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Modulated Structure of the *NC*-type ($N = 5{\cdot}5$) Pyrrhotite, $Fe_{1-x}S$*

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Abstract

The modulated structure of the *NC*-type pyrrhotite $Fe_{1-x}S$ with $x = 0{\cdot}09$ has been determined. The analysis is based on a four-dimensional space group, $W^{pna2_1}_{qq1}$, and an anharmonic modulation model with 53 positional, two thermal, and eight occupational parameters including up to fourth-order harmonics. $a = 11{\cdot}952$, $b = 6{\cdot}892$, $c = 5{\cdot}744$ Å. The final R for 404 observed reflections is 0·097. The modulation wave for occupation probability of Fe shows a strong anharmonicity and has a low value in a narrow range corresponding to successive Fe layers perpendicular to the c axis of the fundamental NiAs-type structure. From this and the four-dimensional symmetry, it is concluded that Fe vacancies are distributed spirally along the c axis. The relationship between the usual superstructure model and this four-dimensional description is discussed.

1. Introduction

The diffraction patterns of the *NC*-type pyrrhotites, $Fe_{1-x}S$, in a composition range between Fe_9S_{10} ($x = 0{\cdot}1$) and $Fe_{11}S_{12}$ ($x = 0{\cdot}083$), show characteristic features and common aspects: there are strong main (fundamental) reflections indicating that the fundamental structure is the NiAs-type structure and the satellite reflections appear along the fundamental c axis. All reflections can be assigned with four integers h_i ($i = 1, 2, 3, 4$) and four vectors as

$$\mathbf{h} = h_1\mathbf{a}^* + h_2\mathbf{b}^* + h_3\mathbf{c}^* + h_4\mathbf{k}, \tag{1}$$

where $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ are the unit vectors of the reciprocal lattice for the *C*-centered orthorhombic fundamental cell with $a = 11{\cdot}952$, $b = 6{\cdot}892$ and $c = 5{\cdot}744$ Å (Morimoto, Nakazawa, Nishiguchi & Tokonami, 1970) (these are related to the hexagonal NiAs-type cell constants A, B, C by $a = 2\sqrt{3}A$, $b = 2B$, $c = C$) and $\mathbf{k}$ is given by

$$\mathbf{k} = k_3\mathbf{c}^*. \tag{2}$$

When k_3 (the $\mathbf{c}^*$ component of $\mathbf{k}$) is written as $1/N$, the N value continuously changes with temperature and/or composition from 3 to 6 (Nakazawa & Morimoto, 1971).

In the present case, the composition is $Fe_{10}S_{11}$ ($x = 0{\cdot}09$) and N is 5·54. This shows that this is a modulated structure which has a periodic distortion of atomic position and/or wavy distribution of vacancies with wave vector $\mathbf{k}$. When the period is made approximately commensurate with that of the fundamental cell, the structure is analyzed as a superstructure based on a three-dimensional space group. Koto, Morimoto & Gyobu (1975) analyzed the 6*C*-type pyrrhotite ($N = 6$) by this method. If the period is incommensurate, it can, however, be analyzed on the basis of four-dimensional symmetry as shown by de Wolff (1974) and Janner & Janssen (1977). In the present paper, the *NC*-type structure with $N = 5{\cdot}54$ is analyzed on the basis of a four-dimensional space group with X-ray data collected by Dr M. Tokonami and Mr K. Nishiguchi, Osaka University. As shown later (§ 7), this method can be used not only to analyze the incommensurate structure but also the superstructure such as the 6*C*-type pyrrhotite: the number of parameters is much less than in the three-dimensional analysis.

2. Four-dimensional description

According to (1), $h_1h_2h_3 0$ specify the main (fundamental) reflections while $h_1h_2h_3 \pm n$ specify the *n*th-order satellite reflections. In the crystal used, satellite reflections up to fourth order are observed (see Fig. 1). Equation (1) means that the *NC*-type pyrrhotite has a one-dimensionally modulated structure. Therefore, its symmetry is described by a four-dimensional space group.

The vector (1) corresponds to the reciprocal-lattice point in four-dimensional space R_4 spanned by the unit vectors $\mathbf{b}_1 = \mathbf{a}^*$, $\mathbf{b}_2 = \mathbf{b}^*$, $\mathbf{b}_3 = \mathbf{c}^*$ and $\mathbf{b}_4 = \mathbf{k} + \mathbf{d}^*$, where $\mathbf{d}^*$ is the unit vector perpendicular to the usual three-dimensional space R_3: the reciprocal-lattice points in R_4 are represented by $\mathbf{h}' = h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3 + h_4\mathbf{b}_4$ and the position of observed reflection h in R_3 is regarded as the projection of $\mathbf{h}'$ onto R_3. If the wave

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vector $\mathbf{k}$ is incommensurate with the reciprocal unit vectors $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, that is, k_3 is an irrational number, $\mathbf{h}$ and $\mathbf{h}'$ have one-to-one correspondence. The unit vectors $\mathbf{a}_i$ ($i = 1, 2, 3, 4$) of the direct lattice are defined by $\mathbf{a}_1 = \mathbf{a}$, $\mathbf{a}_2 = \mathbf{b}$, $\mathbf{a}_3 = \mathbf{c} - k_3\mathbf{d}$ and $\mathbf{a}_4 = \mathbf{d}$, where $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are the unit vectors of the fundamental structure which are reciprocal to $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ and $\mathbf{d}$ is the unit vector perpendicular to R_3, $1/d^*$ in length. A vector $\mathbf{x} = x_2\mathbf{a} + x_2\mathbf{b} + x_3\mathbf{c}$ in R_3 is expressed as $\mathbf{x} = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3 + k_3x_3\mathbf{a}_4$ with the unit vectors in R_4. The first three coordinates are the same as the coordinates in R_3 and when the fourth coordinate is written as $k_3x_3 + t$, $t = 0$ means that the vector lies in R_3.

