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Modulated Structure of Wustite ($Fe_{1-x}O$)† (Three-Dimensional Modulation)

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Abstract

The structure of the incommensurate phase of $Fe_{1-x}O$ ($x = 0{\cdot}098$) with a cubic fundamental cell [$a = 4{\cdot}30\,(4)$ Å] has been analyzed on the basis of a six-dimensional expression of the structure factor and a six-dimensional space group P^{Fm3m}_{Pm3m}. The structure is described as a three-dimensionally modulated structure with a wavy distribution of Fe vacancies and a slight displacive modulation with incommensurate wavevectors $\mathbf{k}^1 = 0{\cdot}398\mathbf{a}^*$, $\mathbf{k}^2 = 0{\cdot}398\mathbf{b}^*$, $\mathbf{k}^3 = 0{\cdot}398\mathbf{c}^*$. Methods of obtaining six-dimensional symmetry and the possible form of the modulation wave in the three-dimensionally modulated structure are shown.

1. Introduction

The analysis of CuAu II based on a four-dimensional space group was shown in the previous paper [Yamamoto (1982*b*), hereafter (II)]. In this paper, the structure-factor formula derived in the first paper [Yamamoto (1982*a*), hereafter (I)] is applied to the known structure of wustite, $Fe_{1-x}O$, which has three-dimensional modulation (Koch & Cohen, 1969), to demonstrate an analysis based on the formula and a six-dimensional space group. Because of the non-stoichiometry of this material, the satellite reflections originate from a periodic distribution of vacancies. This density modulation is accompanied by the displacive modulation. Thus wustite is a typical example of three-dimensional density modulations.

† A preliminary report has been published (Yamamoto, Nakazawa & Tokonami, 1979).

The three-dimensional modulation shows characteristic satellite reflections: all reflections are specified by six integers h_1–h_6 as

$$\mathbf{h} = h_1\,\mathbf{a}^* + h_2\,\mathbf{b}^* + h_3\,\mathbf{c}^* + h_4\,\mathbf{k}^1 + h_5\,\mathbf{k}^2 + h_6\,\mathbf{k}^3, \quad (1)$$

where $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*$ are the unit vectors in the reciprocal lattice of the fundamental structure, which is the rock-salt structure in the present case. $\mathbf{k}^1,\mathbf{k}^2,\mathbf{k}^3$ are fractional vectors in the three-dimensional space R_3, each of which cannot be described by an integral linear combination of the others.

Wustite, $Fe_{1-x}O$ with $x = 0{\cdot}098$, has the wavevectors $\mathbf{k}^1 = 0{\cdot}398\mathbf{a}^*$, $\mathbf{k}^2 = 0{\cdot}398\mathbf{b}^*$, $\mathbf{k}^3 = 0{\cdot}398\mathbf{c}^*$. This is a well known example of an incommensurate structure with the three-dimensional modulation. This three-dimensional modulation is analyzed by using data of Koch & Cohen (1969). The aim of the present paper is to describe the method of analyzing the modulated structure with the three-dimensional modulation based on a six-dimensional space group.

2. Six-dimensional space group

The symmetry of a three-dimensionally modulated structure is described by a six-dimensional space group (Janner & Janssen, 1977). The unit vectors of a six-dimensional reciprocal lattice are given by $\mathbf{b}_1 = \mathbf{a}^*$, $\mathbf{b}_2 = \mathbf{b}^*$, $\mathbf{b}_3 = \mathbf{c}^*$, $\mathbf{b}_4 = \mathbf{k}^1 + \mathbf{d}_1$, $\mathbf{b}_5 = \mathbf{k}^2 + \mathbf{d}_2$, $\mathbf{b}_6 = \mathbf{k}^3 + \mathbf{d}_3$, where $\mathbf{d}_1,\mathbf{d}_2,\mathbf{d}_3$ are the unit vectors perpendicular to R_3. The unit vectors reciprocal to these are $\mathbf{a}_1 = \mathbf{a} - \sum_{i=1}^{3} k_1^i\,\mathbf{d}_i$, $\mathbf{b}_2 = \mathbf{b} - \sum_{i=1}^{3} k_2^i\,\mathbf{d}_i$, $\mathbf{b}_3 = \mathbf{c} - \sum_{i=1}^{3} k_3^i\,\mathbf{d}_i$ and $\mathbf{a}_{3+i} = \mathbf{d}_i$ ($i = 1,2,3$), 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 k_1^i,k_2^i,k_3^i are the $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*$ com-

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Table 1. *Symbols for rotation operators in the point group m3m*

The symbol next to an operator is the vector formed from the vector x,y,z by the operator.

