$.

(c_2) hKL are present only if $h+K+L=2n$, where the indices hKL refer to the reciprocal vectors $\mathbf{a}^*\mathbf{B}^*\mathbf{C}^*$, *i.e.* $K=k/2$, $L=l/2$.



k values observed

	●	○	+	×
Aenigmatite	4n (s)	4n+2 (s)	4n+1 (s)	4n+3 (s)
Sapphirine	4n (s)	4n+2 (s)	2n (s)	2n (s)
Sapphirine of Mautia Hill	4n (s)	4n+2 (s)	2n (wm) 2n+1 (nm)	2n (wm) 2n+1 (nm)

Fig. 1. Distribution of intensities in reciprocal space for aenigmatite, sapphirine and sapphirine of Mautia Hill. Sharp reflexions are indicated by (s); (wm) and (nm) indicate respectively wide maxima and narrow maxima on streaks.

(d) In the $h0l$ reciprocal plane sharp reflexions are present only for $h=2n$ (and $l=4n$), the diffuse streaks vanish except for $h=2n+1$ (and $l=2n+1$).

Condition (a) shows that, although the real structure is periodic only in two dimensions with translational vectors $\mathbf{a},\mathbf{b}$, a fictitious structure with electron density $\hat{\varrho}\,(xyz)$ related to the electron density of the real structure by

$$\hat{\varrho}\,(xyz)=\tfrac{1}{2}[\varrho(x,y,z)+\varrho(x,y,z+\tfrac{1}{2})]$$

is periodic in three dimensions. Such a fictitious structure is usually called the *superposition structure.*

From condition (c_1) it follows that the superposition structure has the basic vectors $\mathbf{A}=\mathbf{a}$, $\mathbf{B}=\mathbf{b}/2$, $\mathbf{C}=\mathbf{c}/2$. From condition (c_2) it follows that the superposition structure is body-centred. Condition (d) indicates the presence of n-glide planes perpendicular to $\mathbf{b}$, in the real structure, of a-glide and c-glide planes in the superposition structure.

Only two space groups are thus possible for the superposition structure: Ia and $I2/a$ (corresponding, with another choice of $\mathbf{a}$ and $\mathbf{c}$ axes, to Cc and $C2/c$ respectively) (see Fig. 2). We may assume that the symmetrically equivalent asymmetric units of the superposition structure originate from symmetry-equivalent parts of the real structure. This assumption follows from the assumption that the real structure is built of geometrically equivalent layers.

The n-glide plane deduced from condition (d) links asymmetric units related by it rigidly one to the other. Therefore asymmetric units related in this way should be considered as belonging to the same layer. Thus $P1(n)1$ results as the minimum symmetry of the single layer. The different layers are translationally equivalent and adjacent layers are related by a vector $(2\mathbf{a}+\mathbf{b}-\mathbf{c})/4$