Now we consider the symmetry operator $(\mathsf{R}|\tau)$ for the modulated structure, where R is the rotation operator in R_4 and τ is the translation vector. The rotation R must transform the four-dimensional reciprocal lattice spanned by $\mathbf{b}_i$ ($i = 1, 2, 3, 4$) into itself. From the definition, $\mathbf{b}_4$ is oblique to R_3 whenever the wave vector $\mathbf{k}$ is non-zero. Therefore, R must transform $\mathbf{b}_4$ into either $\mathbf{b}_4$ or $-\mathbf{b}_4$. Since $\mathbf{b}_4$ is $\mathbf{k} + \mathbf{d}$, the symmetry operators are limited to those transforming $\mathbf{k}$ into $\mathbf{k}$ or $-\mathbf{k}$. By these operators, the vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are transformed into an integral linear combination of themselves. When $\mathbf{b}_i$ ($i = 1, 2, 3, 4$) are transformed to $\mathbf{b}'_i$ ($i = 1, 2, 3, 4$) by a rotation R, the matrix elements of R are defined by

$$\mathbf{b}_i = \sum_{j=1}^{4} \mathsf{R}_{ij}\mathbf{b}_j. \tag{3}$$

The condition for R is expressed by using the matrix elements R_{ij} as $\mathsf{R}_{i4} = \mathsf{R}_{4i} = 0$ ($i = 1, 2, 3$) for all symmetry operators and $\mathsf{R}_{44} = 1$ or -1 according as R transforms $\mathbf{k}$ into $\mathbf{k}$ or $-\mathbf{k}$. The matrix elements of the first 3×3 part are the same as the matrix representation of the rotation operator R in R_3 because $\mathbf{b}_1 = \mathbf{a}^*$, $\mathbf{b}_2 = \mathbf{b}^*$, $\mathbf{b}_3 = \mathbf{c}^*$. Thus we have a 4×4 matrix which is $(3 + 1)$-reducible, that is, $\mathsf{R}_{i4} = \mathsf{R}_{4i} = 0$ for $i = 1, 2, 3$. Since the coordinates x_i ($i = 1, 2, 3, 4$) are transformed by the rotation operator like the reciprocal unit vectors $\mathbf{b}_i$, the coordinates are transformed by the symmetry operator $(\mathsf{R}|\tau)$ as follows.

$$x'_i = \{(\mathsf{R}|\tau)\mathbf{x}\}_i = \sum_{j=1}^{4} \mathsf{R}_{ij}x_j + \tau_i, \tag{4}$$

where τ_i is the $\mathbf{a}_i$ component of the translation vector.

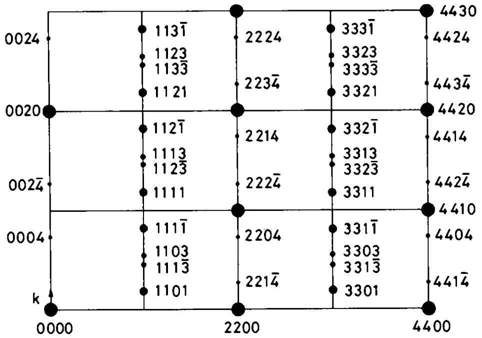

Fig. 1. Schematic view of the diffraction pattern of the *NC*-type pyrrhotite.

For convenience, we use the same symbol for R of $(\mathsf{R}|\tau)$ as in the three-dimensional space group. For example, σ_x represents the mirror plane perpendicular to the a axis and its non-zero elements are given by $\mathsf{R}_{11} = -1$, $\mathsf{R}_{22} = 1$, $\mathsf{R}_{33} = 1$ and $\mathsf{R}_{44} = 1$ because the fundamental cell is orthorhombic and $\sigma_x\mathbf{k} = \mathbf{k}$. The other condition for the symmetry operator is that $(\mathsf{R}|\tau)$ is a symmetry operator in the fundamental structure.

As is well known, the fundamental structure of pyrrhotite is a slightly deformed NiAs-type structure and its unit cell is orthorhombic. In a one-dimensionally modulated structure, the displacement from the fundamental structure is expressed by a plane wave with the wave vector $\mathbf{k}$. Therefore, the atomic position in R_3 is written as

$$x_i = \bar{x}_i + u_i(\bar{x}_4), \quad (i = 1, 2, 3) \tag{5}$$

where $\bar{x}_4 = k_3\bar{x}_3 + t$ and the bar denotes the quantity belonging to the fundamental structure. The four-dimensional description of this structure is as follows (de Wolff, 1974). Its four-dimensional coordinates are the same as (5) for $i \leq 3$ and the fourth coordinate is given by

$$x_4 = \bar{x}_4 + u_4(\bar{x}_4), \tag{6}$$

where $u_4(\bar{x}_4) = k_3u_3(\bar{x}_4)$. It should be noted that x_4 and $\bar{x}_4$ take any value, and, therefore, the 'atom' in the four-dimensional lattice is continuous along the fourth axis $\mathbf{a}_4$. [In (5) and (6), $\bar{x}_1$, $\bar{x}_2$, $\bar{x}_3$ are independent of $\bar{x}_4$.] Because the rotation operator R is $(3 + 1)$-reducible, $(\mathsf{R}|\tau)$ must transform the first three coordinates, $\bar{x}_1$, $\bar{x}_2$, $\bar{x}_3$, of an atom into those of the other atom of the same kind or into themselves. Therefore, the first 3×3 part of R and the projection of τ onto R_3 comprise the usual three-dimensional space group, which is, in general, a subgroup of the space group of the fundamental structure in R_3.

