

The Negative-Quartet Relation from Electron-Density Considerations

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Abstract

On the basis of electron-density considerations, graphic explanations are given of triplets and positive and negative quartets. It is shown that the number of useful negative relations will always be much smaller than the number of useful positive relations.

Introduction

The most important relation used in direct methods is the triplet or \sum_2 relation:

$$\varphi_{\mathbf{H}} + \varphi_{\mathbf{K}} + \varphi_{-\mathbf{H}-\mathbf{K}} \simeq 0 \quad (1)$$

for large values of

$$E_3 = N^{-1/2} |E_{\mathbf{H}} E_{\mathbf{K}} E_{-\mathbf{H}-\mathbf{K}}|. \quad (2)$$

Although the triplet relation in its centrosymmetric form is already implicitly present in the Harker–Kasper inequalities (Harker & Kasper, 1948) and the determinant inequalities of Karle & Hauptman (1950), the first explicit formulation was given by Sayre (1952), Cochran (1952) and Zachariasen (1952). The non-centrosymmetric form of (1) was first formulated by Cochran (1955), although again this expression was implicitly present in many older papers.

Structures can be phased reliably with (1). In symmorphic space groups (*e.g.* $P1$, $P1$) and polar space groups (*e.g.* $P2_1$), however, the most consistent solution often is an artefact. Also, the selection of a good set of reflections to start a phase determination with (1) is too often a problem. In such cases additional information is necessary to arrive at the solution of the phase problem and this information may be obtained from quartet relations:

$$\varphi_{\mathbf{H}} + \varphi_{\mathbf{K}} + \varphi_{\mathbf{L}} + \varphi_{-\mathbf{H}-\mathbf{K}-\mathbf{L}} = p \quad (3)$$

for large values of

$$E_4 = N^{-1} E_{\mathbf{H}} E_{\mathbf{K}} E_{\mathbf{L}} E_{-\mathbf{H}-\mathbf{K}-\mathbf{L}}, \quad (4)$$

in which p may have any value. The following special cases can be distinguished.

(1) $p \simeq 0$

For large values of E_4 the most probable value of p is 0. This relationship, now commonly referred to as a positive quartet, was already known as the \sum_5 formula (Hauptman & Karle, 1953) and independently it was derived by Simerska (1956). Later it was shown (Schenk, 1973*a*) that, for a successful application, it is of paramount importance to include the cross terms $\mathbf{H} + \mathbf{K}$, $\mathbf{K} + \mathbf{L}$ and $\mathbf{H} + \mathbf{L}$. Only when these terms are strong does the positive quartet give a reliable indication.

(2) $p \simeq \pi$

Again, for large E_4 , but now for small values of the cross terms, the negative-quartet relation with $p = \pi$ is obtained (Hauptman, 1974; Schenk, 1974).

(3) $p \simeq \pm\pi/2$

For large E_4 and moderate values of $|E_{\mathbf{H}+\mathbf{K}}|$, $|E_{\mathbf{K}+\mathbf{L}}|$ and $|E_{\mathbf{H}+\mathbf{L}}|$ these enantiomorph-specific quartets are found (Hauptman, 1975), which can be used in an enantiomorph-specific figure of merit (FOM) to be used in space groups like $P2_1$ (van der Putten & Schenk, 1979).

The precursor of the negative-quartet relation was the two-dimensional analogue (Schenk & de Jong, 1973; Schenk, 1973*b*)

$$\varphi_{\mathbf{H}} + \varphi_{\mathbf{H}} + \varphi_{-\mathbf{H}+\mathbf{K}} + \varphi_{-\mathbf{H}-\mathbf{K}} \simeq \pi \quad (5)$$

for large $|E_{\mathbf{H}}|$, $|E_{-\mathbf{H}+\mathbf{K}}|$ and $|E_{-\mathbf{H}-\mathbf{K}}|$ and small $|E_{\mathbf{K}}|$.

Although this relation followed from a generalization of one of the Harker–Kasper inequalities in $P1$, it was shown by a graphical method to hold for any space group (Schenk, 1973*b*).

The main object of this paper is to explain the negative-quartet relationship (4) with $p \simeq \pi$ in terms of the electron-density distribution in the crystal. Similar treatments will be given for the triplets of the \sum_2 relationships, the special negative quartet (5) and the positive-quartet relationship (4) with $p \simeq 0$. Simple physical pictures such as this are attractive for teaching purposes (*e.g.* Schenk, 1971, 1979), and may, moreover, point the way for new developments (*e.g.* Schenk, 1973*b*).

