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.

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

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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.

Conditions for Friedel's law

Let us consider a crystal containing N kinds of atoms. The crystal can be divided into N substructures so that the pth substructure, S_p, is composed of atoms of only the pth kind. If the origin of S_p is chosen according to a convenience due to the symmetry of S_p, the structure amplitude F for a reflexion with a given index $\mathbf{h}$ is written as follows:

$$\begin{aligned} F(\mathbf{h}) &= \textstyle\sum_p F_p(\mathbf{h}) \exp (2\pi i\mathbf{h} \, . \, \mathbf{u}_p) \\ &\equiv \textstyle\sum_p f_p(\mathbf{h}) G_p(\mathbf{h}) \exp (2\pi i\mathbf{h} \, . \, \mathbf{u}_p) \,, \end{aligned} \qquad (1)$$

where $\mathbf{u}_p$ is the vector from the origin of the crystal to that of S_p, f_p is the atomic scattering factor for atoms in S_p, and F_p and G_p are the structure factor and effective geometrical structure factor for S_p respectively.† The summation is taken over substructures. Generally f_p has a form

$$\begin{aligned} f_p &= f_p^0 + \Delta f_p' + i\Delta f_p'' \\ &\equiv f_p' + if_p'' \,. \end{aligned}$$

We assume here that $f'' \neq 0$, hence‡

$$f(\mathbf{h}) = f(-\mathbf{h}) \neq f^*(-\mathbf{h}) \qquad (2)$$

while

$$G(\mathbf{h}) = G^*(-\mathbf{h}) \,. \qquad (3)$$

Using relations (1), (2) and (3), we obtain

$$\begin{aligned} \Delta I &\equiv |F(\mathbf{h})|^2 - |F(-\mathbf{h})|^2 \\ &= -4 \textstyle\sum_{p>q} (f_p'' f_q' - f_q'' f_p') \, . \, \mathrm{Im} \, [G_p(\mathbf{h}) G_q^*(\mathbf{h}) \\ &\quad \times \exp \{2\pi i\mathbf{h} \, . \, (\mathbf{u}_p - \mathbf{u}_q)\}] \,, \end{aligned} \qquad (4)$$

where $\mathrm{Im}(z)$ is the imaginary part of z.

Now, define the phase factor α_p by

$$G_p = |G_p| \exp (i\alpha_p) \,.$$

Then, ΔI vanishes and Friedel's law holds if either

$$G_p = 0 \quad \text{for all } p \text{ except for one,} \qquad (5\text{-}1)$$

or

$$\alpha_p - \alpha_q + 2\pi\mathbf{h} \, . \, (\mathbf{u}_p - \mathbf{u}_q) = n\pi \quad (n\text{: integer}) \qquad (5\text{-}2)$$

for any combination of p and q, for any $\mathbf{h}$.

Examples

Equation (4) states that: (i) a centrosymmetric crystal always gives centrosymmetric diffraction patterns, since all $\mathbf{u}_p$'s can be taken to be (000) and G_p's are real, (ii) $\Delta I = 0$ if the crystal contains no anomalous scatterers, and (iii) a crystal consisting of only one kind of atom gives always centrosymmetric diffraction patterns.§ In this section, we examine several structures, other than these three cases, for which Friedel's law is always valid. For simplicity, crystals containing only two kinds of atom are considered. In this case we can take $\mathbf{u}_1 = (000)$ and $\mathbf{u}_2 = \mathbf{u}$; and the conditions for Friedel's law are given by

$$G_1 = 0 \qquad (6\text{-}1)$$

or

$$G_2 = 0 \qquad (6\text{-}2)$$

or

$$\alpha_1 - \alpha_2 - 2\pi\mathbf{h} \, . \, \mathbf{u} = n\pi \qquad (6\text{-}3)$$

for any $\mathbf{h}$.