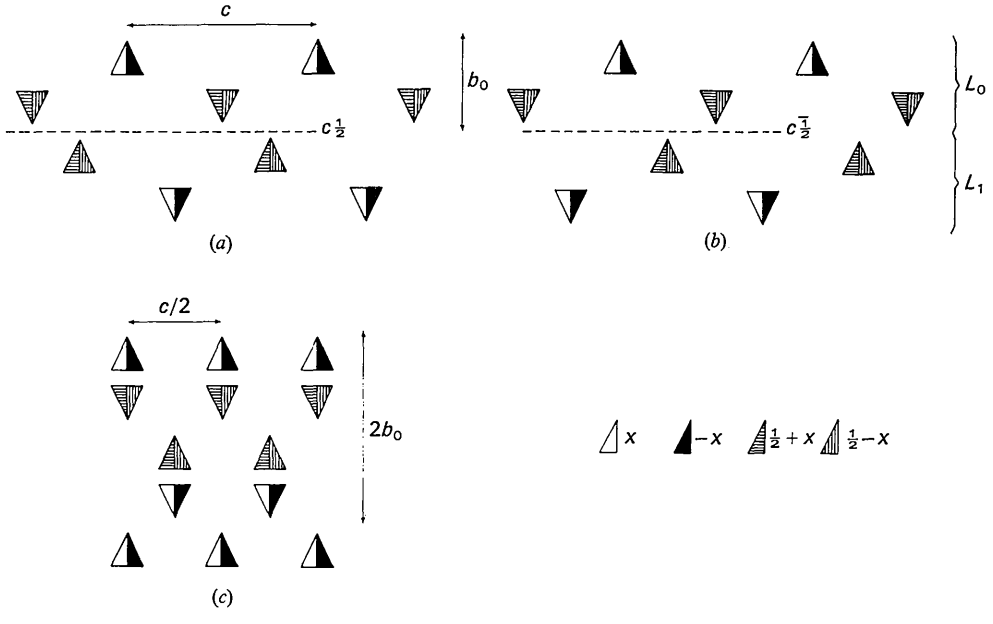


Fig. 2. (a), (b) The two possible positions of layer L_1 relative to L_0. (c) The superposition structure.

or $(2\mathbf{a}+\mathbf{b}+\mathbf{c})/4$ corresponding to the translational vector $(\mathbf{a}+\mathbf{B}+\mathbf{C})/2$ producing the body-centring of the superposition structure. The result of the symmetry of the single layer and of these translations is the OD-groupoid family:

$$\begin{gathered} P\,1(n)1 \\ \{1(c_{\frac{1}{4}})1\} \end{gathered}$$

and the space group of the corresponding superposition structure is *Ia*. The only other family (space group of superposition structure *I*2/*a*) compatible with the quoted observed facts is

$$\begin{gathered} P\,1(2/n)1 \\ \left\{\ 1\left(\frac{2_2}{c_{\frac{1}{4}}}\right)1\ \right\} . \end{gathered}$$

In either of these cases, a pair of layers linked by the glide operation $c_{\frac{1}{4}}$ indicated in the symbol is geometrically equivalent to a pair linked by a glide operation $c_{\bar{\frac{1}{4}}}$ with translational component in the opposite direction. The disordered structure is characterized by a stacking of layers which is not periodic corresponding to these two possibilities.

Fig. 2(*a*) and (*b*) shows schematically the symmetry of two adjacent layers L_0 and L_1 and the two possibilities for their relative position; Fig. 2(*c*) shows the superposition structure. The higher symmetry $P\,1(2/n)1$ was assumed for the single layer.

Discussion of the position of maxima on the streaks

In either of the two OD-groupoid families deduced above, there exist two essentially different family members of maximum degree of order: one in which all glide operations converting any one layer into the subsequent one have the same translational component [to be called MDO$_1$ if the glide operation is $(c_{\frac{1}{4}})$, MDO$_1'$ if it is $(c_{\bar{\frac{1}{4}}})$], and another (MDO$_2$) in which glide operations $(c_{\frac{1}{4}})$ and $(c_{\bar{\frac{1}{4}}})$ alternate. MDO$_1$, MDO$_1'$ and, in the case of the OD-groupoid family of higher symmetry, MDO$_2$ deserve the name 'of maximum degree', because all triples of consecutive layers are geometrically equivalent and similar statements hold for all quadruples, for quintuples and for higher *n*-tuples. Although in the case of MDO$_2$ in the family of lower symmetry there are two kinds of triples, $(L_{2n},L_{2n+1},L_{2n+2})$ on the one hand and $(L_{2n-1},L_{2n},L_{2n+1})$ on the other, it has to be called a structure of maximum degree of order as well, because no structure is possible containing triples of only one kind.