Strong and weak structure factors

If the atoms lie in the neighbourhood of the set of planes **H**, as indicated in Fig. 1(a), the reflection has a large intensity, while the intensity is small if the atoms are randomly distributed (Fig. 1b). This follows directly from the structure factor expression

$$F_{\mathbf{H}} = |F_{\mathbf{H}}| \exp i\varphi_{\mathbf{H}} = \sum_{j=1}^N f_j \exp [2\pi i(hx_j + ky_j + lz_j)] \quad (6)$$

because a large $F_{\mathbf{H}}$ will only be found if the atoms lie near positions for which $hx_j + ky_j + lz_j \simeq \text{constant}$ for all j . Conversely, a strong intensity of **H** implies that the electron density will peak in planar regions which lie $d_{\mathbf{H}}$ apart. The choice of the origin with respect to these planar regions of electron density defines the phase $\varphi_{\mathbf{H}}$ in (6).

Large and small structure factor amplitudes thus may be used to predict where in the unit cell electron density can approximately be expected.

Large $|E_{\mathbf{H}}|$, $|E_{\mathbf{K}}|$ and $|E_{-\mathbf{H}-\mathbf{K}}|$: the triplet relationship

If two reflections **H** and **K** are both strong then the electron density is likely to be found in the

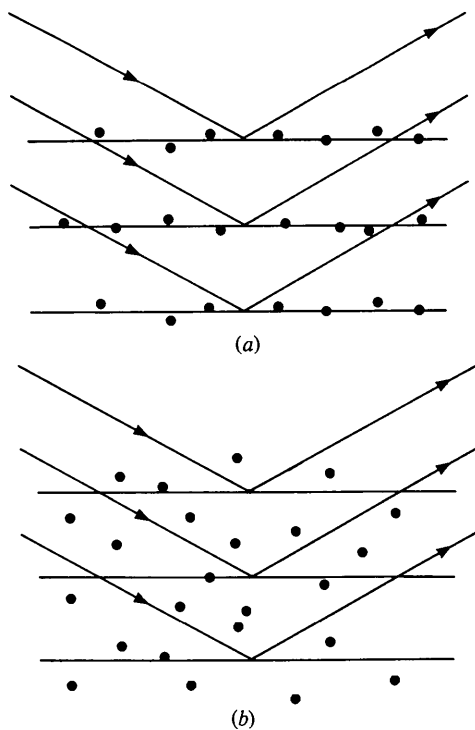


Fig. 1. A reflected beam has a high intensity when the atoms lie in the neighbourhood of the set of planes **H** (a) and a weak intensity when the atoms are spread out randomly with respect to the planes **H** (b).

neighbourhood of both sets of equidistant planes **H** and **K**, that is to say the electron density will be found near the lines of intersection of the planes **H** and **K** as indicated in projection in Fig. 2. A large $|E|$ for the reflection $-\mathbf{H} - \mathbf{K}$ implies furthermore that the electron density will also peak in planes lying $d_{-\mathbf{H}-\mathbf{K}}$ apart. It is therefore most likely that these planes run through the lines of intersection of the planes **H** and **K**, in other words that the three sets of planes have their lines of intersection in common (Fig. 2).

By choosing an origin *O* at an arbitrary point the triplet phase relationship can be found from a planimetric theorem, proved in Fig. 3:

$$AO/AD + BO/BE + CO/CF = 2, \quad (7)$$

which is equivalent to

$$\varphi_{-\mathbf{H}-\mathbf{K}} + \varphi_{\mathbf{H}} + \varphi_{\mathbf{K}} = 0 \text{ (modulo } 2\pi\text{)}. \quad (8)$$

Since the origin is arbitrary (8) is completely general; relations of this type are usually called structure invariants, although a better name would be origin invariants.