The fundamental structure has the space group *Ccmm* (D_{2h}^{17}) and the lattice constants $a = 5{\cdot}976$, $b = 3{\cdot}446$, $c = 5{\cdot}744$ Å. The atomic positions of Fe and S are shown in Table 1. It is noted that a and b are half of those in the modulated structure. This is because an $F(1, 2, 4)$-centered lattice is taken in the modulated structure. (See the next section.) The space group *Ccmm* consists of 16 elements which are generated by $(C_{2x}|0,0,\frac{1}{2})$, $(C_{2y}|0,0,0)$, $(I|0,0,0)$ and the centering translation of the C-centered lattice, $(E|\frac{1}{2},\frac{1}{2},0)$, where the translation vector τ is represented by its $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ components. When a and b are doubled, these generators are expressed as $(C_{2x}|0,0,\frac{1}{2})$, $(C_{2y}|0,0,0)$, $(I|0,0,0)$ and $(E|\frac{1}{4},\frac{1}{4},0)$. From the above consideration, 32 elements generated by $(C_{2x}|0,0,\frac{1}{2},\tau_4)$, $(C_{2y}|0,0,0,\tau_4)$ and $(I|0,0,0,\tau_4)$ and the four centering translations mentioned in the next section are the symmetry operators of the modulated structure because these transform **k** into **k** or −**k**. The fourth component τ_4 in each operator must be determined so that the extinction rules are satisfied.

3. Extinction rules and space group

In the four-dimensional representation mentioned in the previous section, the extinction rules are given by

$$\left.\begin{aligned} h_1 + h_2 &= 2n \quad &(7)\\ h_2 + h_4 &= 2n \quad &(8)\\ h_1 + h_4 &= 2n \quad &(9)\end{aligned}\right\} \text{ for general reflections}$$

$$h_2 + 2h_3 + h_4 = 4n \quad \text{for } 0h_2\,h_3\,h_4 \tag{10}$$

$$h_1 + h_4 = 4n \quad \text{for } h_1\,0h_3\,h_4 \tag{11}$$

$$h_3 = 2n \quad \text{for } 00h_3\,h_4, \tag{12}$$

where n is an integer. The schematic view of the diffraction pattern is shown in Fig. 1. As derived from formula (13) in § 4 or from analogy with the usual three-dimensional space group, the first three rules are attributed to the non-primitive Bravais lattice with the centering translations $(E|\frac{1}{2},\frac{1}{2},0,0)$, $(E|\frac{1}{2},0,0,\frac{1}{2})$, $(E|0,\frac{1}{2},0,\frac{1}{2})$, which is called an $F(1, 2, 4)$-centered lattice (Wondratschek, Bulow & Neubuser, 1971). The fourth to sixth rules are explained by the presence of the symmetry elements $(\sigma_x|\frac{1}{4},\frac{1}{4},\frac{1}{2},\frac{1}{4})$, $(\sigma_y|\frac{1}{4},\frac{1}{4},0,\frac{1}{4})$ and $(C_{2z}|0,0,\frac{1}{2},0)$. These symmetry operators (Table 2) generate a space group. In the same table, de Wolff's notation of symmetry operators are also listed. This is the space group $W^{pna2_1}_{qq1}$ in the symbols of Janner, Janssen & de Wolff (1979) or number 04/01/004 in the table of four-dimensional space groups by Brown, Bulow, Neubuser, Wondratschek & Zassenhaus (1978) and agrees with the space group determined by Wondratschek (1979, private communication).

Table 1. *Atomic positions in the fundamental structure (Ccmm)*

Atom	Position	$\bar{x}_1$	$\bar{x}_2$	$\bar{x}_3$
Fe	4(*a*)	0	0	0
S	4(*c*)	$-\frac{1}{6}$	0	$-\frac{1}{4}$

Table 2. *Symmetry operators in the four-dimensional space group of the NC-type pyrrhotite*

The second expression is de Wolff's notation for the four-dimensional symmetry operators.

F(1,2,4) centered lattice
$(E|0,0,0,0)$, $(\sigma_x|\frac{1}{4},\frac{1}{4},\frac{1}{2},\frac{1}{4})$, $(\sigma_y|\frac{1}{4},\frac{1}{4},0,\frac{1}{4})$, $(C_{2z}|0,0,\frac{1}{2},0)$

$(0,0,0,0;\ \frac{1}{2},\frac{1}{2},0,0;\ \frac{1}{2},0,0,\frac{1}{2};\ 0,\frac{1}{2},0,\frac{1}{2})$ +
$x,y,z,\xi;\ \frac{1}{4}-x,\ \frac{1}{4}+y,\ \frac{1}{2}+z, \frac{1}{4}+\xi; \frac{1}{4}+x, \frac{1}{4}-y,\ z,\ \frac{1}{4}+\xi; -x,\ -y,\ \frac{1}{2}+z,\ \xi$

There are four Fe and four S atoms in the fundamental cell as shown in Table 1 and therefore 16 Fe and 16 S sites in the unit cell of the modulated structure. Sixteen sulfur atoms occupy a 16-fold general position of this space group, but there are less than 16 Fe atoms occupying this general position. The mean occupation probability of Fe is 0·91 ($Fe_{10}S_{11}$).

4. Model for the structure

As shown by Koto, Morimoto & Gyobu (1975), the *NC*-type pyrrhotite has a wavy distribution of Fe vacancies and associated displacement of atoms. To analyze such a structure, a general structure-factor formula has been derived (Yamamotò *et al.*, 1979). The structure factor in the present case is given by*

$$\begin{aligned} F(h_1\,h_2\,h_3\,h_4) = \sum_{\mu(\mathrm{R}|\tau)} a^\mu \int_0^1 \mathrm{d}\bar{x}_4^\mu\, f^\mu(\mathbf{h})\, P^\mu(\bar{x}_4^\mu) \\ \times \exp\Big\{-B^\mu(\bar{x}_4^\mu)h^2 \\ + 2\pi i \sum_j [h_j(Rx^\mu(\bar{x}_4^\mu))_j + h_j\tau_j]\Big\}, \end{aligned} \tag{13}$$

where $f^\mu(\mathbf{h})$ is the atomic scattering factor of the μth non-equivalent atom, a^μ is its multiplicity, P^μ is the occupation probability, B^μ is the isotropic temperature factor and x^μ is the positional vector which is written as $\bar{x}^\mu + u^\mu(\bar{x}_4^\mu)$ with $\bar{x}^\mu$ the positional vector in the fundamental structure and u^μ the displacement. The quantities P^μ, B^μ and u^μ are periodic functions of the fourth coordinate $\bar{x}_4^\mu$ in the fundamental structure. We call this a modulation function or modulation wave. The summation of (R|τ) is taken over all symmetry operators mentioned before, and μ runs over all non-equivalent atoms. The suffix i runs from one to four. In the present case, the non-equivalent atoms are only two, so that Fe is indicated by $\mu = 1$ and S by $\mu = 2$ in the following. The temperature factor B^μ is a periodic function of $\bar{x}_4^\mu$ but, in the present analysis, the isotropic temperature factor is assumed to be independent of $\bar{x}_4^\mu$ for simplicity.