E	xyz	I	$\bar{x}\bar{y}\bar{z}$	C_{4x}^{+}	$x\bar{z}y$	S_{4x}^{-}	$\bar{x}z\bar{y}$
C_{2x}	$x\bar{y}\bar{z}$	σ_x	$\bar{x}yz$	C_{4y}^{+}	$zy\bar{x}$	S_{4y}^{-}	$\bar{z}\bar{y}x$
C_{2y}	$\bar{x}y\bar{z}$	σ_y	$x\bar{y}z$	C_{4z}^{+}	$\bar{y}xz$	S_{4z}^{-}	$y\bar{x}\bar{z}$
C_{2z}	$\bar{x}\bar{y}z$	σ_z	$xy\bar{z}$	C_{4x}^{-}	$xz\bar{y}$	S_{4x}^{+}	$\bar{x}\bar{z}y$
C_{31}^{+}	zxy	S_{61}^{-}	$\bar{z}\bar{x}\bar{y}$	C_{4y}^{-}	$\bar{z}yx$	S_{4y}^{+}	$z\bar{y}\bar{x}$
C_{32}^{+}	$\bar{z}x\bar{y}$	S_{62}^{-}	$z\bar{x}y$	C_{4z}^{-}	$y\bar{x}z$	S_{4z}^{+}	$\bar{y}xz$
C_{33}^{+}	$\bar{z}\bar{x}y$	S_{63}^{-}	$zx\bar{y}$	C_{2a}	$yx\bar{z}$	σ_{da}	$\bar{y}\bar{x}z$
C_{34}^{+}	$z\bar{x}\bar{y}$	S_{64}^{-}	$\bar{z}xy$	C_{2b}	$\bar{y}\bar{x}\bar{z}$	σ_{db}	yxz
C_{31}^{-}	yzx	S_{61}^{+}	$\bar{y}\bar{z}\bar{x}$	C_{2c}	$z\bar{y}x$	σ_{dc}	$\bar{z}y\bar{x}$
C_{32}^{-}	$y\bar{z}\bar{x}$	S_{62}^{+}	$\bar{y}zx$	C_{2d}	$\bar{x}zy$	σ_{dd}	$x\bar{z}\bar{y}$
C_{33}^{-}	$\bar{y}z\bar{x}$	S_{63}^{+}	$y\bar{z}x$	C_{2e}	$\bar{z}\bar{y}\bar{x}$	σ_{de}	zyx
C_{34}^{-}	$\bar{y}\bar{z}x$	S_{64}^{+}	$yz\bar{x}$	C_{2f}	$\bar{x}\bar{z}\bar{y}$	σ_{df}	xzy

ponents of $\mathbf{k}^i$. Any reciprocal-lattice vector $\mathbf{h}'$ in R_6 is $\mathbf{h}' = \sum_{i=1}^{6} h_i \mathbf{b}_i$. The observed reflection (1) is regarded as the projection of this six-dimensional lattice point onto the usual three-dimensional space spanned by $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*$.

A symmetry operator in R_6 transforms the reciprocal lattice in R_6 into itself. The lattice type mentioned above strongly limits the types of symmetry operators.

From the transformation property of the reciprocal unit vectors $\mathbf{b}_i = \sum_{j=1}^{6} R_{ij} \mathbf{b}_j$ (a primed letter represents the quantity after transformation) we have $R_{ij} = 0$ for $i \leq 3, j \geq 4$ and $i \geq 4, j \leq 3$ (Janner & Janssen, 1977).† The first 3×3 part of this matrix is the same as the matrix representation of the rotation operator in the usual three-dimensional space R_3 because $\mathbf{b}_1 = \mathbf{a}^*$, $\mathbf{b}_2 = \mathbf{b}^*$, $\mathbf{b}_3 = \mathbf{c}^*$. The remaining 3×3 part is equal to the first 3×3 part in the present case because the former is the transformation matrix for the wavevectors and $\mathbf{k}^1,\mathbf{k}^2,\mathbf{k}^3$ are parallel to $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*$ and have the same length.

