Modulated Structure of CuAu II (One-Dimensional Modulation)

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Abstract

The long-period antiphase-domain structure of CuAu II with an orthorhombic fundamental cell [$a = 3.956$ (3), $b = 3.972$ (2), $c = 3.976$ (2) Å] is analyzed on the basis of a four-dimensional expression of the structure factor and a four-dimensional space group. This analysis requires half the number of parameters of the usual three-dimensional analysis based on the superstructure model because its four-dimensional symmetry is higher than its three-dimensional symmetry. The structure is described as a modulated structure with highly anharmonic substitutional modulation and a slight displacive modulation with a commensurate wavevector $k = 0.1b^*$.

1. Introduction

The structure-factor formula for a modulated structure derived in a previous paper [Yamamoto (1982); hereafter (I)] is a generalization of a structure-factor formula derived by de Wolff (1974) in three points: de Wolff's formula is extended to cover the cases in which a modulated structure has both density and displacive modulations; the dimension of modulation is higher than one; and some wavevectors of the modulation wave are commensurable with the fundamental reciprocal lattice while others are incommensurable. This extension makes it possible to analyze the superstructure based on a multi-dimensional description.

In this paper, we apply the formula to CuAu II which has one-dimensional substitutional and displacive modulations with a commensurable wavevector. As stated in (I), the displacive modulation plays an essential role in determining the modulation wave for substitutional modulation. To demonstrate the analysis of a superstructure based on the new method, the known structure of CuAu II (Okamura, Iwasaki & Ogawa, 1968) is employed. It is a typical example of substitutional modulation in which one site is occupied by two atoms with fractional occupation probabilities. This substitutional modulation has a long period represented by the wavevector $k = 0.1b^*$. This is a
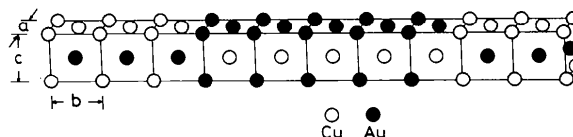

Fig. 1. The ideal antiphase-domain structure of CuAu II.

well known antiphase-domain structure (see Fig. 1) which has a block-type modulation wave with wavevector k for the occupation probability of Cu and Au.

The symmetry of a one-dimensionally modulated incommensurate structure is described by a four-dimensional space group based on a fictitious four-dimensional lattice (de Wolff, 1974; Janner & Janssen, 1977). This multi-dimensional description is also effective in the commensurate (super-) structure as shown by Valentine, Cavin & Yakel (1977). Since the structure-factor formula derived in (I) is expressed in terms of four-dimensional space R_4, the analysis based on the four-dimensional space group can easily be performed. In this paper, the analysis based on the formula and the four-dimensional symmetry is demonstrated using the data of Okamura *et al.* (1968).

2. Four-dimensional space group

In the four-dimensional description, to all reflections are assigned four integers $h_1, \ldots, h_4$:

$$h = h_1 a^* + h_2 b^* + h_3 c^* + h_4 k, \quad (1)$$

where a^*, b^*, c^* are the unit vectors in the reciprocal lattice of the fundamental structure which has an orthorhombic unit cell with $a = 3.956$, $b = 3.972$, $c = 3.676$ Å and k is the wavevector of the modulation wave represented by $0.1b^*$. Fig. 2 shows a schematic view of the diffraction pattern. In this case the higher-order satellite reflections are very weak, so that the correspondence between the lattice points in R_4 and the observed reflections can be regarded as one-to-one. Therefore, from the figure, the following extinction rules are obtained for general reflections $h_1h_2h_3h_4$:
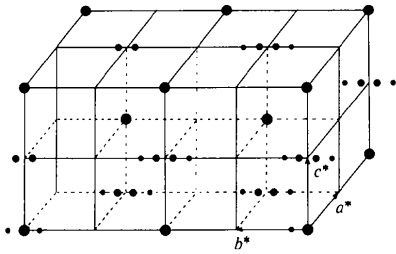
$$h_1 + h_2 = 2n, \quad (2)$$

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Fig. 2. The diffraction aspect of CuAu II after Ogawa & Watanabe (1954) and Okamura, Iwasaki & Ogawa (1968).

$$h_1 + h_3 + h_4 = 2n, \tag{3}$$

$$h_2 + h_3 + h_4 = 2n, \tag{4}$$

where n is an integer. These rules are derived from the following considerations.

