Crystal Structure of γ'_2 Martensite in Au-47.5 at% Cd Alloy

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Crystal structure of the γ'_2 martensite in a Au-47.5 at% Cd alloy has been analyzed by the single crystal X-ray diffraction method. The lattice constants were $a=0.4859(11)$, $b=0.3151(1)$ and $c=0.4766(1)$ nm. The space group was Pcm, with 4 atoms in the unit cell as Ölander reported. The structure was refined by the full-matrix least squares method to a final R factor of 4.7%, noticeably improved from that of Ölander. Moreover, the amount of shift of each atom from the ideal stacking positions in the hcp structure was discussed by using a hard sphere model of atoms; *e.g.* atoms in each layer are not arranged centro-symmetric.

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I. Introduction

The Au-47.5 at% Cd alloy has attracted much attention of researchers for many years for the shape memory effect⁽¹⁾ and early application of the phenomenological crystallographic theory⁽²⁾ and a unique property called rubber-like behavior⁽³⁾⁻⁽⁴⁾. The phenomenological theory was successfully applied to this alloy to predict the crystallographic parameters such as the habit plane, the shape strain in the martensitic transformation⁽²⁾. The rubber-like behavior occurs by a reversible twin boundary movement after stabilization (aging) in the γ'_2 martensitic state for about 50.4 ks (14 h) or so at room temperature⁽⁴⁾. The origin for the phenomenon still remains unsolved, but it is clearly related to the stabilization effect. Lieberman *et al.*⁽⁵⁾ proposed a mechanism, in which a twinning process is separated into twinning shear and shuffles, and that twinning shear occurs instantaneously but shuffling occurs gradually during aging. The stabilization effect increases the A_s temperature (reverse transformation start temperature) in general. The effect was observed in other β -phase alloys, such as Cu-Zn-Al and Cu-Al-Ni, and it is a serious problem in the practical applications of shape memory alloys⁽⁶⁾⁻⁽⁸⁾. The stabilization effect in this respect was also found in an Au-Cd alloy⁽⁹⁾. The origin for the stabilization is not understood yet, and the re-ordering of martensite is proposed to be responsible for the phenomenon⁽⁷⁾.

The first step to understand the above behavior is to know the crystal structure of the martensite. Besides, if there is a structural change on aging or stabilization, it is very important to know the accurate structure in the martensitic phase. Furthermore, an exact equiatomic alloy Au-50 at% Cd shows a different mechanical

Table 1 The lattice constants of γ'_2 martensite in Au-47.5 at% Cd alloy.

at% Cd	a (nm)	b (nm)	c (nm)	Reference
47.5	0.4861	0.3150	0.4765	Ölander ⁽¹²⁾
47.6	0.4861	0.3150	0.4765	Byström and Almin ⁽²¹⁾
47.5	0.48644	0.31540	0.47645	Chang ⁽²²⁾
47.5	0.4859(11)	0.3151(1)	0.4766(1)	Present study

behavior⁽¹⁰⁾ and has a different crystal structure⁽¹¹⁾. In order to clarify the difference between Au-50 at% Cd and Au-47.5 at% Cd, it is also important to determine the crystal structure accurately.

The structure of the γ'_2 martensite was first analyzed by Ölander⁽¹²⁾ in 1932 by using the X-ray powder diffraction method. The space group they reported was Pcm, and their lattice constants are shown in Table 1, along with those measured by others. The positional parameters they determined will be described later. In 1977, Tadaki and Shimizu⁽¹³⁾ re-examined the crystal structure by using a hard sphere model and gave atomic positions derived from the model, which were different from those reported by Ölander. They calculated structure factors for both structures and compared them with observed electron diffraction patterns. Although they concluded their positional parameters were more reliable than Ölander's, the comparison was not quantitative. No quantitative analysis has been made for this martensite since Ölander's work. One of possible reasons for this lies in the difficulty of obtaining a single crystal of the martensite.

In this paper, structure determination of a Au-47.5 at% Cd alloy is carried out by using a single crystal obtained under a tensile stress.

II. Experimental

An alloy ingot with nominal composition of Au-47.5 at% Cd was prepared by melting 99.99% Au and

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Table 2 The observed transformation temperatures.