A pure MDO$_1$ structure would have reflexions at the positions indicated for aenigmatite; MDO$_1'$ would have reflexions at positions with the *k* values for different crosses interchanged. Thus a disordered structure in which regions MDO$_1$ and MDO$_1'$ alternate would have maxima at $k=2n+1$ for all crosses (*i.e.* the narrow maxima of sapphirine from Mautia Hill). A pure MDO$_2$ structure would have reflexions at all crosses $k=2u$ (if referred to the same reciprocal axes $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*$), *i.e.* at the position of the wide maxima of sapphirine from Mautia Hill. Thus the occurrence of the narrow and wide maxima in the diffraction pattern of this mineral is explained by the assumption that in the disordered sample investigated there are present large regions MDO$_1$ and MDO$_1'$ and smaller regions contributing to the reflexions at $k=2n$. The fact that the wide maxima are, at least in diffraction patterns of some samples, more intense than the narrow maxima indicates that the regions MDO$_1$ and MDO$_1'$ occupy, all in all, a smaller volume of the crystal than the regions corresponding to MDO$_2$. The broadness of the maxima at $k=2n$ indicates that the domains contributing to them can only be of very limited thickness, perhaps between 10 and 50 layers each, whereas the coherent regions of MDO$_1$ and MDO$_1'$ must have an extension at least one order of magnitude larger. These observations are in keeping with the hypothesis put forward by one of us (Merlino, 1973) that the samples which show this effect are the results of a solid-state reaction which converts the original MDO$_1$ single crystal or MDO$_1$/MDO$_1'$ twin with large coherent domains gradually into a multitude of narrow coherent domains originating from nuclei of MDO$_2$, MDO$_2'$, MDO$_2''$ and MDO$_2'''$ cropping up independently when the conditions (temperature and/or pressure) change. Here the three dashed MDO$_2$ domains are obtained from the undashed one by shifts of $\mathbf{c}/2$, $(2\mathbf{a}+\mathbf{b}+\mathbf{c})/4$ and $(2\mathbf{a}+\mathbf{b}-\mathbf{c})/4$ respectively plus integral multiples of the lattice constants.

Deduction and discussion of the Fourier transform in its dependence on the structure of a single layer and the stacking of layers

The equipoints of a single layer L_0 are

$$[L_0]=(x,y,z;\ x+\tfrac{1}{2},\bar{y},z+\tfrac{1}{2}) .$$

and thus for its Fourier transform $F_0(h,\eta,l)$

$$F_0(h,\eta,l)=(-1)^{h+l}\,.\,F_0(h,\bar{\eta},l)$$

holds.

All layers are translationally equivalent; the translation converting any layer L_{q-1} into its successor L_q is equal to

$$\mathbf{t}_q=\mathbf{a}/2+\mathbf{b}_0+\beta_q\mathbf{c}/4$$

where β_q is $+1$ or -1, and $\mathbf{b}_0$ is perpendicular to $\mathbf{a}$ and $\mathbf{c}$ but different from the basic vector $\mathbf{b}$ to which the formal indexing referred (see above). η refers to this new scaling.

The equipoints of L_p may now be expressed in terms of the equipoints of L_{p-1} or of L_0:

$$\begin{aligned}[L_p]&=[L_{p-1}]+(\tfrac{1}{2},1,\beta_p/4)\\ &=[L_0]+(p/2,p,\tfrac{1}{4}\sum_{q=1}^{p}\beta_q) .\end{aligned}$$

The sum $\sum\limits_{q=1}^{p}\beta_q$ is even for *p* even, and odd for *p* odd;

we may, therefore, replace it by

$$\sum_{q=1}^{p} \beta_q = 2m_p + p$$

where the numbers m_p are integral and depend on the stacking:

$$[L_p] = [L_0] + (p/2, p, m_p/2 + p/4) .$$

Thus the Fourier transform of a layer L_p is related to the Fourier transform of L_0 by

$$F_p = \exp\left\{2\pi i\left[\left(\frac{h}{2} + \eta + \frac{l}{4}\right)p + \frac{lm_p}{2}\right]\right\} . F_0$$

and the Fourier transform $F(h\eta l)$ of the structure is

$$F(h\eta l) = \sum_p F_p = S(h\eta l) . F_0$$

with

$$S(h\eta l) = \sum_p \exp\left\{2\pi i\left[\left(\frac{h}{2} + \eta + \frac{l}{4}\right)p + \frac{lm_p}{2}\right]\right\} .$$

For l even we obtain with $l = 2L$

$$S(h\eta l) = \sum_p \exp\left\{2\pi i\left[\left(\frac{h+L}{2} + \eta\right) p\right]\right\} .$$