Since the three-dimensional sublattice spanned by $\mathbf{b}_1,\mathbf{b}_2,\mathbf{b}_3$ is cubic, we can consider 48 rotation operators included in the three-dimensional point group $m3m$ (see Table 1). Corresponding to these, there are 48 rotation operators in R_6 which have the same matrix elements in the two block-diagonal parts and transform the reciprocal lattice in R_6 into itself.

To determine the symmetry operators $(\mathsf{R}|\boldsymbol{\tau})$ in R_6, the translation vector $\boldsymbol{\tau}$ must be determined from the extinction rules. The satellite reflections appear only around the fundamental reflections allowed by the F-centered lattice of the fundamental NaCl-type structure (see Fig. 1). Therefore, the extinction rules of wustite for general reflections are

$$h_1 + h_2 = 2n, \tag{2}$$

$$h_2 + h_3 = 2n, \tag{3}$$

$$h_1 + h_3 = 2n, \tag{4}$$

where n is an integer.

An important concept for determining the space group of the modulated structure is the average structure, from which we can find the $\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3$ components of non-primitive translation $\boldsymbol{\tau}$. This is defined by the electron density integrated with respect to x_4,x_5,x_6. The electron density of $\rho(x_1,\ldots,x_6)$ in R_6 is invariant for the symmetry operators in R_6: when x_i $(i = 1,\ldots,6)$ are transformed into x_i' $(i = 1,\ldots,6)$ by $(\mathsf{R}|\boldsymbol{\tau})$, the electron density fulfills $\rho(x_1',\ldots,x_6') = \rho(x_1,\ldots,x_5)$. Then, after integration, we have $\hat{\rho}(x_1',x_2',x_3') = \hat{\rho}(x_1,x_2,x_3)$ for the electron density of the average structure. This expression shows that the electron density of the average structure is invariant for the symmetry operator which is given by the first 3×3 part of R and τ_1,τ_2,τ_3 ($\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3$ components of $\boldsymbol{\tau}$) because R is (3 + 3)-reducible. These symmetry operators are included in a three-dimensional space group of the average structure.

In the present case, the space group of the average structure is expected to be one of $Fm3m$, $F\bar{4}3m$, $F432$ from the extinction rules for the fundamental reflections. It is known that the fundamental structure of wustite is of the NaCl type (space group $Fm3m$ and Fe and O are located at 0,0,0 and $\frac{1}{2}$,0,0), but Fe partially occupies the tetrahedral site $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ (Koch & Cohen, 1969). In this case possible space groups of the average structure are $Fm3m$ and $F\bar{4}3m$. In $F\bar{4}3m$, there are two tetrahedral sites $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ and $\frac{3}{4},\frac{3}{4},\frac{3}{4}$, but these are equivalent in $Fm3m$. In order to determine the average structure, structure analyses based on these space groups were made using 42 fundamental reflections (six reflections suspected of secondary extinction were dropped). For $F\bar{4}3m$, the model in which the site $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ is partially occupied by Fe was employed. Parameters in both cases are only the temperature factors and an occupation ratio between the octahedral and tetrahedral Fe sites. In both cases, the tetrahedral site was slightly occupied with an occupation probability less than 0·01

† We take the centered lattice whenever the wavevectors lie on the first Brillouin-zone boundary of the fundamental structure. In the centered lattice, the wavevectors are in the Brillouin zone and the relations mentioned above are fulfilled by any three-dimensionally modulated structures.

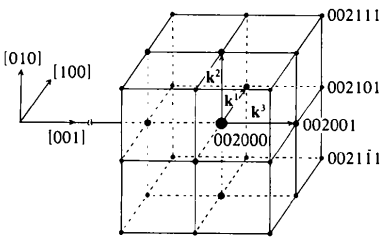

Fig. 1. Satellite reflections around the 002000 fundamental reflection after Koch & Cohen (1969). $\mathbf{k}^1,\mathbf{k}^2,\mathbf{k}^3$ show the wavevectors of the modulation wave.

and almost the same R factor was obtained ($R = 0{\cdot}06$). Thus both possibilities are considered in the following.