As mentioned in (I), the reciprocal lattice in R_4 is spanned by the unit vectors $\mathbf{b}_1 = \mathbf{a}^*$, $\mathbf{b}_2 = \mathbf{b}^*$, $\mathbf{b}_3 = \mathbf{c}^*$, $\mathbf{b}_4 = \mathbf{k} + \mathbf{d}$. This lattice is transformed into itself by the symmetry operator $(R|\tau)$ in R_4. From the definition, $\mathbf{b}_4$ is oblique to R_3 whenever $\mathbf{k}$ is nonzero. Therefore, the rotation operator R in R_4 is limited to that transforming $\mathbf{b}_4$ into $\mathbf{b}_4$ or $-\mathbf{b}_4$ and $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ into their integral linear combinations. When a transformed vector is represented by a primed letter, the matrix element of the rotation operator, R_{ij}, is defined by

$$\mathbf{b}'_i = \sum_{j=1}^{4} R_{ij}\,\mathbf{b}_j. \tag{5}$$

Then the above statement is expressed by $R_{i4} = R_{4i} = 0$ ($i = 1, 2, 3$) and $R_{44} = \pm 1$. The double sign is plus or minus according as R transforms $\mathbf{k}$ into $\mathbf{k}$ or $-\mathbf{k}$ because $\mathbf{b}_4 = \mathbf{k} + \mathbf{d}$. [We take a centered lattice in the modulated structure whenever $\mathbf{k}$ is on the Brillouin-zone boundary of the fundamental structure. In this centered lattice, $\mathbf{k}$ is in the Brillouin zone (see Yamamoto & Nakazawa, 1982).] Thus we have a (3 + 1)-reducible matrix for any symmetry operator in R_4. The matrix elements of the first 3×3 part are the same as those in R_3 since $\mathbf{b}_1 = \mathbf{a}^*$, $\mathbf{b}_2 = \mathbf{b}^*$, $\mathbf{b}_3 = \mathbf{c}^*$. From this fact, it is convenient to use the same symbol for R as in R_3.[†] For example, C_{2x} has the nonzero elements $R_{11} = 1$, $R_{22} = -1$, $R_{33} = -1$, $R_{44} = -1$ since the fundamental structure is orthorhombic and $\mathbf{k}$ is parallel to the b axis.

Another condition for the symmetry operator is: $(R|\tau)$ is also the symmetry operator in the fundamental structure. The fundamental structure in R_4 is defined by the limiting case of infinitesimal distortion [see (I)]. It is natural in the present case to consider a three-dimensional fundamental structure belonging to the

space group $Fmmm$. Cu and Au atoms are located at $\frac{1}{4},\frac{1}{4},0$ with the occupation probability of $\frac{1}{2}$. The other three positions are obtained by the centering translations $(E|\frac{1}{2},\frac{1}{2},0)$, $(E|\frac{1}{2},0,\frac{1}{2})$, $(E|0,\frac{1}{2},\frac{1}{2})$. These are the fourfold special positions $4(a)$ of $Fmmm$. [For the sake of comparison with the result of Okamura *et al.* (1968), the coordinate system with an origin different from that in *International Tables for X-ray Crystallography* (1969) is taken.] This space group is generated by $(C_{2x}|0,\frac{1}{2},0)$, $(C_{2y}|\frac{1}{2},0,0)$, $(I|0,0,0)$ and the centering translations. Corresponding to this, we can consider the space group in R_4 which is generated by $(C_{2x}|0,\frac{1}{2},0,\tau_4)$ $(C_{2y}|\frac{1}{2},0,0,\tau_4)$, $(I|0,0,0,\tau_4)$ and the centering translations $(E|\frac{1}{2},\frac{1}{2},0,\tau_4)$, $(E|\frac{1}{2},0,\frac{1}{2},\tau_4)$ and $(E|0,\frac{1}{2},\frac{1}{2},\tau_4)$. The fourth non-primitive translation, τ_4, must be determined in each operator so that the resulting space group in R_4 gives the extinction rules mentioned before.

