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Application of Modulated Structure Analysis to Two-Dimensional Antiphase-Domain Structure of $Au_{2+x}Cd_{1-x}$

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Abstract

The two-dimensional antiphase-domain structures of $Au_{2+x}Cd_{1-x}$, which are two-dimensionally modulated structures with a hexagonal cell [a = 2·919 (4), c = 4·808 (7) Å] and the wavevectors $\mathbf{k}^1 = N(\mathbf{a}^* + \mathbf{b}^*)/M$, $\mathbf{k}^2 = N(-\mathbf{a}^* + 2\mathbf{b}^*)/M$, were considered based on the five-dimensional description of modulated structures. The refinement of the structure with N/M = 3/7 (7a structure) of Au_2Cd was carried out by using a model with two positional, two thermal and one occupational parameters based on the five-dimensional space group $P_{p6}^{P6_3/mmc}{}_{1mm}$ and gave R factors of 0·065, 0·049 and 0·17 for all, fundamental and satellite reflections, respectively. The displacement wave was almost longitudinal in agreement with a previous result. This method reduces the number of parameters to one eighth of that in the usual three-dimensional analysis. The 9a structure (N/M = 4/9) has the same five-dimensional space group and its five-dimensional structure is isomorphic with that of the 7a structure.

Introduction

There exist many binary alloys with one- and two-dimensional long-period superlattices (Cowley, Cohen, Salamon & Wuensch, 1979). These structures are regarded as modulated structures with incommensurate or commensurate wavevectors and can be analyzed on the basis of a unified theory of the modulated structure analysis (de Wolff, 1974; Janner & Janssen, 1977; Yamamoto, 1982*a*). In this theory, an n-dimensionally modulated structure is described in a (3 + n)-dimensional space and its symmetry is designated by a (3 + n)-dimensional space group. The

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one-dimensional antiphase-domain structure of CuAu II has been refined by the application of this theory (Yamamoto, 1982*b*) and its efficiency has been confirmed. This method is more efficient for the structure analysis of a two-dimensional antiphase-domain structure with a simple modulation: the number of parameters is much less than that of the usual three-dimensional analysis and the structure can be analyzed by using only the main and observed satellite reflections. Here, we consider the two-dimensional antiphase-domain structure of $Au_{2+x}Cd_{1-x}$ based on a five-dimensional space group.

In many two-dimensional antiphase-domain structures, higher-order satellites are not observed but the usual three-dimensional analysis requires these reflections in the refinements because each parameter almost equally affects all satellite reflections. On the other hand, in the method employed here, each parameter strongly contributes to only limited satellite reflections and we can ignore the parameters which mainly contribute to the non-observed satellite reflections and we can drop these reflections in the refinement.

Methods of obtaining multi-dimensional symmetry and possible modulation wave forms were shown in the case of a three-dimensional modulation of wustite $Fe_{1-x}O$ (Yamamoto, 1982*c*). The symmetry operators of a multi-dimensional space group are obtained from the symmetry operators of the average structure and the extinction rules. Their rotational parts are obtained from the point group of the average structure and the transformation matrix of the wavevectors. All the point groups of the average structures are the subgroups of the cubic $m3m$ or the hexagonal $6/mmm$. We treated wustite as an example with a simple three-dimensional modulation and with the highest symmetry $m3m$. In this paper, we treat a hexagonal system with the highest symmetry and carry out the five-dimensional analysis of the known structure of Au_2Cd by use of the X-ray data of Watanabe & Iwasaki (1982). The present study clarifies the close relation between a series of $Au_{2+x}Cd_{1-x}$ alloy structures.

Five-dimensional description

Diffraction patterns observed in Au–Cd alloys with about 33% Cd are assigned by using five integers $h_1 - h_5$: $\mathbf{h} = h_1\mathbf{a}^* + h_2\mathbf{b}^* + h_3\mathbf{c}^* + h_4\mathbf{k}^1 + h_5\mathbf{k}^2$, where $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ are the unit vectors reciprocal to the unit vectors of the hexagonal cell with $a = 2{\cdot}919\,(4)$, $c = 4{\cdot}818\,(7)$ Å and the wavevectors $\mathbf{k}^1$, $\mathbf{k}^2$ are represented by $N(\mathbf{a}^* + \mathbf{b}^*)/M$, $N(-\mathbf{a}^* + 2\mathbf{b}^*)/M$ (see Fig. 1). N/M changes continuously from 3/7 to 4/9 with the chemical compositions, indicating that the structures are incommensurate (Hirabayashi, Yamaguchi, Hiraga, Ino, Sato & Toth, 1970). The present analysis is concerned with the case of $N/M = 3/7$ (7*a* structure).