The components τ_4,τ_5,τ_6 are obtained from the extinction rules including satellite reflections. The extinction rules (2)–(4) imply that there exist the centering translations $(E|\frac{1}{2},\frac{1}{2},0,0,0,0)$, $(E|\frac{1}{2},0,\frac{1}{2},0,0,0)$, $(E|0,\frac{1}{2},\frac{1}{2},0,0,0)$ [where the translation vector $\boldsymbol{\tau}$ is represented by its $\mathbf{a}_i$ $(i = 1,\ldots,6)$ components], indicating that the Bravais lattice is non-primitive. We call this an $F(1,2,3)$-centered lattice for convenience. There is no additional extinction rule attributed to the presence of hyper glide planes or hyper screw axes. Therefore, we can take $\boldsymbol{\tau} = 0$ for 48 symmetry operators which have the same matrix elements for the block-diagonal 3×3 parts as those of the point group $m3m$. The resulting space group is generated from these and the centering translations of the $F(1,2,3)$-centered lattice.

3. Modulation wave

The waveform of the modulation function is limited when atoms are located at the special positions in the space group of the average structure. We consider the NaCl-type fundamental structure and ignore Fe atoms in the tetrahedral sites for a while. Then the space group is $Fm3m$ and Fe is located at 0,0,0 and O at $\frac{1}{2}$,0,0. In these special positions, the coordinates are transformed into themselves under 48 operators because the site-symmetry group is $m3m$ in both sites. Corresponding to these, there are 48 operators in the space group in R_6 for which the modulation function is invariant. These construct the site-symmetry group G_s in R_6. The group G_s for the Fe site is generated by the five operators $(C_{2x}|0,0,0,0,0,0)$, $(C_{2z}|0,0,0,0,0,0)$, $(\sigma_{da}|0,0,0,0,0,0)$, $(C_{31}^{+}|0,0,0,0,0,0)$ and $(I|0,0,0,0,0,0)$, and G_s for the O site is generated by $(C_{2x}|0,0,0,0,0,0)$, $(C_{2z}|1,0,0,0,0,0)$, $(\sigma_{da}|\frac{1}{2},-\frac{1}{2},0,0,0,0)$, $(C_{31}^{+}|\frac{1}{2},-\frac{1}{2},0,0,0,0)$ and $(I|1,0,0,0,0,0)$ (for the symbols, see Table 1).

The modulation functions in the three-dimensional modulation are generally written as

$$x_l^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu}) = \bar{x}_l^{\mu} + \tfrac{1}{2}\Big\{\sum_{n_1,n_2,n_3} u^{\mu}_{l(n_1,n_2,n_3)}\, f^{\mu}_{pw} + \text{c.c.}\Big\}, \quad (5)$$

$$B^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu}) = \tfrac{1}{2}\Big\{\sum_{n_1,n_2,n_3} B^{\mu}_{(n_1,n_2,n_3)}\, f^{\mu}_{pw} + \text{c.c.}\Big\}, \quad (6)$$

$$P^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu}) = \tfrac{1}{2}\Big\{\sum_{n_1,n_2,n_3} P^{\mu}_{(n_1,n_2,n_3)}\, f^{\mu}_{pw} + \text{c.c.}\Big\}, \quad (7)$$

where f^{μ}_{pw} is the plane wave $\exp\{2\pi i[n_1\bar{x}_4^{\mu} + n_2\bar{x}_5^{\mu} + n_3\bar{x}_6^{\mu}]\}$ and we take isotropic temperature factors. The notation is the same as in (I): $x_l^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu})$ is the positional vector of the μth atom in the unit cell, $B^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu})$ is the isotropic temperature factor, and $P^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu})$ is the occupation probability of the μth atom; these are continuous functions of $\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu}$ (the bar denotes quantities belonging to the fundamental structure). There are only two independent atoms in the present case, so that Fe and O are specified by $\mu = 1$ and $\mu = 2$, respectively.

For any operator in G_s, the modulation functions must be invariant. The possible modulation-wave forms are obtained from the following formulae. For atomic position, we have

$$x_l^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu}) = \frac{1}{N}\sum_{(\mathsf{R}|\boldsymbol{\tau})} \{(\mathsf{R}|\boldsymbol{\tau})\, \mathbf{x}^{\mu}(\bar{x}_4',\bar{x}_5',\bar{x}_6')\}_i, \quad (8)$$

where N is the order of G_s and $\bar{x}'_{3+i} = \sum_{j=1}^{6} R^{-1}_{3+i,j}(\bar{x}_j^{\mu} - \tau_j)$. The sum of $(\mathsf{R}|\boldsymbol{\tau})$ is over all elements of G_s. Similarly, for the isotropic temperature factor and the occupation probability, we have