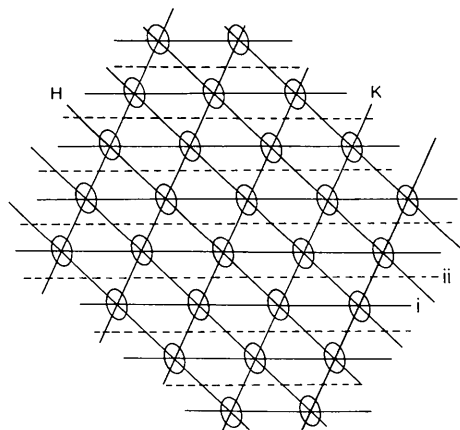


Fig. 2. If the reflections **H** and **K** both have a high intensity, then the electron density will probably lie in the neighbourhood of the intersecting lines of the two sets of equidistant planes defined by **H** and **K**. When $-\mathbf{H} - \mathbf{K}$ is also a strong reflection it is more likely that the planes of high density of $-\mathbf{H} - \mathbf{K}$ run through the intersecting lines (planes *i*) than just in-between (planes *ii*).

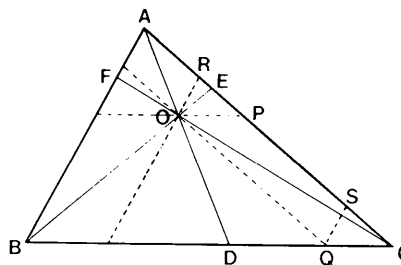


Fig. 3. In an arbitrary triangle *ABC* an origin *O* has been chosen arbitrarily. Theorem: $AO/AD + BO/BE + CO/CF = 2$. Proof: $AO/AD = AP/AC$; $CO/CF = CR/AC$, $BO/BC = AS/AC$; because $RP = SC$, $AP + CR + AS = 2AC$.

In Fig. 2 the ideal situation is sketched; of course a small shift of the planes of largest density of $-\mathbf{H} - \mathbf{K}$ does not affect the reasoning given above. However, the most unlikely position for these planes is the one indicated by the broken lines in Fig. 2 because then the planes $-\mathbf{H} - \mathbf{K}$ of largest electron density just clear the lines of intersection of \mathbf{H} and \mathbf{K} .

The Σ_2 relation has a probability character and this is emphasized with the \simeq sign in (8) and then (1) follows. Clearly the triple product E_3 (equation 2) is large when all three reflections \mathbf{H} , \mathbf{K} and $-\mathbf{H} - \mathbf{K}$ have large $|E|$ values.

Large $|E_{\mathbf{H}}|$, $|E_{-\mathbf{H}+\mathbf{K}}|$, $|E_{-\mathbf{H}-\mathbf{K}}|$ and small $|E_{\mathbf{K}}|$: Harker-Kasper relations

From one of the Harker-Kasper inequalities for $\bar{1}$ it follows that if \mathbf{H} , $\mathbf{H} - \mathbf{K}$ and $\mathbf{H} + \mathbf{K}$ are strong reflections and \mathbf{K} is weak the sign product

$$S(\mathbf{H} + \mathbf{K})S(\mathbf{H} - \mathbf{K}) = -1 \quad (9)$$

(e.g. Woolfson, 1961). As is true for all Harker-Kasper relations this relation also is valid only in very

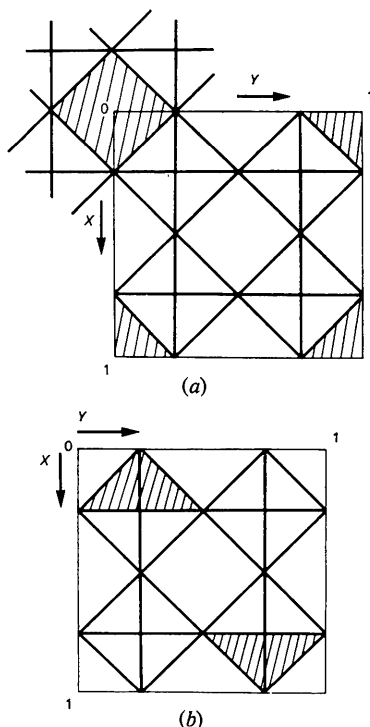


Fig. 4. The thicker lines are those for which the Fourier components $\cos(2\pi x, 0, 0)$, $\cos(0, 2\pi y, 0)$, $\cos(2\pi x, 2\pi y, 0)$ and $\cos(2\pi x, -2\pi y, 0)$ are zero, 100, 110 and $1\bar{1}0$ are strong reflections. If $S(100) = S(110) = S(1\bar{1}0) = +1$ then a concentration of electron density can be expected in the shaded part of (a). If $S(100) = S(1\bar{1}0) = +1$ and $S(110) = -1$, then a concentration of electron density can be expected in another part of the cell, which is shaded in (b). It can easily be checked that in case (a) 010 will be strong and in case (b) 010 will be small.

small structures ($N \leq 20$). Schenk & de Jong (1973) showed that for larger structures the relations may still be useful if the conditions for the magnitude of the E values involved are relaxed. The relation can be interpreted geometrically (Schenk, 1973b). In Fig. 4 the reasoning is given for a typical example.