The $G(1,2)$-centered lattice (Wondratschek, Bülow & Neubüser, 1971) having the centering translations $(E|\frac{1}{2},\frac{1}{2},0,0)$, $(E|\frac{1}{2},0,\frac{1}{2},\frac{1}{2})$, $(E|0,\frac{1}{2},\frac{1}{2},\frac{1}{2})$ gives the extinction rules (2)–(4). Since all extinction rules are explained by the centering translations, we can take $(C_{2x}|0,\frac{1}{2},0,0)$, $(C_{2y}|\frac{1}{2},0,0,0)$ and $(I|0,0,0,0)$ together with the centering translations of the $G(1,2)$-centered lattice as the generating elements.[*] (From the fundamental structure and the extinction rules, two other space groups are also possible having the three-dimensional part $Fmm2$. These possibilities will be discussed later.) The space group employed maintains three centering translations, which are present in the fundamental structure, in a different form while the three-dimensional space group $Imam$ (Okamura *et al.*, 1968) loses some of them and cannot explain the systematic extinction rules (2)–(4). This shows that the four-dimensional space group describes the symmetry of the superstructure of CuAu II more efficiently.

3. Modulation wave

As shown in (I), the modulation waves for the atomic position, isotropic temperature factor and occupation probability are given by

$$x_i^\mu(\bar{x}_4^\mu) = \bar{x}_i^\mu + \left[\frac{1}{2}\sum_n u_{in}^\mu \exp\{2\pi i n \bar{x}_4^\mu\} + \text{c.c.}\right] \tag{6}$$

$$B^\mu(\bar{x}_4^\mu) = \frac{1}{2}\sum_n B_n^\mu \exp\{2\pi i n \bar{x}_4^\mu\} + \text{c.c.} \tag{7}$$

$$P^\mu(\bar{x}_4^\mu) = \frac{1}{2}\sum_n P_n^\mu \exp\{2\pi i n \bar{x}_4^\mu\} + \text{c.c.} \tag{8}$$

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† Janner & Janssen (1977) used a primed symbol for R when $R_{44} = -1$. Unprimed symbols are used in this paper to unify the notation for all modulated structures since such notation is impossible for two- or higher-dimensional modulations.

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* Rigorously speaking, in addition, one generator for the translations $(E|0,0,0,1)$ is necessary. The entire list of superspace groups for one-dimensionally modulated structures by de Wolff, Janner & Janssen (1981) became available after the present work was completed. According to this, the space group employed is $L^{Fmmm}_{1\bar{1}1}$.

In the present case, Cu and Au occupy the same position, so that when the independent Cu and Au atoms are represented by $\mu = 1$ and 2, we have $u_{in}^1 = u_{in}^2$, $B_n^1 = B_n^2$ ($n = 0, 1, 2, \ldots$) and $P_0^1 = P_0^2 = \frac{1}{2}, P_n^1 = -P_n^2$ ($n = 1, 2, \ldots$). Since these atoms are located at the special position in the fundamental structure, their coordinates $\frac{1}{4},\frac{1}{4},0$ in R_3 do not change by the symmetry operators $(E|0,0,0)$, $(C_{2x}|0,\frac{1}{2},0)$, $(C_{2y}|\frac{1}{2},0,0)$, $(C_{2z}|\frac{1}{2},\frac{1}{2},0)$, $(I|\frac{1}{2},\frac{1}{2},0)$, $(\sigma_x|\frac{1}{2},0,0)$, $(\sigma_y|0,\frac{1}{2},0,)$ and $(\sigma_z|0,0,0)$ in $Fmmm$. The coordinates $x_1^\mu, x_2^\mu, x_3^\mu, x_4^\mu$ are functions of $\bar{x}_4^\mu$ in the four-dimensional description of modulated structures. Therefore, these functions must be invariant under the corresponding symmetry operations, which form the site-symmetry group G_s generated by $(C_{2x}|0,\frac{1}{2},0,0)$, $(C_{2y}|\frac{1}{2},0,0,0)$ and $(I|\frac{1}{2},\frac{1}{2},0,0)$. This condition constrains the shape of the modulation function as shown in the following.