$M_s(K)$	$M_f(K)$	$A_s(K)$	$M_i(K)$	
337	337	346	351	aging for less than 0.5×3.6 ks
337	337	351	356	aging for 30×3.6 ks

99.9999% Cd at 1273 K in a sealed quartz tube filled with Ar gas. The ingot was again sealed and re-melted at 1173 K in 27 mm diameter quartz tube filled with Ar, which was connected with thinner quartz tube, and the molten alloy was poured into a thinner part (4 mm diameter) of the tube. A single crystal of the parent phase was made by the Bridgman method in a carbon mould which was encapsulated in the other quartz tube filled with Ar. The mass of the alloy was measured before and after melting, and the loss in mass was confirmed to be negligible. The specimen was spark cut to a square pillar with $1 \text{ mm} \times 1 \text{ mm} \times 50 \text{ mm}$. The transformation temperatures were determined by measuring the electrical resistivity as a function of temperature. The results are shown in Table 2. To make a single crystal of the martensite, we applied a tensile stress and held it for about 86.4 ks (24 h) to stabilize the martensite. Back reflection Laue photographs of the stabilized specimen after releasing the tensile stress showed Bragg spots from a single crystal, confirming that the single crystal was obtained. Tiny specimens for X-ray diffraction were made by electro-polishing in a solution which consists of hydrochloric acid: phosphoric acid: glycerine = 3:2:3. Polystyrene was put on a part of specimens so that tiny crystals were cut off without any stress. To avoid the reverse transformation of the specimen, the temperature of the solution was kept below 283 K, and the applied voltage for electro-polishing was 8 V. We obtained nine specimens in total. Cylindrical Laue photographs confirmed that one of the specimens was a single crystal specimen. Thus it was used for the following X-ray diffraction experiment. The shape of the specimen is approximately a triangular prism of about $10 \mu\text{m}$ high and the basal plane is a triangle with sides about 130, 160 and $180 \mu\text{m}$ long.

An ENRAF NONIUS four-circle X-ray diffractometer (CAD-4) with graphite monochromatized $\text{MoK}\alpha_1$ radiation ($\lambda = 0.070926 \text{ nm}$) was used to determine the lattice constants and to collect intensity data. The lattice constants were determined by using 12 independent reflections with $47^\circ < 2\theta < 54^\circ$. The a , b and c -axes defined by Ölander correspond to the b , a and c -axes, respectively, in the present paper. The axes were chosen in the same way as those of Cu-Al-Ni alloy⁽¹⁴⁾; that is, the stacking direction of the close packed plane was chosen as the c -axis and a row of the same kind of atoms was chosen as the a -axis. The unit cell was found to be orthorhombic and the results are shown in Table 1 along with those determined by previous workers by the powder diffraction method. There was a large standard deviation on the a -axis because some $0k0$ and $00l$ reflections, which were not effective in determining the a -axis, were used to determine the lattice constants. To collect the intensity data,

a $2\theta-\omega$ scan mode with the scanning width of $\Delta\omega = 1.4 + 0.75 \tan \theta$ was used. The scanning speed was variable depending on a ratio of standard deviations of intensity ($\sigma(I)$) and intensity (I); i.e. $\sigma(I)/I$ of each reflection. A total of 1626 reflection data with $2\theta < 78^\circ$ were collected. The back ground was measured at each end of the scan.

III. Refinement and Results

The reflection data were corrected for the Lorentz-polarization factor. Reflections with $|F_0| < 3\sigma(|F_0|)$ were excluded from the data. Figure 1(a) shows the inten-

Fig. 1. The intensity distribution of $0kl$ reciprocal plane. The radii of the circles are proportional to F_0 . (a) Intensity distribution without correction. Reflections which should not appear by the extinction rule are indicated by arrows. (b) The intensity distribution with absorption correction, which gives the final R factor.

sity distribution of the $0kl$ reciprocal lattice plane, which was determined by four-circle diffractometer measurements. From the figure the systematic absences were found to be $0kl$ for $l \neq 2n$. There were twelve reflections that should not appear by the extinction rule, as indicated by the arrows. However, these reflections were weak and appeared at random within the extinction rule. Thus discarding these reflections, 1387 reflections remained for use in the structure analysis.