(i) *Crystals consisting of two geometrically identical substructures*

First, assume that the geometrical structures of two substructures are exactly the same. The conditions (6) become

$$G_1 = G_2 = 0 \qquad (7\text{-}1)$$

or

$$\mathbf{h} \, . \, \mathbf{u} = n/2 \qquad (7\text{-}2)$$

for any $\mathbf{h}$. The relation (7-1) is trivial. The combination of two centrosymmetric substructures under the condition (7-2) always gives a centre of inversion to the crystal. On the other hand, under the same condition, two non-centrosymmetric substructures form a non-centrosymmetric composite structure for which Friedel's law always holds irrespective of the space-group symmetry of the substructures presumed.

Fig. 1 illustrates one of the simplest examples of this type. The space-group is $P2_1$ (b axis unique), and $\mathbf{u} = (0,\frac{1}{2},0)$.

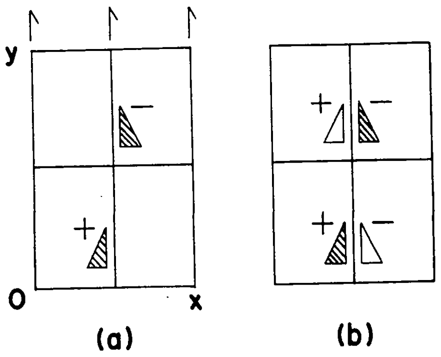

Fig. 1. A simple example of the non-centrosymmetric structure which gives centrosymmetric diffraction patterns. (a) Basic substructure with the space group $P2_1$, comprised of polar 'molecules' as represented by triangles. (b) A composite structure consisting of two substructures with $\mathbf{u} = (0,\frac{1}{2},0)$. Shaded and open triangles compose the substructures 1 and 2 respectively. The structure is non-centrosymmetric, while Friedel's law holds even with anomalous dispersion.

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† $\mathbf{h} \equiv (hkl)$; $\mathbf{u} \equiv (uvw)$; uvw as fractions.

‡ Note that $f(\mathbf{h}) = f^*(-h)$ if the imaginary part of f is due only to the effect of bonding electrons or acentric thermal vibrations of the atom. In that case Friedel's law holds.

§ For the case of an element in which atoms in different crystallographic sites are in different bonding states, see Chandrasekaran (1968).

(ii) *Two different non-centrosymmetric substructures*

Even when a crystal is composed of two different non-centrosymmetric substructures S_1 and S_2, the relation (6-3) may hold if a proper systematic correlation exists between α_1 and α_2. For example, assume that S_1 and S_2 have face-centred and body-centred structures respectively, both being derived from the geometrically identical primitive cell. In this case $G_1=2G_2$ for reflexions with all even hkl, and for these reflexions equation (6-3) reduces to

$$\mathbf{h}\,.\,\mathbf{u}=n/4\,.$$

For reflexions of other types, either (6-1) or (6-2) is valid.

(iii) *One centrosymmetric substructure S_1 and one non-centrosymmetric substructure S_2*

In this case we may take $\mathbf{u}=(000)$. The relation (6-3) reduces to

$$\alpha_2=0 \quad \text{or} \quad \pi\,.$$

The conditions for Friedel's law are satisfied if, for example, S_1 is face-centred, S_2 is body-centred and if all the xyz parameters in S_2 are limited to multiples of $\frac{1}{4}$ as shown in Fig. 2.

(iv) *Two different centrosymmetric substructures*

In this case, equation (6-3) becomes

$$\mathbf{h}\,.\,\mathbf{u}=n/2\,. \tag{8}$$

Non-centrosymmetric structures for which the relations (6-1), (6-2) or (8) are valid do exist. Consider a hexagonal crystal with atoms in the following positions (coordinates referred to each origin of the substructure):

$$\begin{aligned} S_1\colon &\quad \pm(\tfrac{2}{3},\tfrac{1}{3},\tfrac{1}{4});\\ S_2\colon &\quad \pm(\tfrac{1}{3},\tfrac{1}{3},\tfrac{1}{4};\quad \tfrac{2}{3},0,\tfrac{1}{4};\quad 0,\tfrac{2}{3},\tfrac{1}{4});\\ &\quad \mathbf{u}=(0,0,\tfrac{1}{4})\,. \end{aligned}$$