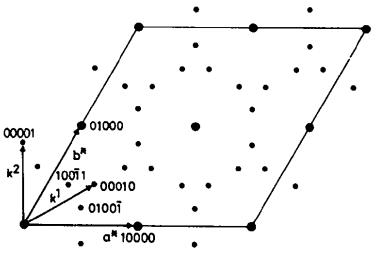

Fig. 1. A schematic view of the diffraction pattern in $Au_{2+x}Cd_{1-x}$.

The structure is commensurate (Watanabe & Iwasaki, 1982) but all the reflections are uniquely assigned by the above formula because the higher-order satellite reflections are very weak and not observed (Yamamoto, 1982*a*). The extinction rule is $h_3 = 2n$ for $h_1h_1h_3h_40$. This is explained by a hyper-glide plane mentioned below. The symmetry operators in a five-dimensional space group are obtained from the symmetry operators in the three-dimensional space group of the average structure and the above extinction rule (Yamamoto, 1982*c*).

The average structure is the hexagonal close-packed structure with $P6_3/mmc$. As the corresponding five-dimensional space group, we take the space group $P^{P6_3/mmc}_{p6\ 1\ mm}$ which is generated by $(S_3^-|0,0,\frac{1}{2},0,0)$, $(\sigma_{v3}|0,0,0,0,0)$, $(I|0,0,0,0,0)$ and generating elements for the lattice translations, where we use the space-group symbol of de Wolff, Janner & Janssen (1981). Symbols for the symmetry operators are the same as those in the previous paper (Yamamoto, 1982*c*). For the rotational part, we use the symbol in the three-dimensional space group because the first 3×3 part of the rotation matrix is the same as in the usual three-dimensional point group. The extinction rule is explained by the hyper-glide plane $(\sigma_{d3}|0,0,\frac{1}{2},0,0)$ in this space group.

There is one independent Au/Cd site in the average structure which is located at the special position 2(*c*) of $P6_3/mmc$: $\frac{1}{3},\frac{2}{3},\frac{1}{4}$, the site symmetry of which is $\bar{6}m2$. Corresponding to this group, the site symmetry group in the five-dimensional space is generated by $(S_3^-|0,1,\frac{1}{2},0,0)$ and $(\sigma_{v3}|1,1,0,0,0)$. This constrains the forms of the modulation waves (Yamamoto, 1982*c*). Neglecting higher-order harmonics, we have

$$\begin{aligned}\mathbf{u}(\bar{x}_4,\bar{x}_5) = U_1[&-(\mathbf{a}+\mathbf{b})\sin\bar{x}_4 + \mathbf{b}\sin(-\bar{x}_5)\\ &+ \mathbf{a}\sin(\bar{x}_5-\bar{x}_4)] + U_2[(-\mathbf{a}+\mathbf{b})\cos\bar{x}_4\\ &-(\mathbf{a}+2\mathbf{b})\cos(\bar{x}_5-\bar{x}_4)\\ &+(2\mathbf{a}+\mathbf{b})\cos(-\bar{x}_5)] \qquad (1)\end{aligned}$$

for the displacement wave, where $\mathbf{u}(\bar{x}_4,\bar{x}_5)$ is the displacement vector parallel to the usual three-dimensional superplane: $u(\mathbf{k}^1.\bar{\mathbf{x}},\ \mathbf{k}^2.\bar{\mathbf{x}})$ gives the displacement of the atom located at $\bar{x}$ in the fundamental structure. U_1 is the amplitude of the triple longitudinal waves and U_2 is the amplitude of the triple

transverse waves lying in the *ab* plane. Similarly, we have

$$P(\bar{x}_4,\bar{x}_5) = P_0 + P_1[\cos \bar{x}_4 + \cos(-\bar{x}_5) + \cos(-\bar{x}_4 + \bar{x}_5)] \quad (2)$$

and

$$B(\bar{x}_4,\bar{x}_5) = B_0 + B_1[\cos \bar{x}_4 + \cos(-\bar{x}_5) + \cos(-\bar{x}_4 + \bar{x}_5)] \quad (3)$$