This explanation is not restricted to centrosymmetric structures; for non-centrosymmetric space groups the relation is

$$\varphi_{\mathbf{H}} + \varphi_{\mathbf{H}} + \varphi_{-\mathbf{H}+\mathbf{K}} + \varphi_{-\mathbf{H}-\mathbf{K}} \simeq \pi \quad (10)$$

for $|E_{\mathbf{H}}|$, $|E_{-\mathbf{H}+\mathbf{K}}|$, $|E_{-\mathbf{H}-\mathbf{K}}|$ large and $|E_{\mathbf{K}}|$ small (Schenk, 1973b).

This relationship is a quartet, but because \mathbf{H} occurs twice it is still two-dimensional.

The positive-quartet relation

For the positive-quartet relation

$$\varphi_{\mathbf{H}} + \varphi_{\mathbf{K}} + \varphi_{\mathbf{L}} + \varphi_{-\mathbf{H}-\mathbf{K}-\mathbf{L}} \simeq 0, \quad (11)$$

three strong reflections \mathbf{H} , \mathbf{K} and \mathbf{L} are combined so that the electron density must be found in the sets of planes given in Fig. 5. As a result the electron density will be found near the points of intersection of the three planes, which is indicated for only a few planes from the sets in Fig. 6. Then for a strong reflection $-\mathbf{H} - \mathbf{K} - \mathbf{L}$ it is much more likely that it will run with its plane of maximum electron density through the point of intersection (Fig. 7a) than that it will just clear these points (Fig. 7b). Then the quartet relation (11) follows from the theorem of Fig. 8 for an arbitrary origin O (Fig. 7a):

$$AO/AA' + BO/BB' + CO/CC' + DO/DD' = 3, \quad (12)$$

which is equivalent to the quartet relation (11).

This quartet relation is not a reliable one compared with the triplet relation because of the factor N^{-1} in E_4 (equation 4), whereas in E_3 (equation 2) only a term

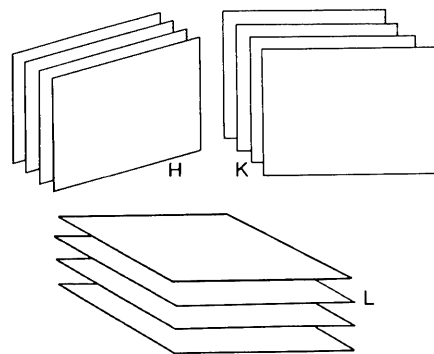


Fig. 5. If the reflections \mathbf{H} , \mathbf{K} and \mathbf{L} are strong, then the electron density will probably lie in the neighbourhood of the three sets of equidistant planes defined by \mathbf{H} , \mathbf{K} and \mathbf{L} .

$\mathcal{N}^{-1/2}$ appears. Therefore, the reliability was improved by constructing the same quartet from two triplets:

$$\begin{aligned} \varphi_{\mathbf{H}} + \varphi_{\mathbf{K}} + \varphi_{-\mathbf{H}-\mathbf{K}} &\simeq 0 \\ \frac{\varphi_{\mathbf{L}} + \varphi_{-\mathbf{H}-\mathbf{K}-\mathbf{L}} + \varphi_{\mathbf{H}+\mathbf{K}}}{\varphi_{\mathbf{H}} + \varphi_{\mathbf{K}} + \varphi_{\mathbf{L}} + \varphi_{-\mathbf{H}-\mathbf{K}-\mathbf{L}}} &\simeq 0, \end{aligned} \quad (13)$$

which holds for large E_4 and large $|E_{\mathbf{H}+\mathbf{K}}|$ (Schenk, 1973a).