From the transformation properties of a vector and a scalar, the atomic position, isotropic temperature factor and occupation probability at $\mathbf{x}^\nu = (R|\tau)\,\mathbf{x}^\mu$ are given by

$$x_i^\nu(\bar{x}_4^\nu) = [(R|\tau)\,\mathbf{x}^\mu(\bar{x}_4^\mu)]_i = \sum_{j=1}^4 R_{ij}\,x_j^\mu(\bar{x}_4^\mu) + \tau_i \quad (9)$$

$$B^\nu(\bar{x}_4^\nu) = (R|\tau)\,B^\mu(\bar{x}_4^\mu) = B^\mu(\bar{x}_4^\mu) \quad (10)$$

$$P^\nu(\bar{x}_4^\nu) = (R|\tau)\,P^\mu(\bar{x}_4^\mu) = P^\mu(\bar{x}_4^\mu). \quad (11)$$

The special position $\mathbf{x}^\mu$ must fulfill

$$x_i^\mu(\bar{x}_4^\mu) = \sum_{j=1}^4 R_{ij}\,x_j^\mu[R_{44}^{-1}(\bar{x}_4^\mu - \tau_4)] + \tau_i \quad (12)$$

for all elements of G_s, where we use $\bar{x}_4^\mu = R_{44}^{-1}(\bar{x}_4^\mu - \tau_4)$ in (9). One method of finding the modulation function of the special position is to solve (12) for the generating elements of G_s. From $(C_{2y}|\frac{1}{2},0,0,0)$, we have $x_1^\mu(\bar{x}_4^\mu) = -x_1(\bar{x}_4^\mu) + \frac{1}{2}$, $x_3(\bar{x}_4^\mu) = -x_3^\mu(\bar{x}_4^\mu)$. Similarly, from $(I|\frac{1}{2},\frac{1}{2},0,0)$, we obtain $x_2^\mu(\bar{x}_4^\mu) = -x_2^\mu(-\bar{x}_4^\mu) + \frac{1}{2}$. $(C_{2x}|0,\frac{1}{2},0,0)$ does not give any additional conditions. From the transformation properties (10) and (11) for a scalar, similar considerations lead to $B^\mu(\bar{x}_4^\mu) = B^\mu(-\bar{x}_4^\mu)$ and $P^\mu(\bar{x}_4^\mu) = P^\mu(-\bar{x}_4^\mu)$. These conditions and (6)–(8) give $u_{1n}^\mu = u_{3n}^\mu = 0$, Re $u_{2n}^\mu = 0$, Im $B_n^\mu =$ Im $P_n^\mu = 0$, where Re and Im are the real and imaginary parts.

Since the wavevector $\mathbf{k}$ is $0 \cdot 1\mathbf{b}^*$ and is commensurable with the fundamental reciprocal lattice, the structure-factor formula is given by

$$F_{\mathbf{h}} = \tfrac{1}{10} \sum_{\mu(R|\tau)} p^\mu \sum_{\nu=0}^9 f^\mu(\mathbf{h})\,P^\mu(\bar{x}_4^\mu)$$

$$\times \exp\left[- B^\mu(\bar{x}_4^\mu)\,h^2 \right.$$

$$\left. + 2\pi i \sum_{i=1}^4 \{h_i[R\mathbf{x}^\mu(\bar{x}_4^\mu)]_i + h_i\tau_i\} \right], (13)$$

where $\bar{x}_4^\mu = \mathbf{k}.\bar{\mathbf{x}}^\mu + v/10$, $x_4^\mu(\bar{x}_4^\mu) = \mathbf{k}.\mathbf{x}^\mu(\bar{x}_4^\mu) + v/10$ and p^μ is the multiplicity of the μth independent atom in the fundamental cell. There are four atomic sites in the fundamental cell, only one of which is independent. The modulation waves of the other three Cu and Au atoms are obtained from those of the independent Cu and Au atoms by the centering translations and (9)–(11). Therefore, $\mu = 1, 2$ in the above formula and $(R|\tau)$ refers to three centering translations and the identity operator $(E|0,0,0)$. The other symmetry operators included in the space group are not necessary because these do not produce new atomic positions. In the actual analysis, the reflections which are not observed due to the centering translations are dropped. Then the centering translations are also unnecessary because each atom produced by these operators gives the same contribution for observed reflections as the independent atoms. Formula (13) needs the coordinate only at the discrete points $\bar{x}_4^\mu = k_2\bar{x}_2^\mu + v/10$ ($v = 0, 1, \ldots, 9$). Therefore, x_2^1, B^1, P^1 in (6)–(8) are expressed by the Fourier terms up to $n = 5$ and from the restriction for the Fourier coefficients u_{2n}^1, B_n^1, P_n^1, we have only sine terms for u_2^1 and cosine terms for B^1 and P^1 in (6)–(8). Thus, the analysis needs five positional, six thermal and six occupational parameters. Of these, one occupational parameter P_0^1 is fixed at $\frac{1}{2}$ from the composition of the crystal used. On the other hand, 10 positional, 10 thermal and 10 occupational parameters are necessary in the usual analysis (Okamura et al., 1968). This corresponds to using both sine and cosine terms for u_2^1, B^1, P^1.