For a large number of layers this expression vanishes except for integral values of $(h+L)/2 + \eta$, *i.e.* except for integral values of $\eta/2$ which we may indicate by

$$\frac{\eta}{2} = K \ (K \text{ integral})$$

and

$$h + K + L = 2n .$$

These conditions are the conditions observed for the sharp reflexions and lead to the appropriate scaling in the **b*** direction. As for the sharp reflexions $k = 2K$, this leads to the relation $k = 4\eta$ or $\eta = k/4$ for all the reflexions and maxima on the streaks. For the maxima, *i.e.* for l odd and $\eta = k/4$ with k integral:

$$S(hkl) = \sum_p \exp\left\{2\pi i\left[\left(\frac{h}{2} + \frac{k+l}{4}\right)p + \frac{lm_p}{2}\right]\right\} .$$

For the narrow maxima corresponding to MDO_1 and MDO_1' respectively:

$$S(hkl) = \sum_p (-1)^{\left(h + \frac{k+l}{2}\right)p + m_p} .$$

With the abbreviations

$$\sum_{p'} (-1)^{m_{2p'}} = R \quad \text{and} \quad \sum_{p''} (-1)^{m_{2p''+1}} = Q$$

this becomes

$$S(hkl) = R + (-1)^{h + \frac{k+l}{2}} Q$$

or

$$S(hkl) = R + Q \text{ for } 2h + k + l = 4n$$

$$S(hkl) = R - Q \text{ for } 2h + k + l = 4n + 2 .$$

If, therefore, as in the diffraction pattern of aenigmatite, the reflexions with $2h + k + l = 4n$ are missing, we may conclude that $R = -Q$; if the whole intensity distribution, including the narrow maxima, shows monoclinic symmetry, this may either be because $R = 0$, because $Q = 0$ or because there is a statistical distribution of mosaic regions with various R and Q values.

For the wide maxima of the Mautia Hill sample and the reflexions of sapphirine, $k = 2n$ and thus

$$\begin{aligned} S(hkl) &= \sum_p (-1)^{(h+k)p + m_p}\, i^{lp} \\ &= \sum_{p'} (-1)^{m_{2p'} + p'} + i^l \sum_{p''} (-1)^{h+k+m_{2p''+1}+p''} . \end{aligned}$$

Thus for all sets of points with l odd and k even the absolute value $|S(hkl)|$ is the same.

Aenigmatite and sapphirine as OD structures

The close structural relations between aenigmatite and sapphirine are reflected in the relationship between their unit cells. In fact the triclinic aenigmatite cell with $a = 10{\cdot}406$, $b = 10{\cdot}813$, $c = 8{\cdot}926$ Å, $\alpha = 104°56'$, $\beta = 96°52'$, $\gamma = 125°12'$ (Kelsey & McKie, 1964) can be described in terms of a fourfold pseudo-monoclinic cell, plainly related to those of sapphirine and Mautia sapphirine (Table 1).

The crystal structure of aenigmatite was obtained by Merlino (1970) assuming that the asymmetric unit of this mineral, apart from its chemical composition, would be the same as that of sapphirine. Thus if we can prove that aenigmatite is actually an OD structure, we prove at the same time that sapphirine is also an OD structure.

In Table 2 we give the atomic coordinates in aenigmatite referred to the triclinic cell as well as the corresponding coordinates referred to the monoclinic cell as given in the present work (transformation matrix $[00\bar{1}/\frac{1}{2}\frac{1}{4}\frac{3}{4}/\frac{1}{2}\frac{\bar{1}}{4}\frac{1}{4}]$). The triclinic coordinates were derived from those given by Fang, Robinson & Ohya in the paper of Cannillo *et al.* (1971), because of their low standard deviations. The following modifications were made:

(1) The origin was translated $+\mathbf{b}/2$ relative to the old one;

(2) Some atoms were substituted by symmetry-equivalent atoms.

The substitutions used are given in Table 3, the resulting atomic coordinates (with the Roman numeral indicating the substitution used) in Table 2, with reference to the triclinic and fourfold pseudo-monoclinic cell. It can be observed that all the atoms have y_m coordinates with values $|y_m| \le \frac{1}{8}$, which assures that all the atoms listed belong to the same layer L_0.