$$B^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu}) = \frac{1}{N}\sum_{(\mathsf{R}|\boldsymbol{\tau})} B^{\mu}(\bar{x}_4',\bar{x}_5',\bar{x}_6'), \quad (9)$$

$$P^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu}) = \frac{1}{N}\sum_{(\mathsf{R}|\boldsymbol{\tau})} P^{\mu}(\bar{x}_4',\bar{x}_5',\bar{x}_6'), \quad (10)$$

and for the anisotropic temperature factor, we have

$$B^{\mu}_{ij}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu}) = \frac{1}{N}\sum_{(\mathsf{R}|\boldsymbol{\tau})} \{\mathsf{R}B^{\mu}(\bar{x}_4',\bar{x}_5',\bar{x}_6')\,\tilde{\mathsf{R}}\}_{ij}. \quad (11)$$

Substituting the right-hand sides of (5)–(7) into (8)–(10), we have the possible Fourier terms in Table 2, where the Fourier terms with $n_1 = n_2 = n_3 = 1$ and higher-order terms are dropped because $h_1h_2h_3$ ±1 ±1 ±1 and $h_1h_2h_3$ 200 *etc.* are weak and almost all such reflections are not observed.

Now we consider the model with tetrahedral Fe atoms which is specified by $\mu = 3$. The tetrahedral position is the special position defined by the site-symmetry group which is generated by $(C_{2x}|0,\frac{1}{2},\frac{1}{2},0,0,0)$, $(C_{2z}|\frac{1}{2},\frac{1}{2},0,0,0,0)$, $(\sigma_{db}|0,0,0,0,0,0)$ and

Table 2. *The Fourier terms for the octahedral* Fe *and* O *sites appearing in the modulation functions* $u_l^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu})$, $B^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu})$ *and* $P^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu})$

In the following, $c(1,2,3)$, $s(1,-2,3)$ *etc.* mean $\cos 2\pi(\bar{x}_4^{\mu} + 2\bar{x}_5^{\mu} + 3\bar{x}_6^{\mu})$, $\sin 2\pi(\bar{x}_4^{\mu} - 2\bar{x}_5^{\mu} + 3\bar{x}_6^{\mu})$ *etc.* Possible Fourier terms for Fe and O are the same.

Displacement

Coefficient	Fourier term
(1) Im $u_{1(100)}$	$s(1,0,0)\,\mathbf{a}_1 + s(0,1,0)\,\mathbf{a}_2 + s(0,0,1)\,\mathbf{a}_3$
(2) Im $u_{1(110)}$	$[s(1,1,0) + s(1,0,1) + s(1,-1,0) + s(1,0,-1)]\,\mathbf{a}_1$ + $[s(0,1,1) + s(1,1,0) + s(0,1,-1) + s(-1,1,0)]\,\mathbf{a}_2$ + $[s(1,0,1) + s(0,1,1) + s(-1,0,1) + s(0,-1,1)]\,\mathbf{a}_3$

Isotropic temperature factor and occupation probability

Coefficient	Fourier term
(1) Re $B_{(000)}$, Re $P_{(000)}$	$c(0,0,0)$
(2) Re $B_{(100)}$, Re $P_{(100)}$	$c(1,0,0) + c(0,1,0) + c(0,0,1)$
(3) Re $B_{(110)}$, Re $P_{(110)}$	$c(1,1,0) + c(0,1,1) + c(1,0,1)$ + $c(1,-1,0) + c(0,1,-1) + c(-1,0,1)$

Table 3. *Additional Fourier terms for the tetrahedral site*

The Fourier terms for this site are given by the terms in Table 2 and the following terms.

Displacement

Coefficient	Fourier term
(1) Re $u_{1(011)}$	$[c(0,1,1)-c(0,-1,1)]\,\mathbf{a}_1$ $+[c(1,0,1)-c(-1,0,1)]\,\mathbf{a}_2$ $+[c(1,1,0)-c(1,-1,0)]\,\mathbf{a}_3$

($C_{31}^{+}|0,0,0,0,0,0$). This position necessitates the Fourier terms shown in Table 3 in addition to those in Table 2 because of the low site symmetry. In this model, there are two possibilities for the space group in R_6 corresponding to the space groups of the average structure: $Fm3m$ and $F\bar{4}3m$. These are written as P_{Pm3m}^{Fm3m} and $P_{P\bar{4}3m}^{F\bar{4}3m}$ according to Janssen (1980, private communication). In $P_{P\bar{4}3m}^{F\bar{4}3m}$, the Fourier terms in Table 3 are also possible for the octahedral Fe and O sites because the site symmetry is the same as that in the tetrahedral site.