4. Structure refinement

A full-matrix least-squares program written by the author was used for the refinement. In the program, $\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$ is minimized, where w is a weight factor. (Unit weights were used in the present analysis.) The refinement was started from the parameters $u_{2n}^1 = B_n^1 = 0$ for $n = 1, 2, \ldots, 5$, $P_n^1 = 0$ for $n = 2, \ldots, 5$ and $P_1^1 = \frac{1}{2}, B_0^1 = 1$ Å². This structure has only a harmonic modulation wave for the occupation probability.

First, $u_{21}^1, u_{23}^1, P_1^1, P_3^1, B_0^1, B_1^1, B_3^1$ were refined by using the main, first-order satellite and third-order satellite reflections because these reflections are strong and the parameters largely contribute to such reflections. After three cycles, $R = 0 \cdot 13$ was obtained for observed reflections. Next, all parameters were refined by using reflections up to the fifth-order satellite reflections. The R value obtained was $0 \cdot 10$ for observed reflections. At this stage, the modulation function for the occupation probability was plotted. The curve showed a non-physical feature, viz the occupation probability largely exceeded one in some regions and was smaller than zero in other regions. It was noticed that this was

Table 1. *The positional parameters* (×10⁴), *thermal parameters* (×10²) *and occupational parameters* (×10²) *in* CuAu II

Each parameter is the Fourier coefficient of the modulation wave for Cu which corresponds to the Fourier term (FT) in the first two lines. The standard deviations are in parentheses.

FT: (1) $\cos 0 = 1$; (2) $\cos 2\pi\bar{x}_4$; (3) $\sin 2\pi\bar{x}_4$; (4) $\cos 4\pi\bar{x}_4$; (5) $\sin 4\pi\bar{x}_4$; (6) $\cos 6\pi\bar{x}_4$; (7) $\sin 6\pi\bar{x}_4$; (8) $\cos 8\pi\bar{x}_4$; (9) $\sin 8\pi\bar{x}_4$; (10) $\cos 10\pi\bar{x}_4$; (11) $\sin 10\pi\bar{x}_4$.

FT	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
(a) Present work											
u_2			88 (14)		−11 (17)		−40 (16)		−27 (15)		−6 (12)
B	122 (12)	102 (21)		65 (17)		45 (17)		5 (15)		−14 (9)	
P	0	62 (2)		−3 (1)		−23 (2)		0 (1)		9 (1)	
(b) Okamura *et al.* (1968)											
u_2	3	0	136	8	48	26	−24	21	−13	0	15
B	128	84	5	2	7	−28	1	−28	−1	−6	0
P	0	57	1	−3	0	−16	−2	1	0	7	0

because the sign of P_3^1 was wrong. Correcting the sign, the final refinement converged to $R = 0.096$. [The appearance of a subminimum with such a small R value is considered to be due to the small displacement as stated in (I).] The final R value is comparable to the value $R = 0.107$ obtained by Okamura *et al.* (1968). The final parameters are listed in Table 1 together with those of Okamura *et al.* As shown in the table, the usual analysis includes extra parameters corresponding to cosine terms for u_2^1 and sine terms for B^1 and P^1. These terms are small as expected.*

5. The structure in three-dimensional space

The structure has a block-type modulation wave for the occupation probability (see Fig. 3). The block-type function has the amplitudes Re $P_0^1 = 0.5$, Re $P_1^1 = 0.6366$, Re $P_3^1 = -0.2122$, Re $P_5^1 = 0.1273$.... As seen in Table 1, the present result is closer to the block-type function than that of Okamura *et al.* However, these have common features: in both cases the amplitude P_5^1 is small compared with that of the

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36660 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
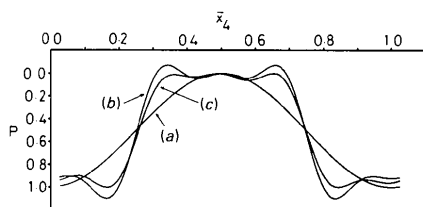

Fig. 3. The modulation functions for the occupation probability of Cu. (*a*) Starting point. (*b*) Final result. (*c*) Okamura, Iwasaki & Ogawa (1968).

block-type function. This makes the slope small near the antiphase boundary. Fig. 4 shows the modulation wave for the displacement along the *b* axis.