This can be understood by drawing the $\mathbf{H} + \mathbf{K}$ reflection into Fig. 6 as illustrated in Fig. 9. Reflection $\mathbf{H} + \mathbf{K}$ strong indicates that the electron density will be found near the intersections of \mathbf{H} and \mathbf{K} . A similar reasoning holds for the other cross terms. In con-

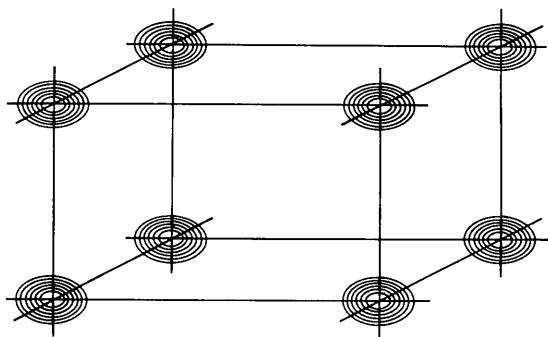
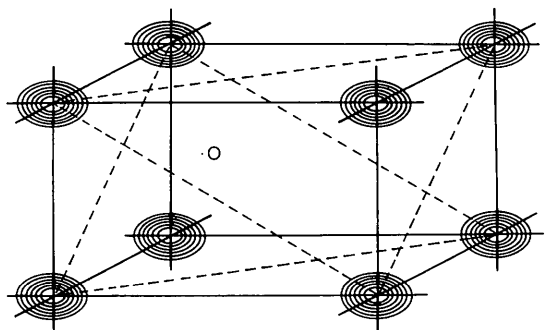
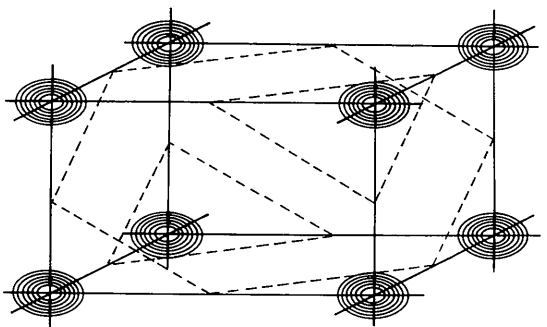


Fig. 6. The electron density will be found near the points of intersection of the three sets of planes \mathbf{H} , \mathbf{K} and \mathbf{L} .



(a)



(b)

Fig. 7. If reflection $-\mathbf{H} - \mathbf{K} - \mathbf{L}$ has also a large intensity, it is more likely that its planes of maximum intensity run through the points of intersection of \mathbf{H} , \mathbf{K} and \mathbf{L} (a) than that they run clear of them (b).

clusion, large values of E_4 , $|E_{\mathbf{H}+\mathbf{K}}|$, $|E_{\mathbf{K}+\mathbf{L}}|$ and $|E_{\mathbf{H}+\mathbf{L}}|$ indicate that the positive quartet (1) is likely to be true. This positive-quartet relationship proved to be reliable (Schenk, 1973a).

The negative-quartet relation

We can make one further point. When the sum of the four phases

$$\varphi_{\mathbf{H}} + \varphi_{\mathbf{K}} + \varphi_{\mathbf{L}} + \varphi_{-\mathbf{H}-\mathbf{K}-\mathbf{L}} \simeq \pi, \quad (14)$$

the resulting relation is referred to as the negative-quartet relation and such relations exist for reasonable intensities for \mathbf{H} , \mathbf{K} , \mathbf{L} and $-\mathbf{H} - \mathbf{K} - \mathbf{L}$.

The planes of maximum density for the four reflections involved in (14) are indicated in Fig. 10. It can be seen that at all indicated positions three of the four planes intersect. If atoms are located at these points the resulting unitary structure factors of \mathbf{H} , \mathbf{K} , \mathbf{L} and $-\mathbf{H} - \mathbf{K} - \mathbf{L}$ will be 0.5, because three atoms lie in the planes and one lies halfway between. Thus for a

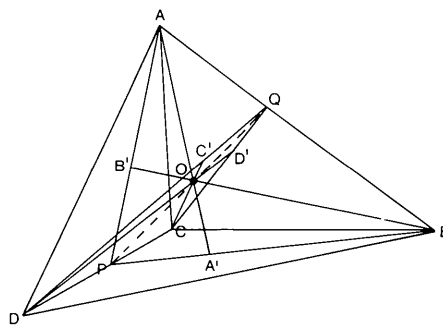


Fig. 8. O is an arbitrary point in an arbitrary tetrahedron. Theorem: $AO/AA' + BO/BB' + CO/CC' + DO/DD' = 3$. Proof: From Fig. 3 it follows that $AO/AA' + BO/BB' + PO/PQ = 2$ and $CO/CC' + DO/DD' + QO/PQ = 2$. By taking the sum $AO/AA' + BO/BB' + CO/CC' + DO/DD' = 4 - PO/PQ - QO/PQ = 3$.