Every atom of the list has a symmetry-related atom at coordinates x_m, y_m, z_m (space group $P\bar{1}$), apart from M(1) and M(2) which are located on inversion centres. It can be observed that in general the atoms can be collected in groups of four atoms with coordinates approximately related to each other as x_m, y_m, z_m; $\frac{1}{2}-x_m, y_m, \frac{1}{2}-z_m$; $\bar{x}_m, \bar{y}_m, \bar{z}_m$ and $\frac{1}{2}+x_m, \bar{y}_m, \frac{1}{2}+z_m$, as to be expected for atoms of a layer with plane space group $P1(2/n)1$ which is indicated by the OD-groupoid family deduced above. As noted above M(1) and M(2) lie on symmetry centres at $\frac{1}{2},0,\frac{1}{2}$, and 0,0,0, respectively; M(5), M(6) and M(7) deviate only slightly from the special positions on the twofold axes and are approximately related through an *n*-glide plane to the equivalent atoms at x_m, y_m, z_m. Thus all the atoms of the layer conform to the ideal symmetry $P2/n$. The deviations from this symmetry are fairly small (mean value 0·08 Å), although statistically highly significant, as compared with the standard deviations in atomic coordinates.

The largest deviations from the ideal symmetry are presented by the two atom pairs 0(8), 0(20) and 0(10), 0(19), 0·18 Å and 0·22 Å respectively. This can be easily understood, as these oxygen atoms with coordinates $|y_m| \simeq \frac{1}{8}$ lie in the outskirts of the layer.

Twinning in aenigmatite and aenigmatite-like minerals

It is well known that aenigmatite of volcanic paragenesis is characteristically polysynthetically twinned on a submicroscopic scale with the *b* axis of the pseudo-

Table 1. *Pseudo-monoclinic cell of aenigmatite compared with the cells of sapphirine and Mautia sapphirine*

	a	*b*	*c*	*β*
Aenigmatite	10·141 Å	29·629 Å	10·406 Å	107°43′ (1)
Sapphirine	9·77	14·54	10·06	110°20′ (2)
Mautia sapphirine	9·85	28·6	9·96	110°30′ (3)

(1) Merlino (1971)
(2) Fleet (1967)
(3) McKie (1963)

Table 2. *Atomic coordinates of aenigmatite, referred to the triclinic and to the fourfold monoclinic cell*

Standard deviations are given in parentheses.
Symmetry equivalent positions are given in Table 3.