for the occupation probability of Au and the isotropic temperature factor. [$P(\mathbf{k}^1.\bar{\mathbf{x}}, \mathbf{k}^2.\bar{\mathbf{x}})$ and $B(\mathbf{k}^1.\bar{\mathbf{x}}, \mathbf{k}^2.\bar{\mathbf{x}})$ represent the occupation probability and temperature factor in three-dimensional space. The occupation probability of Cd is given by $1 - P(\bar{x}_4,\bar{x}_5)$.] Observed satellite reflections were only $h_1h_2h_3 \pm 10$, $h_1h_2h_30 \pm 1$ and $h_1h_2h_3 \pm 1 \mp 1$. Higher-order harmonics which are not included in (1)–(3) mainly contribute to non-observed higher-order satellite reflections and can be dropped in the refinement. The model obtained contains only two parameters for each of the displacements, isotropic temperature factors and occupation probabilities. One of these, P_0, is fixed at 2/3 from the chemical composition of the crystal used. The number of parameters is one eighth of that in the usual analysis (Watanabe & Iwasaki, 1982).

Refinement of the structure

The refinement was carried out by using a restricted least-squares program (written by the author) in which the sum of the squared weighted R factor and squared penalty function is minimized in order to keep the occupation probability within the physically reasonable range $0 < P(\bar{x}_4,\bar{x}_5) < 1$ (Yamamoto, 1981). The penalty function (PF) used is

$$\mathrm{PF} = \left\{(g^2/49) \sum_{\nu_1,\,\nu_2=1}^{7} [r(\bar{x}_4,\bar{x}_5)]^2\right\}^{1/2},$$

where $r(\bar{x}_4,\bar{x}_5)$ and a value $P(\bar{x}_4,\bar{x}_5)$ for $P(\bar{x}_4,\bar{x}_5) < 0$, $P(\bar{x}_4,\bar{x}_5) - 1$ for $1 < P(\bar{x}_4,\bar{x}_5)$ and zero otherwise and $\bar{x}_4 = \mathbf{k}^1.\bar{\mathbf{x}} + \nu_1/M$, $\bar{x}_5 = \mathbf{k}^2.\bar{\mathbf{x}} + \nu_2/M$ ($\bar{\mathbf{x}}$ being the positional vector in the fundamental structure). An appropriate value is taken for g in the refinement. The refinement was initiated from $U_1 = U_2 = 0{\cdot}001$, $B_0 = 0{\cdot}5$ Å^2, $B_1 = 0$ Å^2, $P_1 = -0{\cdot}1$ and an anomalous-dispersion correction and isotropic secondary-extinction correction (Kato, 1976) were made in each cycle. Unit weight was used for all reflections. In the first three cycles, P_1, a scale and an extinction parameter were refined with $g = 1$ and in the succeeding four cycles, all parameters were refined using all observed reflections (23 main and 31 satellite reflections). The final refinement was made with $g = 4$ for three cycles, giving a conventional R factor of 0·065. This is comparable with the R factor of 0·063 for the observed reflections of Watanabe & Iwasaki. The R factors for the main and satellite reflections were 0·049 and 0·17. The final parameters are listed in Table 1 together with the Fourier amplitudes obtained from the result of Watanabe & Iwasaki (1982) and the result of the 9*a* structure (see below). The structure factors are shown in Table 2. As shown in Table 1, the result is essentially the same as that of Watanabe & Iwasaki. In particular, the amplitude of the transverse wave, U_2, is very small and the displacement wave is approximated by the superposition of three longitudinal waves.

Table 1. *The positional* ($\times 10^4$), *thermal* (Å$^2 \times 10^2$) *and occupational* ($\times 10^2$) *parameters*

The standard deviations are in parentheses. (*a*) Present work. (*b*) Watanabe & Iwasaki (1982). (*c*) Hirabayashi *et al.* (1970) (the 9*a* structure).

	U_1	U_2	B_0	B_1	P_0	P_1
(*a*)	25 (11)	5 (8)	127 (8)	30 (7)	67	−22 (4)
(*b*)	32	4	141	63	67	−28
(*c*)					70	−31