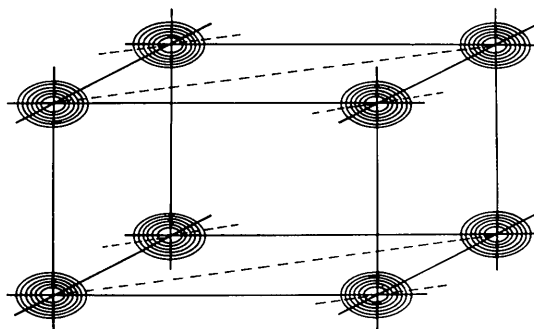


Fig. 9. If \mathbf{H} , \mathbf{K} , \mathbf{L} and $-\mathbf{H} - \mathbf{K} - \mathbf{L}$ are strong and electron density is found near their points of intersection, the $\mathbf{H} + \mathbf{K}$ reflection, indicated with a dotted line, is expected to be strong. Conversely, a large $|E_{\mathbf{H}+\mathbf{K}}|$ supports the quartet relation (11).

negative-quartet relation the reflections **H**, **K**, **L** and $-\mathbf{H} - \mathbf{K} - \mathbf{L}$ will in general not be found amongst the very strongest. The next question to be answered is: what is the intensity of reflection $\mathbf{H} + \mathbf{K}$, if the electron density is located near the marked points of Fig. 10? From Fig. 11 it can be seen that $\mathbf{H} + \mathbf{K}$ will have a small $|E|$ magnitude: an equal number of points of electron-density concentration lies on the $\mathbf{H} + \mathbf{K}$ planes and halfway in-between. As the same holds for the other cross terms it can be stated that the negative-quartet relation (14) is likely to be true for reasonably large values of E_4 and small values of $|E_{\mathbf{H}+\mathbf{K}}|$, $|E_{\mathbf{H}+\mathbf{L}}|$ and $|E_{\mathbf{K}+\mathbf{L}}|$.

In a similar way it can be shown that an enantiomorph-sensitive quartet

$$\varphi_{\mathbf{H}} + \varphi_{\mathbf{K}} + \varphi_{\mathbf{L}} + \varphi_{-\mathbf{H}-\mathbf{K}-\mathbf{L}} \simeq \pm \pi/2 \quad (15)$$

will be found for moderate $|E|$ values of the cross terms.

Concluding remarks

The graphic analysis of triplets and quartets in terms of electron-density considerations leads to a few additional statements.

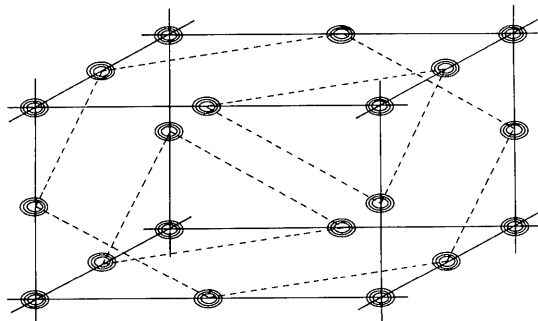


Fig. 10. In the case of the negative-quartet relation the planes of maximum electron density of **H**, **K**, **L** and $-\mathbf{H} - \mathbf{K} - \mathbf{L}$ run as indicated here. At distinct positions three planes intersect and there most probably will the electron density be found.

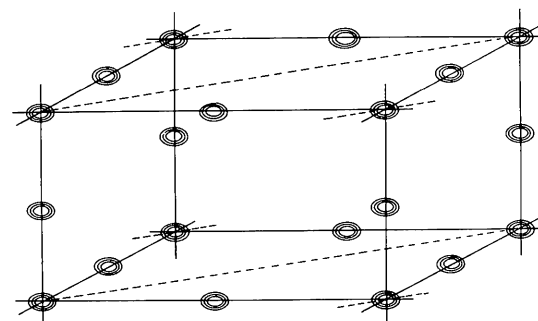


Fig. 11. The reflection $\mathbf{H} + \mathbf{K}$ is indicated with dotted lines. It is easily checked that this reflection is weak, because the electron density is distributed in equal amounts on and between the planes.