The occupation probability and the position of any atom can be obtained from the modulation functions in Figs. 3 and 4. As stated in (I), a vector $\mathbf{x} = x_1\mathbf{a} + x_2\mathbf{b} + x_3\mathbf{c}$ in R_3 is expressed by $x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3 + k_2x_2\mathbf{a}_4$. The occupation probability and the displacement along the *b* axis of the Cu atom are obtained from (9) and (11) by $P^1(k_2\bar{x}_2^1)$ and $u_2^1(k_2\bar{x}_2^1)$, where $\bar{x}_2^1$ is the x_2 coordinate in the fundamental structure. Therefore, Figs. 3 and 4 show the change in the occupation probability of Cu and the displacement of the metal sites along the *b* axis. It should be noted, however, that the satellite reflections with high h_4 index are very weak and the superposition of reflections on R_3 [see (I)] can be neglected in the present case, so that the phase of the modulation waves is not precisely determined. Therefore, the atomic configuration given from the modulation wave shifted by an arbitrary value along the a_4 axis is also equally probable.

For convenience, we call sites dominantly occupied by Cu (Au) atoms Cu (Au) sites. The gentle slope near the antiphase boundary means that the Cu (Au) sites near the boundary are occupied appreciably by Au (Cu) atoms. This shows that CuAu II has considerable disordering in the vicinity of the antiphase boundary as stated by Okamura *et al.* (1968). Fig. 4 shows that Cu sites near the antiphase boundary shift towards the boundary and Au sites displace away
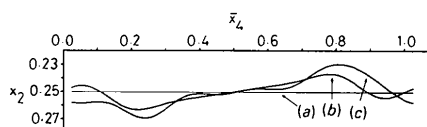

Fig. 4. The modulation functions for the displacement along **b**. (*a*) Starting point. (*b*) Final result. (*c*) Okamura, Iwasaki & Ogawa (1968).

from the boundary. These features will be shown clearly by the Fourier map in § 6. Although there is a small difference between the present result and that of Okamura *et al.*, the two structures are essentially the same.

6. Fourier synthesis

The Fourier synthesis in four-dimensional space gives the electron density based on a four-dimensional lattice which describes the modulated structure (de Wolff, 1974). The electron density of a four-dimensional lattice is

$$\rho(x_1,x_2,x_3,x_4) = \sum_{h_1,h_2,h_3,h_4} F_{h'} \exp\left(2\pi i \sum_{j=1}^{4} h_j x_j\right), (14)$$

where $h' = h_1 b_1 + h_2 b_2 + h_3 b_3 + h_4 b_4$. In the present case, the structure factor $F_{h'}$ in R_4 is approximated by the structure factor F_h in R_3 calculated from (13). One example of the electron density map is shown in Fig. 5(*a*). This represents the projection of $\rho(\frac{1}{4},x_2,x_3,x_4)$ along the a_3 axis since only $h_1 h_2 0 h_4$ reflections were used in the Fourier synthesis. The figure shows a typical feature of substitutional modulation: the peak of electron density runs along the a_4 axis with changing height. The usual three-dimensional space is perpendicular to the a_4 axis. Therefore, the Fourier map in R_3 is given by the section at the solid line normal to the a_4 axis in Fig. 5(*a*). One of these sections is illustrated in Fig. 5(*b*). This is the projection of the electron density along the *c* axis. Strong peaks correspond to the Au sites and weak peaks to the Cu sites. A broken bisector indicates the antiphase boundary. As is clear from the figure, the Cu sites near the antiphase boundary are appreciably occupied by Au, and the Au site near the boundary slightly shifts away from the boundary while the Cu site shifts towards the boundary.
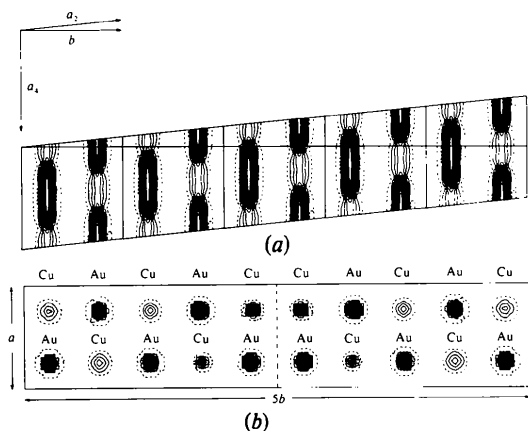