4. Modulated structure

For the refinement of the structure, the same least-squares program was used as in (II). As shown in (I), the structure factor in the present case is written as

$$F_{\mathbf{h}'} = \sum_{\mu(\mathrm{R}|\tau)} p^{\mu} \int_0^1 \mathrm{d}\bar{x}_4^{\mu} \int_0^1 \mathrm{d}\bar{x}_5^{\mu} \int_0^1 \mathrm{d}\bar{x}_6^{\mu}\, f^{\mu}(\mathbf{h}) P^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu}) \times \exp\left[-B^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu})\,h^2 + 2\pi i \sum_j \{h_j[\mathrm{R}\mathbf{x}^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu})]_j + h_j\tau_j\}\right]. \quad (12)$$

The structure was refined first based on P_{Pm3m}^{Fm3m}, neglecting Fe in the tetrahedral site. The integration in (12) was made by using Gauss's method with four divisions. The refinement was started from the structure which has three sinusoidal modulations along the a,b,c axes for the occupation probability and the usual isotropic temperature factor of 0·5 Å^2. To avoid the differential matrix becoming singular, the atomic position is slightly shifted from that of the fundamental structure. The R factor of this starting point was 0·446. Since the satellite reflections with $h_4h_5h_6$ ±100, 0 ± 10 and 00 ± 1 have strong intensity, the five parameters $u_{1(100)}^{\mu}$, $B_{(000)}^{\mu}$ ($\mu = 1, 2$) and $P_{(100)}^{1}$ were refined first by three cycles and $R = 0{\cdot}174$ was obtained using all observed reflections (42 fundamental and 110 satellite reflections measured with Mo $K\alpha$ and Co $K\alpha$ radiations). Next, adding the parameters $u_{1(110)}^{\mu}$ ($\mu = 1$, 2) and $P_{(110)}^{1}$, eight parameters were refined giving $R = 0{\cdot}167$. At this stage, the modulation function for the occupation probability of Fe was plotted and it was noticed that this function takes a large negative value near the origin. In addition, the difference Fourier map (Fig. 2) at $x_3 = 0{\cdot}25$, $x_4 = x_5 = x_6 = 0{\cdot}096$ showed a strong peak near $x_1 = x_2 = 0{\cdot}25$ implying that the atom is located at the tetrahedral site with fractional occupation probability. Therefore, the second model having an Fe atom in this site was considered.

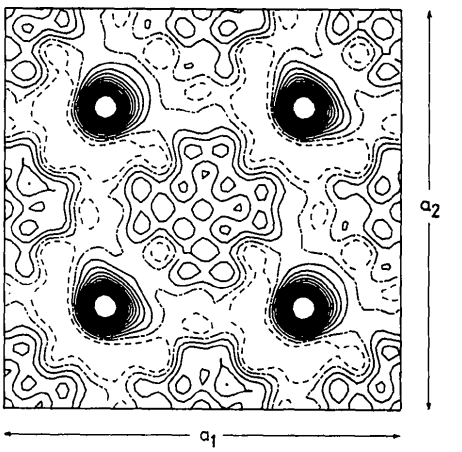

Fig. 2. The difference Fourier map of wustite near the tetrahedral site. The figure shows $\rho_o(x_1,\ldots,x_6) - \rho_c(x_1,\ldots,x_6)$ at $x_3 = \frac{1}{4}$, $x_4 = x_5 = x_6 = 0{\cdot}096$.