1. The condition for a positive quartet that the electron density must lie in the neighbourhood of points is more specific than that for a triplet for which the electron density must lie near lines. This implies that the reflections involved in a quartet must have larger $|E|$ values and thus the reliable and useful quartets will relate the phases of the strongest reflections. They therefore will be particularly helpful at an early stage of the phase determination process. This conclusion was drawn in the first paper on seven-magnitude quartets (Schenk, 1973a) from experimental evidence. Since then quartets have been used with success in the program system *SIMPEL* (Overbeek & Schenk, 1978) for the determination of a large and reliable starting set in terms of the smallest possible number of symbols.

2. With respect to negative quartets it was stated in the preceding section that the intensities of the reflections **H**, **K**, **L** and $-\mathbf{H} - \mathbf{K} - \mathbf{L}$ should be well below maximum otherwise the positive-quartet relation would apply. On the other hand, if these intensities are too small the prediction of the quartet phase sum is again unreliable. Therefore, in general, the number of reliable negative quartets will be much smaller than the number of positive quartets. As a result negative quartets will be more useful as a figure of merit than in the actual phasing procedure.

3. If a negative-quartet relation does not yield exactly π , this implies that the $|E|$'s of the cross terms $\mathbf{H} + \mathbf{K}$, $\mathbf{H} + \mathbf{L}$ and $\mathbf{K} + \mathbf{L}$ are probably not exactly zero. Therefore, in FOM's based on negative quartets, the individual relations must have weights which take into account the magnitudes of $E_{\mathbf{H}+\mathbf{K}}$, $E_{\mathbf{H}+\mathbf{L}}$ and $E_{\mathbf{K}+\mathbf{L}}$. In view of this the negative-quartet FOM NQC (Schenk, 1974) uses empirical weights proportional to $(0.9 - |E|)$ with an $|E|$ threshold of 0.9. The more widely used FOM NQUEST (DeTitta, Edmonds, Langs & Hauptman, 1975) employs the $|E|$'s as threshold values only, which makes it less useful (Gilmore, 1977). On the basis of a theory of Giacovazzo (1975) the weights in NQC were later improved (Schenk, 1975).

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Antiphase Périodique Orientationnelle et Transformation de Phase dans le Fluosilicate de Fer

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Abstract

$\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ above 240 K is described following the structural model previously proposed for $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$ above 300 K: periodic antiphase built on the ordered monoclinic cell of the low-temperature form. In the present case a progressive ordering is observed and the antiphase boundaries are no longer planar but exhibit steps which lead to a mean boundary canted with respect to the *c* hexagonal axis (space group *P3*). Above 240 K a phase transformation occurs with a threefold twinning and a significant lattice deformation. The monoclinic cell (*P2₁/c*) is described.

Introduction

La série des fluosilicates $\text{MSiF}_6 \cdot 6\text{H}_2\text{O}$ (*M* = métal divalent) a été décrite dans les groupes *R3* pour *M* = Co, Ni, Zn (Kodera, Torri, Osaki & Watanabe, 1972; Ray, 1972; Ray, Zalkin & Templeton, 1973), *R3m* pour *M* = Fe, Mg (Hamilton, 1962; Syoyama & Osaki,

1972) et *P3m1* pour *M* = Mn (Kodera, Torri, Osaki & Watanabe, 1972). Dans le cas où *M* = Fe, Mg, nous avons mis en évidence (Jéhanno & Varret, 1975) des réflexions incompatibles avec le groupe d'espace proposé (*R3m*). Pour *M* = Mg, ces réflexions correspondent à des indices entiers et pour *M* = Fe à des indices 'incommensurables'. Toujours fines dans le cas de $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$, elles ne le deviennent dans le cas de $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ que par abaissement de la température. De plus ces deux composés subissent une transformation de phase à *T* ≈ 300 K pour *M* = Mg et *T* ≈ 240 K pour *M* = Fe: la structure devient monoclinique *P2₁/c* (Syoyama & Osaki, 1972; Jéhanno & Varret, 1975; Volland, Hösl, Spiering, Dézsi, Kemény & Nagy, 1978; Chevrier & Jéhanno, 1979).

Nous avons proposé pour le fluosilicate de magnésium à température ambiante (Chevrier & Jéhanno, 1979) une structure basée sur l'alternance périodique d'éléments de la structure basse température (*P2₁/c*) (antiphase à période entière). Nous montrons ici comment le traitement peut être étendu au cas du fluosilicate de fer.