	Coordinates in the triclinic cell			Coordinates in the monoclinic cell		
	x	y	z	$x_m=(y+z)/2$	$y_m=(y-z)/4$	$z_m=-x+(3y+z)/4$
M(1) (i)	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	0
M(2)	0	0	0	0	0	0
M(5)	0·0961 (4)	0·4392 (3)	0·0530 (3)	0·2461 (2)	0·0966 (1)	0·2466 (5)
M(6)	0·5959 (3)	0·4432 (3)	0·0661 (3)	0·2547 (2)	0·0943 (1)	−0·2470 (4)
M(7) (ii)	−0·0030 (4)	0·2434 (4)	0·2577 (3)	0·2506 (3)	−0·0036 (1)	0·2500 (5)
M(3) (ii)	−0·6786 (3)	0·3528 (3)	0·1779 (3)	0·2654 (2)	0·0437 (1)	0·9878 (4)
M(4)	0·7655 (3)	0·3199 (3)	0·1511 (3)	0·2355 (2)	0·0422 (1)	−0·4878 (4)
Na(1) (ii)	−0·7911 (8)	0·1298 (8)	0·3893 (7)	0·2596 (5)	−0·0649 (3)	0·9858 (10)
Na(2)	0·6607 (8)	0·1117 (9)	0·3741 (8)	0·2492 (6)	−0·0656 (3)	−0·4834 (11)
T(1) (iii)	0·5232 (5)	0·2655 (5)	0·6687 (5)	0·4671 (4)	−0·1008 (2)	−0·1569 (6)
T(4) (ii)	−0·7228 (5)	−0·1618 (5)	0·2252 (5)	0·0317 (4)	−0·0968 (2)	0·6578 (6)
T(2) (iii)	0·0136 (5)	0·2637 (5)	0·6534 (5)	0·4586 (4)	−0·0974 (2)	0·3475 (6)
T(3) (ii)	−0·2079 (5)	−0·1565 (5)	0·2416 (4)	0·0426 (3)	−0·0995 (2)	0·1509 (6)
T(5)	0·6487 (5)	0·4448 (5)	0·4447 (5)	0·4448 (4)	0·0000 (2)	−0·2039 (6)
T(6) (ii)	−0·6472 (5)	0·0588 (5)	0·0501 (5)	0·0545 (4)	0·0022 (2)	0·7038 (6)
O(1) (iv)	−0·6458 (14)	0·5641 (14)	0·1621 (13)	0·3631 (10)	0·1005 (5)	1·1094 (18)
O(12) (v)	0·8430 (14)	0·3312 (14)	−0·0612 (12)	0·1350 (9)	0·0981 (5)	−0·6099 (18)
O(2) (i)	0·8611 (14)	0·5666 (13)	0·1807 (12)	0·3737 (9)	0·0965 (5)	−0·3910 (17)
O(11) (vi)	−0·6653 (14)	0·3256 (14)	−0·0709 (12)	0·1274 (9)	0·0991 (5)	0·8918 (18)
O(3) (ii)	−0·4460 (15)	0·4534 (15)	0·2958 (13)	0·3746 (10)	0·0394 (5)	0·8600 (19)
O(13)	0·5233 (15)	0·2108 (14)	0·0393 (12)	0·1251 (9)	0·0429 (5)	−0·3554 (19)
O(4) (vii)	1·0151 (15)	0·4258 (15)	0·2670 (13)	0·3464 (10)	0·0397 (5)	−0·6290 (19)
O(5) (ii)	0·7647 (15)	0·3747 (14)	0·3933 (13)	0·3840 (10)	−0·0047 (5)	1·1441 (19)
O(16)	0·7510 (14)	0·1018 (15)	0·1275 (13)	0·1147 (10)	−0·0064 (5)	−0·6428 (18)
O(6)	0·7541 (15)	0·3843 (14)	0·3902 (13)	0·3873 (10)	−0·0015 (5)	−0·3683 (19)
O(15) (ii)	−0·7583 (15)	0·1060 (16)	0·1120 (13)	0·1090 (10)	−0·0015 (5)	0·8658 (19)
O(7) (viii)	−0·4929 (15)	0·3052 (15)	0·5027 (13)	0·4040 (10)	−0·0494 (5)	0·8475 (19)
O(17)	0·4002 (14)	0·0015 (14)	0·1883 (12)	0·0949 (9)	−0·0467 (5)	−0·3520 (18)
C(8)	0·9575 (14)	0·2755 (14)	0·4871 (12)	0·3813 (9)	−0·0529 (5)	−0·6291 (18)
O(18) (ix)	−1·0637 (16)	0·0147 (16)	0·2264 (14)	0·1206 (11)	−0·0529 (5)	1·1313 (20)
O(9) (viii)	−0·8996 (15)	0·1770 (14)	0·6265 (13)	0·4018 (10)	−0·1124 (5)	1·1890 (19)
O(20)	0·6731 (15)	−0·1374 (15)	0·3366 (13)	0·0996 (10)	−0·1185 (5)	−0·6920 (19)
O(10) (iii)	0·5966 (15)	0·1636 (15)	0·6471 (13)	0·4054 (10)	−0·1209 (5)	−0·3121 (19)
O(19) (ii)	−0·8352 (14)	−0·1351 (14)	0·3183 (12)	0·916 (9)	−0·1134 (5)	0·8153 (18)

Table 3. *Indication of the symmetry-equivalent atom taken for the calculation of* x_m, y_m, z_m (*Table* 2)

The atomic coordinates given by Fang, Robinson & Ohya are called $x, y+\frac{1}{2}, z$

	x	y	z
i	x	$1+y$	z
ii	$-1+x$	y	z
iii	$1-x$	$-y$	$1-z$
iv	$-1+x$	$1+y$	z
v	$1-x$	$-y$	$-z$
vi	$-x$	$-y$	$-z$
vii	$1+x$	y	z
viii	$-x$	$-y$	$1-z$
ix	$-2+x$	y	z

monoclinic cell as twin axis (Kelsey & McKie, 1964).