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* In the previous structure-factor formula by Yamamoto *et al.* (1979), $f^\mu(\mathbf{h})P^\mu(\bar{x}_4^\mu)$ is simply expressed as $f^\mu(\bar{x}_4^\mu)$.

The occupation probability of Fe, P^1, and the positional vector, x^μ, are expressed in terms of the Fourier series:

$$x_i^\mu(\bar{x}_4^\mu) = \bar{x}_i^\mu + \left\{\frac{1}{2}\sum_n u_{in}^\mu \exp 2\pi i n \bar{x}_4^\mu + \text{c.c.}\right\} \qquad (i = 1, 2, 3, 4) \qquad (14)$$

$$P^1(\bar{x}_4^1) = \frac{1}{2}\sum_n P_n^1 \exp 2\pi i n \bar{x}_4^1 + \text{c.c.}, \qquad (15)$$

where u_{in}^μ and P_n^1 are the complex amplitudes of the *n*th order harmonics for the displacement and for the occupation probability, which denote the deviation from the fundamental structure of the NiAs type, and c.c. represents the complex conjugate. As is easily shown from (13), when the displacement is small, the *n*th-order Fourier coefficients u_{in}^μ, P_n^1 mainly contribute to the *n*th-order satellite reflections, $h_1 h_2 h_3 \pm n$. Since the maximum order of observed satellites was four, the Fourier terms up to the fourth-order harmonics must be taken into account. Therefore, n runs from zero to four in the above expressions. There is no restriction for the parameters u_{in}^μ and P_n^1 because all atoms occupy general positions. Thus we have 54 positional, two thermal and nine occupational parameters, of which one occupational parameter P_0^1, representing the average occupation probability, is fixed at 0·91 from the composition of the crystal used and one positional parameter u_{30}^1 is taken to be zero in order to fix the origin.

5. Structure refinement

For the refinement, a full-matrix least-squares program, in which $\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$ is minimized, has been written by one of the authors (AY), where w is the weight factor. Unit weight was used for all reflections (611 reflections) including non-observed reflections and an atomic scattering factor table by Hanson, Herman, Lea & Skillman (1964) was employed. The integral appearing in the structure factor was calculated numerically with Gauss's method with 16 divisions.

Preliminary calculations were made on the basis of many possible symmetries, all of which include the symmetry operator $(E|\frac{1}{4},\frac{1}{4},0,\frac{1}{4})$, since the pseudo-extinction rule $h_1 + h_2 + h_4 = 4n$ exists for general reflections in the data used. Of these, the model with $(E|0,0,0,0)$, $(C_{2z}|0,0,\frac{1}{2},0)$, $(E|\frac{1}{4},\frac{1}{4},0,\frac{1}{4})$, $(C_{2z}|\frac{1}{4},\frac{1}{4},\frac{1}{2},\frac{1}{4})$ gave the best result but provided a large R factor for the first-order satellite reflections. Moreover, these operators do not form any space group in R_4. At this stage, the symmetry operator $(E|\frac{1}{4},\frac{1}{4},0,\frac{1}{4})$ was discarded and $(\sigma_y|\frac{1}{4},\frac{1}{4},0,\frac{1}{4})$ was taken instead. This leads to the space group shown in Table 2. The pseudo-extinction rule can be considered to be due to the special atomic configuration under the general position of this space group: if the x_2 coordinates of Fe and S in Table 1 remain zero in the modulated structure, then $(\sigma_y|\frac{1}{4},\frac{1}{4},0,\frac{1}{4})$ is equivalent to $(E|\frac{1}{4},\frac{1}{4},0,\frac{1}{4})$ and $(\sigma_x|\frac{1}{4},\frac{1}{4},\frac{1}{2},\frac{1}{4})$ is equivalent to $(C_{2z}|\frac{1}{4},\frac{1}{4},\frac{1}{2},\frac{1}{4})$ in the sense that these transform Fe and S into the same positions. Therefore, the pseudo-extinction rule suggests that the displacement along the

Table 3. *The R factor: R including, R′ excluding non-observed reflections; R_n and R_n' represent the R factor for the nth-order reflections*

$R = 0{\cdot}146$	$R_0 = 0{\cdot}064$	$R_1 = 0{\cdot}157$	$R_2 = 0{\cdot}148$	$R_3 = 0{\cdot}330$	$R_4 = 0{\cdot}78$
$R' = 0{\cdot}097$	$R_0' = 0{\cdot}055$	$R_1' = 0{\cdot}115$	$R_2' = 0{\cdot}087$	$R_3' = 0{\cdot}215$	$R_4' = 0{\cdot}36$

Table 4. *The positional parameters* ($\times 10^4$) *and thermal and occupational parameters* ($\times 10^2$) *in the 5·5C-type pyrrhotite*

Each parameter is the Fourier coefficient of the modulation wave corresponding to the Fourier term (FT) in the first line.