The space group is $P6_322$. It is seen that

$$\begin{aligned} F_1&=0 \quad \text{if } h-k=3n \quad \text{and} \quad l=2n+1\,;\\ F_2&=0 \quad \text{if } h-k\neq 3n\,; \end{aligned}$$

and the equation (8) is satisfied if $h-k=3n$ and $l=2n$. Therefore, Friedel's law always holds for this structure. In a structure of this type, the local symmetry seems to be reflected in the symmetry of diffraction patterns.

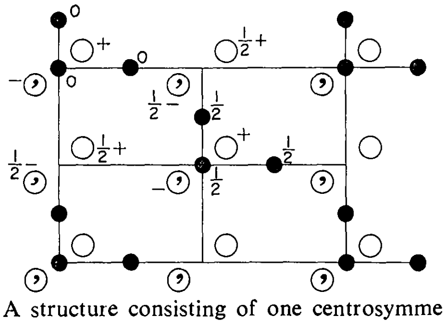

Fig. 2. A structure consisting of one centrosymmetric and one non-centrosymmetric substructure. Substructure 1: face-centred, centrosymmetric, indicated by open circles. Substructure 2: body-centred, non-centrosymmetric, composed of black circles. The composite structure is non-centrosymmetric and gives centrosymmetric diffraction patterns.

The symmetry of the above structure reduces to space group $P6_3$ when $\mathbf{u}$ is shifted to $(00z)$. It is interesting that this deviated structure gives diffraction patterns with a higher Laue symmetry: $6/mmm$ (Iwasaki, 1972).

Vector set and Friedel's law

In this section, geometrical characteristics of a structure, for which Friedel's law holds even with anomalous dispersion, are pointed out. The basic idea is an extension of that involved in the explanation of the diffraction enhancement of symmetry given by Sadanaga & Ohsumi (1974).

Let $\mathbf{u}_{pq}$ be the vector from the qth atom to the pth atom. When anomalous dispersion is not involved, the Patterson peaks corresponding to $\mathbf{u}_{pq}$ and $\mathbf{u}_{qp}$ have the same value, and as far as the diffraction effect is concerned, $\mathbf{u}_{pq}$ is equivalent to $\mathbf{u}_{qp}$. The situation is similar even with anomalous dispersion when the pth and qth atoms are of the same kind, since the phase difference of the X-rays diffracted by these two atoms is determined by their path difference alone. These vectors are 'colourless' in the sense that they are irrelevant to the Bijvoet differences. When all the vectors in a crystal are colourless, the symmetry of the vector set is represented by a certain ordinary (colourless) space group, and usual Friedel's law holds. The case of a crystal of an element is, of course, included in this category.

If different anomalous scatterers are concerned, however, $\mathbf{u}_{pq}$ and $\mathbf{u}_{qp}$ become not equivalent. The imaginary part of the Patterson function, $P_s(\mathbf{u})$, has peaks proportional to $\Delta_{pq}=f''_qf'_p-f''_pf'_q$ and to Δ_{qp} at $\mathbf{u}=\mathbf{u}_{pq}$ and $\mathbf{u}_{qp}$, respectively (Okaya, Saito & Pepinsky, 1955). In conformity with the fact that the function P_s is the Fourier transform of ΔI, the vectors between different kinds of atoms are responsible for the violation of Friedel's law. For simplicity, let us consider a structure consisting of two kinds of atoms and let us call them 'black' and 'white' atoms. According to the P_s peaks at $\mathbf{u}_{pq}$ and $\mathbf{u}_{qp}$, it is very natural to designate a vector from a black atom to a white atom a 'black' vector, and the one from a white to black atoms a 'white' vector. (Note that a black vector is always transformed into a black vector, not white, by an inversion of the coordinate system.) The distribution of these black and white vectors has at least a symmetry of anti-inversion. In a centrosymmetric crystal, black and white vectors with the same magnitude and direction (including sense) always coexist, and the symmetry of the vector set is represented by a 'grey' space group. In a non-centrosymmetric crystal, on the other hand, some white vectors may be eclipsed by black ones while others not; and the black-and-white vector set is generally a superposition of an antisymmetric part and a centrosymmetric grey part, the symmetry of the former being represented by a certain black-and-white space group. In such a case Friedel's law breaks down.