Table 2. *Observed and calculated structure factors* (×4)

h_1	h_2	h_3	h_4	h_5	F_o	F_c	h_1	h_2	h_3	h_4	h_5	F_o	F_c
1	0	0	0	0	199	193	1	1	0	−1	0	40	29
2	0	0	0	0	133	137	2	0	0	−1	1	17	13
3	0	0	0	0	159	168	0	1	0	1	−1	15	10
1	1	0	0	0	251	259	1	0	0	1	0	13	10
2	1	0	0	0	100	104	2	1	0	−1	0	16	14
2	2	0	0	0	133	136	3	0	0	−1	1	25	25
0	0	2	0	0	313	293	1	1	0	1	−1	19	19
1	1	2	0	0	216	239	2	0	0	1	0	7	8
0	0	4	0	0	248	235	3	1	0	−1	0	11	11
1	1	4	0	0	199	188	2	1	0	1	−1	5	8
0	0	6	0	0	178	157	2	0	0	0	1	12	12
1	0	1	0	0	258	272	1	2	0	0	−1	13	14
1	0	2	0	0	178	168	3	0	0	0	1	15	18
1	0	3	0	0	225	227	2	2	0	0	−1	17	20
1	0	4	0	0	122	119	1	1	0	1	0	16	17
1	0	5	0	0	172	160	2	2	0	−1	0	23	25
1	0	6	0	0	78	76	3	1	0	−1	1	8	9
2	0	1	0	0	198	213	0	0	2	1	0	30	23
2	0	2	0	0	115	123	1	1	2	−1	0	33	28
2	0	3	0	0	177	179	1	1	2	1	0	15	16
2	0	4	0	0	92	92	2	2	2	−1	0	21	23
2	0	5	0	0	132	129	0	0	4	1	0	23	21
3	0	2	0	0	147	155	1	1	4	−1	0	25	24
0	1	0	0	−1	25	14	1	1	4	1	0	13	15
1	1	0	0	−1	30	25	2	2	4	−1	0	16	20
2	1	0	0	−1	9	9	0	0	6	1	0	15	17
0	0	0	1	0	38	23	1	1	6	−1	0	17	19

Five-dimensional description of the 9*a* structure

We consider another commensurate structure with $N/M = 4/9$. The three-dimensional space group of this 9*a* structure, $P6_3/mcm$, is different from that of the 7*a* structure, $P6_3/mmc$. However, this appears to have the

same five-dimensional space group because the electron diffraction patterns are similar to those of the $7a$ structure except for the difference in the wavevectors and N/M varies continuously with the chemical composition (Hirabayashi *et al.*, 1970). This suggests that the five-dimensional space groups of these two structures are the same and a series of incommensurate structures with $3/7 < N/M < 4/9$ have the same space group. These are expected to have similar structures.

In order to confirm this, we calculated the Fourier amplitude of the $9a$ structure given by Hirabayashi *et al.* (1970) and confirmed that the distribution of Au atoms is well approximated by (2). This shows that their five-dimensional structures are isomorphic with each other. The Fourier amplitudes P_0 and P_1 of this structure are listed in Table 1.

Summary and concluding remarks

We carried out a five-dimensional analysis of the $7a$ structure based on the theory of modulated structure analysis and obtained essentially the same result as in the more sophisticated analysis based on the usual three-dimensional symmetry. It was shown that the $9a$ structure has the same five-dimensional space group as the $7a$ structure and has a similar five-dimensional structure. The present paper demonstrates that the refinement can be carried out by using only observed reflections and parameters mainly contributing to these reflections. This saves much computing time and reduces effort in analyses of commensurate structures without accompanying higher-order harmonics.

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Atom Distributions in Sigma Phases. I. Fe and Cr Atom Distributions in a Binary Sigma Phase Equilibrated at 1063, 1013 and 923 K*

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Abstract

Extensive single-crystal Mo $K\alpha$ Bragg-diffraction data sets were collected and analyzed from sigma (σ) phases with compositions near $Cr_{48}Fe_{52}$ that had been annealed at three temperatures (1063, 1013 and 923 K) within the region of σ-phase metastability. Precisions of measurement varied from <1% for the relatively few intense diffraction maxima to ~10–20% for the more numerous weak reflections. No clear indication of the absence of a center of symmetry was found in any data set, or in any of the results obtained by least-squares refinements of parameters assuming space group $P4_2/mnm$. Average site-occupation parameters of limited precision (±5–10%) were derived for the five independent sites occupied in the σ structure during the refinement based on each data set. The crystal from the alloy equilibrated at 1013 K was also studied using synchrotron-radiation (SR) Bragg diffraction at photon energies just below the Fe and Cr K absorption edges, where relative differences ($\Delta|f|/|f|$) in the atomic scattering factors of Fe and Cr approach 20–35%. (For Mo $K\alpha$ radiation, $\Delta|f|/|f|$ is 8–11%.) Site-occupation parameters derived from the less numerous

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