FT		1	$\cos 2\pi\bar{x}_4$	$\sin 2\pi\bar{x}_4$	$\cos 4\pi\bar{x}_4$	$\sin 4\pi\bar{x}_4$	$\cos 6\pi\bar{x}_4$	$\sin 6\pi\bar{x}_4$	$\cos 8\pi\bar{x}_4$	$\sin 8\pi\bar{x}_4$
Fe	*x*	−16 (4)	−49 (11)	44 (14)	−12 (46)	−97 (7)	18 (6)	6 (15)	−5 (7)	−4 (4)
	y	−8 (6)	90 (39)	154 (26)	18 (8)	−2 (13)	−25 (40)	53 (20)	−5 (11)	1 (17)
	z	0	−92 (9)	17 (33)	−8 (61)	115 (10)	78 (24)	30 (60)	10 (44)	−34 (12)
	B	121 (6)								
	P	91	−4 (5)	17 (1)	16 (4)	7 (8)	7 (6)	−9 (6)	−8 (1)	0 (8)
S	*x*	−4 (3)	−5 (7)	9 (4)	10 (4)	−3 (10)	17 (8)	6 (13)	−12 (4)	−1 (13)
	y	−1 (6)	3 (10)	−14 (14)	2 (14)	0 (10)	6 (12)	−8 (15)	1 (14)	−1 (15)
	z	124 (22)	−165 (15)	26 (45)	11 (76)	−146 (12)	38 (21)	23 (34)	23 (23)	17 (28)
	B	52 (7)								
	P	100								

b axis is comparatively small: this is, in fact, true for S but Fe has large displacement as shown in the following.

The refinement was started from the final parameters in the best model mentioned above and converged to $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0{\cdot}097$ for all observed reflections after several cycles. The *R* factors for all, main and satellite reflections are listed in Table 3. The *R* factors for the first- and second-order satellite reflections are less than 0·16 and are acceptable values. However, those for the third- and fourth-order satellite reflections are large. This is because their intensities are weak or not observed and, in particular, many fourth-order satellites are not observed. The final parameters are shown in Table 4.* The modulation waves for the occupation probability of Fe and those for the atomic positions of Fe and S are shown in Fig. 2.

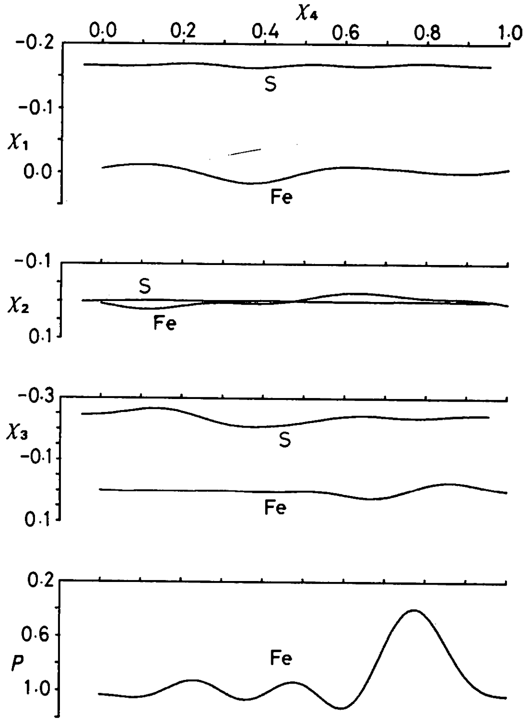

Fig. 2. Modulation waves for the displacement and the occupation probability in the *NC*-type ($N = 5{\cdot}5$) pyrrhotite.

6. Description of the structure

To obtain the arrangements of Fe and S in R_3 and R_4, calculations must be made of the occupation probabilities and atomic positions of equivalent atoms. From the transformation property of a scalar, the occupation probability of the νth equivalent atom related to the μth non-equivalent atom with $\mathbf{x}^\nu = (\mathsf{R}|\tau)\mathbf{x}^\mu$ is given by

$$P^\nu(\bar{x}_4^\nu) = (\mathsf{R}|\tau)P^\mu(\bar{x}_4^\mu) = P^\mu(\bar{x}_4^\mu). \tag{16}$$

Similarly, the atomic position is given by

$$x_i^\nu(\bar{x}_4^\nu) = [(\mathsf{R}|\tau)\mathbf{x}^\mu(\bar{x}_4^\mu)]_i = [\mathsf{R}\mathbf{x}^\mu(\bar{x}_4^\mu)]_i + \tau_i \tag{17}$$

and, for the displacement, we have

$$u_i^\nu(\bar{x}_4^\nu) = [\mathsf{R}\mathbf{u}^\nu(\bar{x}_4^\nu)]_i. \tag{18}$$

The displacement and the occupation probability in R_3 of this atom are given by $\mathbf{u}^\nu(k_3\bar{x}_3^\nu)$ and $P^\nu(k_3\bar{x}_3^\nu)$ (de Wolff, 1974). Thus we can calculate the positions and occupation probabilities of all atoms in R_3 from $\mathbf{x}^\mu(\bar{x}_4^\mu)$ and $P^1(\bar{x}_4^1)$ shown in Fig. 2.

From (16) and (18), the occupation probability and the displacement of the νth atom in R_3 are expressed by

$$P^\nu(k_3\bar{x}_3^\nu) = P^\mu(\bar{x}_4), \tag{19}$$

$$u_i^\nu(k_3\bar{x}_3^\nu) = \sum_{j=1}^{3} \mathsf{R}_{ij}\, u_j^\mu(\bar{x}_4), \quad (i = 1, 2, 3), \tag{20}$$

where $\bar{x}_4 = k_3\bar{x}_3^\mu + \mathsf{R}_{44}^{-1}(k_3\tau_3 - \tau_4)$. These show that the modulation functions in Fig. 2 are regarded as the change of the displacement and occupation probability along the *c* axis since P^ν and $\mathbf{u}^\nu$ for the atom at $\bar{x}_1^\mu, \bar{x}_2^\mu, \bar{x}_3^\mu + n$ $(n = 1, 2, \ldots)$ in the fundamental structure are given by $P^\mu(k_3\bar{x}_3^\mu + k_3 n)$ and $\mathbf{u}^\mu(k_3\bar{x}_3^\mu + k_3 n)$. In particular, for Fe, P^ν and $-u_1^\nu, -u_2^\nu, u_3^\nu$ at $0,0,\bar{x}_3^\nu = (2n - 1)/2$ are given by $P^1(k_3\bar{x}_3^\nu)$ and $u_i^1(k_3\bar{x}_3^\nu)$ $(i = 1, 2, 3)$ because these positions are obtained from 0,0,0 by $(C_{2z}|0, 0, (2n - 1)/2)$ and its corresponding operator in R_4 is $(C_{2z}|0, 0, (2n - 1)/2, 0)$.