In this model, Fe atoms occupy the octahedral site and the tetrahedral site, so that Re $P_{(000)}^{1}$ + Re $P_{(000)}^{3} = 0{\cdot}902$ and there are the two possibilities mentioned before. The refinement based on P_{Pm3m}^{Fm3m} converged to $R = 0{\cdot}111$ giving a mean occupation probability for the tetrahedral site of 0·015 and the difference Fourier map showed no remarkable peak at the tetrahedral site. However, the modulation function for the occupation probability of the octahedral Fe site also took a large negative value at the origin. Therefore, a restricted least-squares method developed in a previous paper (Yamamoto, 1981) was applied after slight modification: the square of the weighted R factor plus the penalty function defined by

$$\tfrac{1}{3}\sum_{\mu=1}^{3} \int_0^1 \mathrm{d}\bar{x}_4 \int_0^1 \mathrm{d}\bar{x}_5 \int_0^1 \mathrm{d}\bar{x}_6 \{g^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu})\}^2 \quad (13)$$

was minimized, where $g^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu})$ takes a value $2P^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu})$ for $P^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu}) < 0$, $2\{1 - P^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu})\}$ for $P^{\mu}(\bar{x}_4^{\mu},\bar{x}_5^{\mu},\bar{x}_6^{\mu}) > 1$ and otherwise zero. This method is effective for constraining the occupation probability within the physically reasonable range. The final refinement was made by using Gauss's integrals with five divisions in order to reduce computational errors.

Table 4. *The R factors in models* 1 *and* 2

R_0 and R_1 represent the R factors for the fundamental and satellite reflections.

		Mo $K\alpha$		Co $K\alpha$
	R	R_0	R_1	R_1
Model 1	0·168	0·065	0·236	0·411
Model 2	0·110	0·057	0·166	0·176

Table 5. *Final parameters in the model including tetrahedral* Fe *atoms (model* 2)

For the coefficients, refer to Tables 2 and 3. The standard deviations are in parentheses. Fe(1) and Fe(2) represent the octahedral and tetrahedral Fe atoms, respectively.

Displacement ($\times 10^4$)

	$-\mathrm{Im}\, u_{1(100)}$	$-\mathrm{Im}\, u_{1(110)}$	$\mathrm{Re}\, u_{1(011)}$
Fe(1)	−139 (4)	−33 (4)	
Fe(2)	256 (161)	−51 (72)	234 (52)
O	78 (19)	109 (14)	

Temperature factor (Å$^2 \times 10^2$)

	$\mathrm{Re}\, B_{(000)}$	$\mathrm{Re}\, B_{(100)}$	$\mathrm{Re}\, B_{(110)}$
Fe(1)	50 (7)	0 (8)	4 (8)
Fe(2)	253 (54)		
O	119 (14)	15 (12)	60 (10)

Occupation probability ($\times 10^2$)

	$\mathrm{Re}\, P_{(000)}$	$\mathrm{Re}\, P_{(100)}$	$\mathrm{Re}\, P_{(110)}$
Fe(1)	77 (1)	−16 (1)	−5 (1)
Fe(2)	6 (1)	6 (1)	3 (1)
O	100		

The model belonging to the space group P^{Fm3m}_{Pm3m} converged to $R = 0{\cdot}110$ after six cycles. Starting from the resulting parameters, the model with the space group $P^{F\bar{4}3m}_{P\bar{4}3m}$ was refined but an improvement of the R factor was not found; therefore, this is rejected. The R factors for the fundamental and satellite reflections in the first model (model 1) and the second model (model 2) are shown in Table 4 and the final parameters in model 2 are shown in Table 5.*

The R factors for the satellite reflections were notably reduced in model 2 (see Table 4), indicating that the tetrahedral site is fractionally occupied by Fe. From Table 5, the mean occupation probability of the tetrahedral Fe site is 0·06.

5. Superstructure model

To compare the result with the previous one (Koch & Cohen, 1969), we calculate the vacancy distribution and displacements of wustite in the case of $k_1^1 = k_2^2 = k_3^3 = \frac{1}{3}$, which corresponds to the $3X$-cell model of Koch & Cohen. The positions and occupation probabilities calculated by using the parameters in Table 5 are shown in Table 6 together with the results of Koch &

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36663 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 6. *Parameters in the* $3X$*-cell model calculated from the parameters in Table* 5, *and the parameters in model* 4 *of Koch & Cohen* (1969)