Fig. 5. (*a*) The electron density in the $x_2 - x_4$ plane at $x_1 = \frac{1}{4}$. The map shows the projection of the electron density $\rho(\frac{1}{4},x_2,x_3,x_4)$ along a_3. (*b*) The section of the usual three-dimensional space at the solid line in Fig. 5(*a*). This is the usual electron density map projected along *c*.

7. Noncentrosymmetric space groups

We analyzed the structure based on the centrosymmetric space group. The possibility of the two noncentrosymmetric groups allowed from the fundamental structure and the extinction rules is considered in this section. One of these is generated by $(\sigma_x|\frac{1}{2},0,0,0)$, $(\sigma_y|0,\frac{1}{2},0,0)$, $(C_{2z}|\frac{1}{2},\frac{1}{2},0,0)$ and the centering translations of a $G(1,2)$-centered lattice and the other is generated by $(\sigma_x|\frac{1}{2},0,0,0)$, $(C_{2y}|\frac{1}{2},0,0,0)$, $(\sigma_z|0,0,0,0)$ and the same centering translations.* The former allows the cosine terms in the modulation function of the x_3 coordinate in addition to the terms allowed by the centrosymmetric space group while the latter allows the cosine terms for x_2 and the sine terms for P other than the centrosymmetric ones. The analysis based on the latter is equivalent to the analysis by Okamura *et al.* (1968) (see Table 1). This is rejected since Okamura's result gives no improvement. The former cannot be rejected from the present analysis because the modulation for x_3 does not affect $h_1 h_2 0 h_4$ used in the present analysis. The analysis using three-dimensional reflections can determine the true space group and structure but this is beyond the scope of the present study.

8. Concluding remarks

The present paper shows that the antiphase-domain structure of CuAu II can be analyzed on the basis of a four-dimensional space group by regarding the structure as a modulated structure. The extinction rules observed in the diffraction pattern are well explained by the four-dimensional space group because of the conservation of the centering translations present in the fundamental structure, so that the number of parameters in the analysis reduces to about a half of that required in the usual analysis based on a three-dimensional space group. The four-dimensional symmetry is higher than or equal to the three-dimensional symmetry (Yamamoto & Nakazawa, 1982). The present study concludes that, in general, the modulated structure is more easily analyzed by the application of the multi-dimensional description of modulated structures.

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* These are written as $L_{1\bar{1}\bar{1}}^{Fmm2}$ and L_{111}^{Fm2m} in the symbol of de Wolff, Janner & Janssen (1981).

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Modulated Structure of Wustite (Fe₁₋ₓO)† (Three-Dimensional Modulation)

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Abstract

The structure of the incommensurate phase of $Fe_{1-x}O$ ($x = 0.098$) with a cubic fundamental cell [$a = 4.30$ (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 $k^1 = 0.398a^*$, $k^2 = 0.398b^*$, $k^3 = 0.398c^*$. 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.

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† 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

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

where a^*, b^*, c^* are the unit vectors in the reciprocal lattice of the fundamental structure, which is the rock-salt structure in the present case. k^1, k^2, 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 $x = 0.098$, has the wavevectors $k^1 = 0.398a^*$, $k^2 = 0.398b^*$, $k^3 = 0.398c^*$. 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 $b_1 = a^*$, $b_2 = b^*$, $b_3 = c^*$, $b_4 = k^1 + d_1$, $b_5 = k^2 + d_2$, $b_6 = k^3 + d_3$, where d_1, d_2, d_3 are the unit vectors perpendicular to R_3. The unit vectors reciprocal to these are $a_1 = a - \sum_{i=1}^{3} k_1^i d_i$, $b_2 = b - \sum_{i=1}^{3} k_2^i d_i$, $b_3 = c - \sum_{i=1}^{3} k_3^i d_i$ and $a_{3+i} = d_i$ ($i = 1,2,3$), where a,b,c are the unit vectors of the fundamental structure which are reciprocal to a^*, b^*, c^* and k_1^i, k_2^i, k_3^i are the a^*, b^*, c^* com-