According to this interpretation, the occupation probability in Fig. 2 shows that the vacancies are concentrated on every two or three Fe layers perpendicular to the *c* axis. (The spacing of successive Fe layers corresponds to $\bar{x}_4 = k_3/2 = 0{\cdot}09$.) The displacements of S atoms along the *a* and *b* axes are small and within 0·05 Å. The Fe atoms are mainly displaced in the *ab* plane except in the vicinity of vacancies. The atomic displacements of Fe and S clearly deviate from single sinusoidal waves and have strong higher-order harmonics. The displacement of S along the *b* axis is small as expected but a large displacement is seen for Fe.

The occupation probability of the other Fe sites is considered in more detail. The sites $\frac{1}{4},\frac{1}{4},n/2$; $\frac{1}{2},0,n/2$; $\frac{1}{4},-\frac{1}{4},n/2$ $(n = 1, 2, \ldots)$ in R_3, which are called *B*, *C*, *D* sites for convenience, are obtained from *A* site $0,0,n/2$ by $(\sigma_y|\frac{1}{4},\frac{1}{4},0)$, $(E|\frac{1}{2},0,0)$ and $(\sigma_y|\frac{1}{4},-\frac{1}{4},0)$. (See Fig. 3.) From (19) and the corresponding symmetry operators $(\sigma_y|\frac{1}{4},\frac{1}{4},0,\frac{1}{4})$, $(E|\frac{1}{2},0,0,\frac{1}{2})$, $(\sigma_y|\frac{1}{4},-\frac{1}{4},0,-\frac{1}{4})$ in R_4, we have

$$P^\nu(k_3 n/2) = P^1(k_3 n/2 - \tau_4), \tag{21}$$

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36288 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

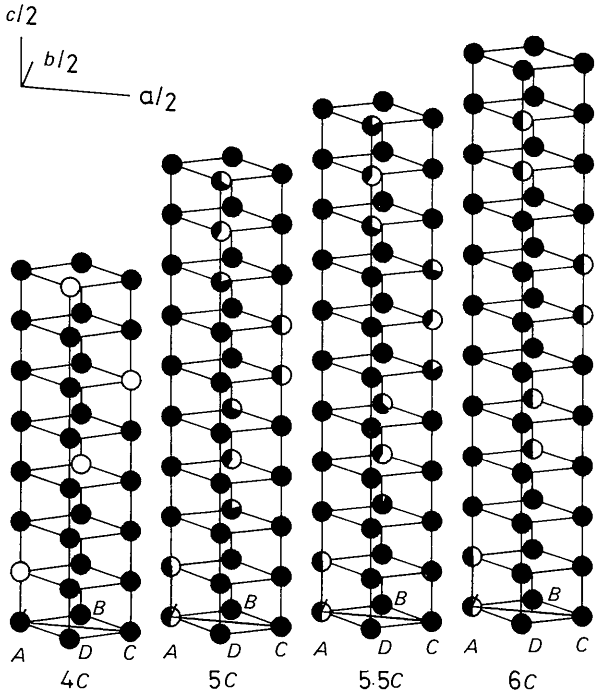


Fig. 3. The vacancy distribution in the 4C-, 5C-, 5·5C- and 6C-type pyrrhotites. The solid part represents the occupation probability of Fe.

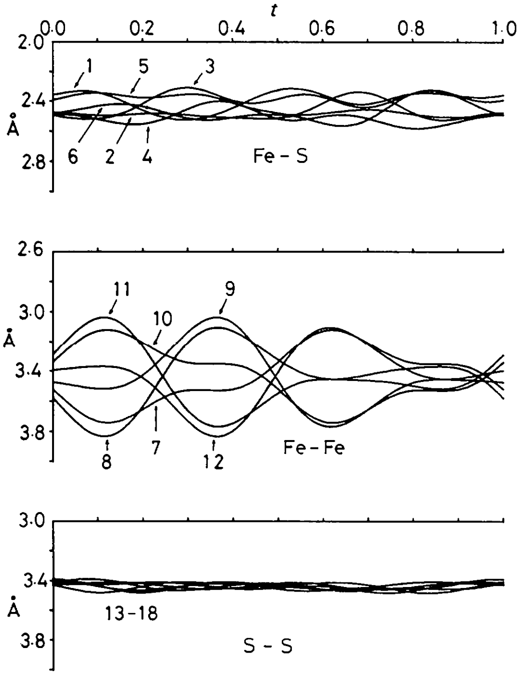


Fig. 4. Interatomic distances between the nearest neighbors. For the numbers of the curves, refer to Fig. 5. $t = \bar{x}_4 - k_3\bar{x}_3$.

Table 5. *The minimum and maximum values of the nearest-neighbour distances in the* 5·5C*-type pyrrhotite and the monoclinic* 4C*-type pyrrhotite*

	5·5C type		4C type	
	min	max	min	max
Fe—S	2·31	2·58	2·322 (9)	2·674 (10)
Fe—Fe	3·03	3·83	2·944 (6)	3·926 (6)
S—S	3·39	3·48	3·450	3·458

where τ_4 takes $\frac{1}{4},\frac{1}{2}$ and $-\frac{1}{4}$ for the B, C and D sites, respectively. In this way, the vacancy distribution of the NC-type pyrrhotite with $N = 5{\cdot}54$ was obtained. This is shown in Fig. 3 as the 5·5C-type pyrrhotite, where the solid part is the occupation probability of Fe and the almost occupied part in Fig. 2 is regarded as completely occupied.