		$3X$-cell model				Model 4 of Koch & Cohen			
	Equipoints	x	y	z	P	x	y	z	P
Fe									
$P\bar{4}3m$	4(*e*)					0·090	0·090	0·090	1·0
$Pm3m$	8(*g*)	0·081	0·081	0·081	0·33				
	1(*a*)	0·0	0·0	0·0	−0·03	0·0	0·0	0·0	0·0
	12(*i*)	0·160	0·160	0·0	0·32	0·166	0·166	0·0	0·0
	6(*e*)	0·326	0·0	0·0	0·53	0·329	0·0	0·0	1·0
	12(*i*)	0·328	0·328	0·0	0·85	0·329	0·329	0·0	1·0
	12(*h*)	0·5	0·163	0·0	0·80	0·5	0·167	0·0	1·0
	24(*m*)	0·327	0·163	0·163	0·71	0·324	0·158	0·158	1·0
	24(*l*)	0·5	0·330	0·166	0·96	0·5	0·333	0·167	1·0
	8 (*g*)	0·331	0·331	0·331	0·93	0·330	0·330	0·330	1·0
	6(*f*)	0·5	0·5	0·333	0·97	0·5	0·5	0·333	1·0
	3(*c*)	0·5	0·5	0·0	1·04	0·5	0·5	0·0	1·0
O									
$Pm3m$	6(*e*)	0·182	0·0	0·0		0·172	0·0	0·0	
	3(*d*)	0·5	0·0	0·0		0·5	0·0	0·0	
	24(*k*)	0·345	0·172	0·0		0·338	0·168	0·0	
	8(*g*)	0·175	0·175	0·175		0·174	0·174	0·174	
	24(*m*)	0·336	0·336	0·163		0·338	0·338	0·160	
	12(*j*)	0·5	0·166	0·166		0·5	0·167	0·167	
	12(*j*)	0·5	0·326	0·326		0·5	0·333	0·333	
	1(*b*)	0·5	0·5	0·5		0·5	0·5	0·5	
	6(*f*)	0·5	0·5	0·156		0·5	0·5	0·167	

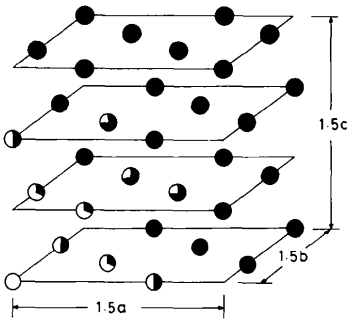

Fig. 3. The vacancy distribution in the $3X$-cell model. The black shading represents the occupation probability of the octahedral Fe site. The almost-occupied sites ($P \geq 0{\cdot}8$) are regarded as completely occupied for simplicity.

Cohen. It is noted that many positional and occupational parameters have approximately the same values as the previous result. The vacancy distribution in the octahedral site is illustrated in Fig. 3, where the black shading represents the occupation probability of Fe. The principal result is similar to the previous one: the vacancies tend to cluster near the origin. However, there is an essential difference in the fact that the sites $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},0,\frac{1}{2}$; $0,\frac{1}{2},\frac{1}{2}$ in R_3 cannot be completely vacant. To obtain Koch's result, we must introduce strong third-order harmonics to make the modulation function block type. This will lead to strong third-order satellite reflections inconsistent with experiment. Another difference exists in the distribution of Fe atoms in the tetrahedral sites. The present model places the octahedral cluster near the origin in contrast to the tetrahedral one in the previous result. The present analysis only gives the statistical structure of wustite, so that this structure may have locally the vacancy cluster with tetrahedral Fe atoms given by Koch & Cohen.

6. Summary and concluding remarks

It has been shown that the three-dimensionally modulated structure of wustite can be analyzed on the basis of a six-dimensional space group. The analysis describes methods of finding the six-dimensional space group from the extinction rules and the space group of the average structure,* and of determining possible modulation-wave forms at the special positions. The refinement was started from a single sinusoidal modulation for the occupation probability of the Fe site and smoothly converged from $R = 0{\cdot}446$ to $0{\cdot}110$.

The method determines the vacancy distribution and atomic positions simultaneously. Thus the method can treat the structure including vacancy ordering, and is applicable whether the ordering is complete or statistical. The method is general, and can be applied to any three-dimensionally modulated structures and, after slight modifications, to two- or n-dimensionally ($n = 4,5,\ldots$) modulated structures.

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* Recently, Janner & Janssen (1979) gave a complete theory for calculating all $(3 + n)$-dimensional modulated-structure space groups based on a knowledge of 3- and n-dimensional space groups. A complete list of space groups for one-dimensionally modulated structures is now available (de Wolff, Janner & Janssen, 1981).

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