In a structure as treated in the present paper, the black and white vectors as a whole form a complete 'grey' set as in a centrosymmetric crystal. In fact, if Friedel's law holds, P_s must vanish over the entire range of $\mathbf{u}$, and this means that each black vector must have its own white mate with the same magnitude and direction and sense. Such a circumstance can be seen, for example, by inspection of Figs. 1 and 2. In summarizing, Friedel's law holds for any crystal involving two kinds of anomalous scatterers, if the symmetry of a black-and-white vector set as defined above is represented by a certain 'grey' space group.

Conclusion

It has been shown that Friedel's law may hold in certain non-centrosymmetric structures other than crystals of elements, even with the anomalous dispersion. For such a crystal, if one exists, the absolute configuration cannot be determined by the conventional X-ray absorption-edge techniques. The point group of such a crystal cannot be detected by a statistical treatment of intensity differences between possible Bijvoet pairs (Ibers, 1967). No structure of this type seems so far to have been recorded, though one may be found in future.

It should be noted that the condition (6-3) is always satisfied for reflexions with some special indices, if the *xyz* parameters of all atoms, as well as the three components of $\mathbf{u}$, are certain rational fractions of the cell edges. For example, the well known zinc-blende structure (space group $F\bar{4}3m$) consists of two geometrically identical substructures with $\mathbf{u}=(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. Thus, the relation (6-3) holds if indices *hkl* are all even. The centric intensity distribution in these reflexions, in part, arises entirely from the special arrangement of atoms or of substructures. A partial Friedel's law of this type, not as a result of the space-group symmetry, is quite common in a number of crystals of inorganic compounds.

In connexion with this it should be added also that Friedel's law may hold to a very good approximation in several non-centrosymmetric molecular crystals. Practically this problem is sometimes important. Consider a crystal containing atoms of a large atomic number and non-anomalous light atoms. When the heavy atoms are arranged with a certain kind of symmetry higher than that of the crystal, they contribute only to reflexions with certain special indices according to the local symmetry. In such a case, these reflexions often exhibit pseudocentric patterns owing to the large contribution of heavy atoms to diffracted intensities, whereas other reflexions show partially centrosymmetric diffraction patterns. In a 'pseudo-Friedel' case of this type, some difficulties may occur in the determination of the absolute configuration.

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Systematic Errors in Polarization Corrections for Crystal-Monochromatized Radiation

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The polarization expressions for crystal-monochromatized radiation have been evaluated for both molybdenum and copper radiations under a variety of conditions in order to show the magnitude of the systematic error introduced by the use of an inappropriate expression. The effect of the polarization expression on the extinction correction is also discussed.

The expression for the polarization correction for crystal-monochromatized radiation is well known for the case of the double-crystal spectrometer. In this geometry, hereinafter referred to as 'normal' geometry, the monochromator crystal lies in the equatorial plane of a three- or four-circle diffractometer with its rotation axis perpendicular to the equatorial plane. The beam incident on the monochromator crystal is randomly polarized and thus can be represented as the sum of two equal components polarized parallel ($\chi=90°$) and perpendicular ($\chi=0°$) to the equatorial plane of the diffractometer. The relative intensities of the components are:

$$I_{\parallel}=I_{\perp}=\tfrac{1}{2}I_0 .$$

Since the intensity of radiation diffracted in a particular direction is proportional to $\sin^2\varphi$, where φ is the angle between the electric vector and the direction of ob-