Since the specimen is approximately triangular prism, the absorption correction was made by the program provided on the CAD-4 system. The absorption coefficient of the alloy is calculated to be $\mu = 1.22 \times 10^5 \text{ m}^{-1}$ from the International Tables for X-ray Crystallography III⁽¹⁵⁾. After averaging equivalent reflections, 257 independent reflections were obtained. From the systematic absences of $0kl$ for $l \neq 2n$, the possible space groups are Pcm̄m, Pc2m and Pcm2₁. The values of atomic scattering factor f_0 and anomalous dispersion corrections, f' and f'' , used in the refinement were taken from the International Table for X-ray Crystallography IV⁽¹⁶⁾. The initial positions of atoms in Pcm̄m are chosen at the position given by Ölander⁽¹²⁾; i.e. 2e and 2f site in the International Table for X-ray Crystallography I⁽¹⁷⁾. For other space groups, atoms are placed in the same way as Pcm̄m with the condition that two Au atoms and two Cd atoms should be in the unit cell and no extra condition is added for the extinction rule; i.e. 2c site was chosen for space group Pc2m and 2a and 2b site for Pcm2₁. The atomic positional parameters, the anisotropic temperature factors and the scale factor were refined by the full-matrix least squares program, RADIEL⁽¹⁸⁾, for the above possible three space groups. Since the alloy is not stoichiometric, it was assumed that Au occupies one site and Cd_{0.95}Au_{0.05} occupies the other site. The positional parameters refined in this stage and the R and weighted R factor for each space group are the following:

Pcm̄m (No. 51):

Au(2e):	0.2003(1)	0	1/4;
	−0.2003(1)	0	3/4
Cd(2f):	0.7050(3)	1/2	1/4;
	−0.7050(3)	1/2	3/4

$$R = 9.68\%, wR = 10.70\%$$

Pc2m (No. 28):

Au(2c):	0.2004(4)	0.009(4)	1/4;
	−0.2004(4)	0.009(4)	3/4
Cd(2c):	0.7050(7)	1/2	1/4;
	−0.7050(7)	1/2	3/4

$$R = 9.34\%, wR = 10.62\%$$

Pcm2₁ (No. 26):

Au(2b):	0.2003(4)	1/2	0.257(9);
	−0.2003(4)	1/2	0.757(9)
Cd(2a):	0.7051(8)	0	1/4;
	−0.7051(8)	0	3/4

$$R = 9.35\%, wR = 10.60\%$$

Here, Cd represents Cd_{0.95}Au_{0.05} and the number in a parenthesis represents the space group number in the International Table for X-ray Crystallography I⁽¹⁷⁾. The

values in the parentheses followed positional parameters represent standard deviations. The R factor is defined by

$$R = \frac{\sum |F_o - F_c|}{\sum |F_o|},$$

and weighted R factor by

$$wR = \frac{\sum w(F_o - F_c)^2}{\sum wF_o^2},$$

where w is the reciprocal of the square of the standard deviation $\sigma(|F_o|)$ of each reflection.

We adopted the highest symmetry space group Pcm̄m, which has the smallest amount of parameters among the three, from the following reasons. First, the positional parameters x of Au and Cd in Pcm̄m, Pc2m and Pcm2₁ are nearly the same within the standard deviations. Secondly, the values of the parameter y of Pc2m and z of Pcm2₁ are nearly as same as those of Pcm̄m within three times of the standard deviations. Furthermore, the weighted R factors are almost the same in those three.

Integrated intensity I_t is represented by the multiplication of the Lorentz-polarization factor (Lp), square of structure factor $F_o^2 (= I_o)$ and the transmission factor A , which is calculated from the shape, the volume and the orientation of the specimen in the experiment; i.e. $I_t = k(Lp)AI_o$, where k is a constant. An absorption correction is to calculate the transmission factor and to obtain I_o . The specimen we used was made by electropolishing, and the shape is approximately a triangular prism but it has irregular faces. Since the intensities (I_o) of equivalent reflections corrected did not show a good agreement, we re-made the absorption correction on the assumption that the irregular faces are represented by five faces of triangular prism. As the absorption coefficient μ is large enough, a small change of face indices of the crystal or the volume of the crystal changes the transmission factor A greatly, so $F_o (= I_o^{1/2})$ was affected greatly. Thus we changed crystal faces and volume little by little to get better weighted R factor and better agreement of equivalent reflections. Figure 1(b) represents the intensity distribution after the final absorption correction. The final R factor and the weighted R factor with the refinement of positional parameters and anisotropic temperature factors are 4.8% and 5.1%, respectively, as shown in Table 3. Observed structure factors, F_o , which were averaged into independent reflections, and calculated structure factors, F_c , are shown in Table 4. Final atomic parameters are shown in Table 5. Calculations were carried out with a FACOM M780/20 computer at Science Information Processing Center in the University of Tsukuba.

Table 3 R and weighted R factors of γ_2' martensite in Au-47.5at%Cd alloy.