To determine the relative positions of the atoms, inter-atomic distances are calculated. It is convenient to illustrate this as a function of $t = \bar{x}_4 - k_3\bar{x}_3$ instead of writing down atomic distances for many pairs of atoms. Such a figure is shown in Fig. 4. (For the number of each curve, refer to Fig. 5.) This shows the change of atomic distance along the c axis. The atomic distance at the νth cell apart from the origin by $\bar{x}^{\nu}$ is represented by the value at $t = k_3\bar{x}_3^{\nu}$ (mod 1). Distances between sulfur atoms show small changes compared with those between sulfur and iron or iron and iron. The minimum and maximum values of these distances are listed in Table 5. These values are comparable with those of the monoclinic 4C-type pyrrhotite (Tokonami, Nishiguchi & Morimoto, 1972) given in the same table.

The modulated structure of pyrrhotite described above is more clearly visualized with the Fourier map in R_4. The electron density of the four-dimensional lattice is obtained from

$$\rho(x_1,x_2,x_3,x_4) = \frac{1}{V}\sum_{h_1,h_2,h_3,h_4} F_{\mathbf{h}'} \exp 2\pi i \sum_{j=1}^{4} h_j x_j, \quad (22)$$

where V is the unit-cell volume of the fundamental structure. Fig. 6(a) shows $\rho(0,0,x_3,x_4)$ over six cells.

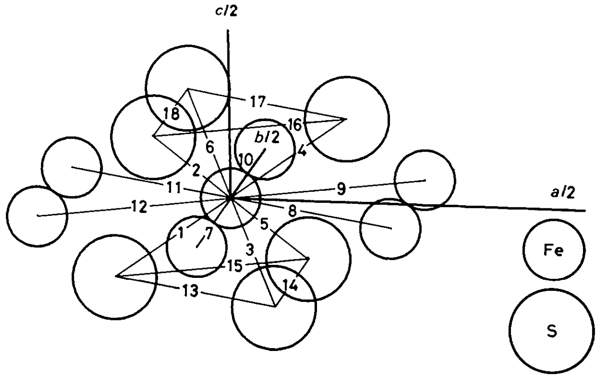


Fig. 5. The nearest-neighbor distances shown in Fig. 4.

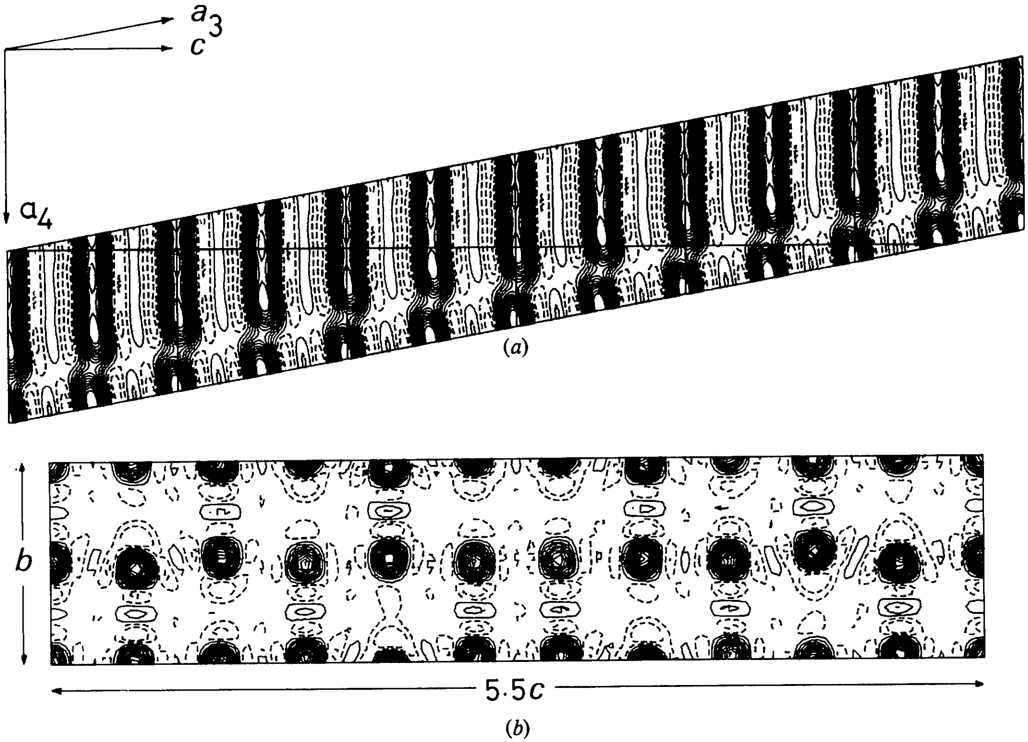
The strong peaks along the a_4 axis correspond to Fe atoms and the low density range in the peaks shows the part of low occupation probability appearing in Fig. 2. The curve of the peak in the vicinity of this low occupation range represents the displacement of Fe along the c axis as is clear from Fig. 2. The real three-dimensional space is the section perpendicular to the a_4 axis, which is represented by a solid line in the figure (de Wolff, 1974). This section in the *bc* plane is illustrated in Fig. 6(*b*). This is the usual Fourier map of the *bc* plane, in which all peaks correspond to Fe atoms. Corresponding to the displacement along the a_2 axis in Fig. 2, a large displacement of Fe atoms along the b axis is seen.

7. Relation between space groups in R_3 and R_4

The diffraction patterns of the *NC*-type pyrrhotite have common aspects in different temperatures and/or different compositions. Except for the slight change in intensity, the only difference is the interval of the satellites. To treat such structures systematically, it is convenient to take a four-dimensional description. Then this series of structures can be described by the same four-dimensional space group. In some particular cases (commensurate cases) such as $N = 5$, 5·5, 6, the usual superstructure model is also available. In the following, the cases of $N = 5$, 5·5 and 6 are called the 5*C*, 5·5*C* and 6*C* types for convenience. These have, however, different three-dimensional space groups and their symmetries are lower than the four-dimensional one as shown in the following.

If $k_3\tau_3 = \tau_4$, (20) shows that x^ν is obtained from x^μ by the symmetry operator $(\mathrm{R}|\tau_1, \tau_2, \tau_3)$ in R_3. In other words, if and only if an operator in R_4 fulfils $k_3\tau_3 = \tau_4$, the corresponding symmetry operator in a space group in R_3 exists. Therefore, the three-dimensional symmetry is, in general, lower than the four-dimensional one.