Similar polysynthetic twinning occurs in two other minerals, isostructural with aenigmatite, namely rhönite, $Ca_2(Mg,Fe^{+2})_4Fe^{+3}TiAl_3Si_3O_{20}$, (Walenta, 1969) and krinovite, $Na_2Mg_4Cr_2Si_6O_{20}$, (Merlino, 1972). The diffraction patterns of such twins (Walenta, 1969; Merlino, 1972) show that they are built of alternating ordered regions with structures MDO$_1$ and MDO$_1'$ with common boundary layers. This twinning is in keeping with the definition of OD twins by Dornberger-Schiff & Grell-Niemann (1961).

We may thus conclude that sapphirine, Mautia sapphirine and aenigmatite are members of isomorphous families of OD structures, and that the same is probable – in spite of their very different chemical composition – of rhönite and krinovite.

Aenigmatite and sapphirine are ordered members of their family, Mautia sapphirine is a disordered member. The twinned structures of aenigmatite, rhönite and krinovite correspond to an intermediate degree of ordering: the twin individuals may be considered as periodic OD structures, but the twins are non-periodic OD structures, as the twinning violates the periodicity.

References

Cannillo, E., Mazzi, F., Fang, J. H., Robinson, P. D. & Ohya, Y. (1971). *Amer. Min.* **56**, 427–446.

Dornberger-Schiff, K. (1956). *Acta Cryst.* **9**, 593–601.

Dornberger-Schiff, K. (1964). *Abh. dtsch. Akad. Wiss. Kl. Chem. Geol. Biol.* **3**.

Dornberger-Schiff, K. (1966). *Lehrgang über OD-Strukturen.* Berlin: Akademie Verlag.

Dornberger-Schiff, K. & Grell-Niemann, H. (1961). *Acta Cryst.* **14**, 167–177.

Fleet, S. G. (1967). *Miner. Mag.* **36**, 449–450.

Kelsey, C. H. & McKie, D. (1964). *Miner. Mag.* **33**, 986–1001.

McKie, D. (1963). *Miner. Mag.* **33**, 635–645.

Merlino, S. (1970). *Chem. Commun.* pp. 1288–1289.

Merlino, S. (1972). *Z. Kristallogr.* **136**, 81–88.

Merlino, S. (1973). *Contrib. Miner. Petrol.* In the press.

Moore, P. B. (1968). *Nature, Lond.* **218**, 81–82.

Moore, P. B. (1969). *Amer. Min.* **54**, 31–49.

Walenta, K. (1969). *Z. Kristallogr.* **130**, 214–230.

Acta Cryst. (1974). A**30**, 173

On the Non-Centrosymmetric Structures which Produce Centrosymmetric Diffraction Patterns even with Anomalous Dispersion

By Hitoshi Iwasaki

The Institute of Physical and Chemical Research, Rikagaku Kenkyusho, Wako-shi, Saitama 351, Japan

(*Received* 7 *July* 1973; *accepted* 11 *September* 1973)

The geometrical conditions that a structure gives centrosymmetric diffraction patterns have been investigated. It is shown that Friedel's law may hold for certain non-centrosymmetric structures containing two or more kinds of anomalous scatterer. Therefore, their absolute configurations can never be established by ordinary absorption-edge techniques. The geometrical characteristics of such a structure are discussed in terms of a vector set.

Introduction

When a non-centrosymmetric crystal contains anomalous scatterers for a given incident radiation Friedel's law does not hold and the crystal will give non-centrosymmetric diffraction patterns with a symmetry which is in general proper to the point group of the crystal. However, there may be exceptions. An obvious exception is found in the well-known fact that the diffraction patterns from a non-centrosymmetric crystal are always centrosymmetric even with anomalous dispersion when the crystal consists of only one kind of atom [*i.e.* the crystal of an element, such as α-manganese (space group $I\bar{4}3m$), metallic selenium and tellurium (both $P3_121$ or $P3_221$)].

In the present paper, it is pointed out that there may exist certain kinds of non-centrosymmetric structures, other than elements, for which Friedel's law is always valid even in the case involving X-ray anomalous dispersion.