We consider the 6*C*-type pyrrhotite. In this case, $k_3 = \frac{1}{6}$, so that according to the above argument, only $(E|0,0,0)$, $(\sigma_x|\frac{1}{4},\frac{1}{4},\frac{3}{2})$ remain in R_3 and primitive translation operators are given by $(E|\frac{1}{2},\frac{1}{2},0)$, $(E|\frac{1}{2},0,3)$, $(E|0,\frac{1}{2},3)$. These operators generate the monoclinic space group *Fd* in agreement with a result of Koto *et al.* (1975). On the other hand, the 5*C*-type pyrrhotite has no rotational symmetry except for $(E|0,0,0)$ and the primitive translations are $(E|\frac{1}{2},\frac{1}{2},0)$, $(E|\frac{1}{2},-\frac{1}{2},0)$ and $(E|0,0,5)$, so that the space group is triclinic *C*1. The numbers of symmetry operators are eight in *Fd* and two in *C*1, while the four-dimensional space group includes 16 operators. Consequently, the three-dimensional analysis will necessitate double parameters even in the 6*C*-type pyrrhotite. These facts indicate that the usual method is inconvenient for analyzing the *NC*-type pyrrhotite because the three-dimensional symmetry is



(*a*)

(*b*)

Fig. 6. (*a*) The electron density of the 5·5*C*-type pyrrhotite in the x_3x_4 plane, $\rho(0,0,x_3,x_4)$, over six cells. The solid line perpendicular to the a_4 axis corresponds to the usual three-dimensional space. (*b*) The electron density map of the 5·5*C*-type pyrrhotite in the *bc* plane, which is the section of the four-dimensional structure of (*a*) at the solid line.

low, so that many parameters are needed and the symmetry is different *depending on the period of modulation.*

8. Structure of the *NC*-type pyrrhotite

From the similarity in the diffraction intensities of the *NC*-type pyrrhotite with different composition, we can infer the structures of the 5*C*- (Fe_9S_{10}) and 6*C*-type ($Fe_{11}S_{12}$) pyrrhotites based on the present analysis. The vacancy distributions of the 5*C*- and 6*C*-type pyrrhotites in Fig. 3 are calculated under the assumption that the modulation wave for the occupation probability does not change with change in chemical composition and that the compositional change is only effected by the extension or subtraction of the almost occupied part in Fig. 2. These models of vacancy distribution agree well with those proposed previously by Koto *et al.* (1975) and, thus, indicate that the *NC*-type pyrrhotite with any composition is a similar structure in which the vacancies are concentrated on two or three successive sites in a row of iron atoms along the *c* axis. Such vacant sites are distributed spirally according to the symmetry: $(\sigma_y|\frac{1}{4},\frac{1}{4},0,\frac{1}{4})$, $(E|\frac{1}{2},0,0,\frac{1}{2})$, $(\sigma_y|\frac{1}{4},-\frac{1}{4},0,-\frac{1}{4})$. A similar spiral distribution of vacancies in the 4*C*-type pyrrhotite has previously been explained by the maximum separation of vacancies (Bertaut, 1953).

In connection with this vacancy distribution, an interesting characteristic in the atomic displacements (§ 6) is that the direction and quantity of the displacements are almost centrosymmetrical around the vacant sites (around $t = 0{\cdot}8$ in Fig. 4). This indicates that all irregularities induced by the presence of the vacancy are compensated around the vacancy. The range of such deformation spreads from $t = 0{\cdot}6$ to $t = 1{\cdot}0$ in Fig. 4, that is, over thirty ångströms, suggesting that the long-range Coulomb interactions between vacancies may play an important role in the wavy distribution of vacancies in the fundamental NiAs-type structure.

9. Conclusion

The present study showed that the *NC*-type pyrrhotites are systematically described with the four-dimensional description of modulated structures. The analysis of the *NC*-type pyrrhotite with $N = 5{\cdot}54$ was made by the application of the four-dimensional analysis, which is easier than the usual analysis based on a three-dimensional space group and the superstructure model.

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References

BERTAUT, E. F. (1953). *Acta Cryst.* **6**, 557–561.
BROWN, H., BULOW, R., NEUBUSER, J., WONDRATSCHEK, H. & ZASSENHAUS, H. (1978). *Crystallographic Groups of Four-Dimensional Space.* New York: Wiley.
HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
JANNER, A. & JANSSEN, T. (1977). *Phys. Rev. B*, **15**, 643–658.
JANNER, A., JANSSEN, T. & DE WOLFF, P. M. (1979). *AIP Conf. Proc.* No. 53. *Modulated Structures*–1979, *Kailua Kona, Hawaii*, edited by J. M. COWLEY, J. B. COHEN, M. B. SALAMON & B. J. WUENSCH, pp. 81–83. New York: American Institute of Physics.
KOTO, K., MORIMOTO, N. & GYOBU, A. (1975). *Acta Cyst.* B**31**, 2759–2764.
MORIMOTO, N., NAKAZAWA, H., NISHIGUCHI, K. & TOKONAMI, M. (1970). *Science*, **168**, 964–966.
NAKAZAWA, H. & MORIMOTO, N. (1971). *Mater. Res. Bull.* **6**, 345–357.
TOKONAMI, M., NISHIGUCHI, K. & MORIMOTO, N. (1972). *Am. Mineral.* **57**, 1066–1080.
WOLFF, P. M. DE (1974). *Acta Cryst.* A**30**, 777–785.
WONDRATSCHEK, H., BULOW, R. & NEUBUSER, H. (1971). *Acta Cryst.* A**27**, 523–535.
YAMAMOTO, A., NAKAZAWA, H. & TOKONAMI, M. (1979). *AIP Conf. Proc.* No 53. *Modulated Structures*–1979, *Kailua Kona, Hawaii*, edited by J. M. COWLEY, J. B. COHEN, M. B. SALAMON & B. J. WUENSCH, pp. 84–86. New York: American Institute of Physics.