Reference	$R(\%)$	$wR(\%)$
Ölander ⁽¹²⁾	22.0	22.6
Tadaki <i>et al.</i> ⁽¹³⁾	8.1	9.3
Present study	4.8	5.1

Table 4 Observed and calculated structure factors of γ_2' martensite in Au-47.5at% Cd.

$h k l$	F_o	F_c	$h k l$	F_o	F_c	$h k l$	F_o	F_c
0 0 2	373.29	396.89	2 2 2	213.43	202.25	4 3 0	12.96	7.83
0 0 4	276.79	265.23	2 2 3	129.89	123.30	4 3 1	39.08	40.83
0 0 6	171.79	171.79	2 2 4	162.85	154.01	4 3 2	16.03	7.38
0 0 8	109.53	107.12	2 2 5	90.79	89.20	4 3 3	35.87	35.58
0 1 0	146.60	103.35	2 2 6	105.66	106.93	4 3 5	27.46	27.35
0 1 2	86.28	91.94	2 2 7	57.39	59.57	4 4 0	40.53	38.12
0 1 4	71.28	71.21	2 3 0	36.52	39.19	4 4 1	99.55	97.41
0 1 6	47.05	49.57	2 3 1	33.04	32.63	4 4 2	38.96	35.68
0 1 8	29.58	31.23	2 3 2	37.48	36.57	4 4 3	91.93	85.53
0 2 0	322.67	311.40	2 3 3	30.82	28.25	4 4 4	30.47	29.53
0 2 2	264.09	274.83	2 3 4	28.88	29.76	5 0 0	65.80	65.20
0 2 4	212.33	204.36	2 3 5	22.04	21.45	5 0 1	10.75	9.99
0 2 6	145.14	139.57	2 3 6	21.77	21.43	5 0 2	60.62	60.56
0 3 0	54.93	54.86	2 4 0	118.94	109.06	5 0 3	10.29	8.43
0 3 2	46.18	51.07	2 4 1	77.57	73.56	5 0 4	48.02	48.91
0 3 4	40.69	41.40	2 4 2	110.59	101.60	5 0 6	33.92	35.01
0 3 6	28.17	29.61	2 4 3	63.59	64.15	5 1 0	197.86	195.70
0 4 0	133.81	143.03	2 4 4	82.97	83.20	5 1 1	18.72	11.78
0 4 2	117.98	132.98	2 4 5	49.11	49.53	5 1 2	179.43	180.27
0 4 4	106.08	108.40	2 5 0	14.85	13.23	5 1 3	15.64	10.03
0 5 0	17.56	18.51	2 5 1	15.00	11.44	5 1 4	139.31	144.06
0 5 2	21.88	17.42	2 5 2	14.48	12.47	5 1 5	11.83	7.60
1 0 0	40.33	39.13	2 5 3	12.32	10.12	5 1 6	102.98	103.43
1 0 1	107.21	100.98	3 0 0	80.97	77.89	5 2 0	48.65	49.93
1 0 2	37.22	33.98	3 0 1	47.43	43.82	5 2 1	10.41	8.14
1 0 3	83.33	81.43	3 0 2	73.08	71.01	5 2 2	46.42	46.54
1 0 4	27.64	25.53	3 0 3	38.42	37.73	5 2 3	13.14	7.03
1 0 5	64.19	59.62	3 0 4	58.56	55.87	5 2 4	37.94	37.91
1 0 6	18.57	17.55	3 0 5	27.57	28.47	5 2 5	11.75	5.42
1 0 7	38.22	39.24	3 0 6	41.29	39.05	5 2 6	25.82	27.49
1 0 8	10.83	10.99	3 0 7	16.78	19.04	5 3 0	123.12	126.78
1 1 0	106.34	120.40	3 1 0	236.81	234.33	5 3 1	23.48	7.99
1 1 1	335.95	370.07	3 1 1	184.05	178.65	5 3 2	128.94	118.57
1 1 2	102.05	101.85	3 1 2	208.76	208.56	5 3 3	16.38	7.01
1 1 3	295.88	277.82	3 1 3	151.17	144.13	5 3 4	102.19	97.37
1 1 4	77.02	71.62	3 1 4	157.51	157.03	5 3 5	10.62	5.47
1 1 5	191.25	188.38	3 1 5	105.06	103.17	5 4 0	22.81	22.94
1 1 6	49.39	47.48	3 1 6	106.66	108.19	5 4 2	23.95	21.56
1 1 7	120.99	122.05	3 1 7	64.00	68.50	6 0 0	41.51	39.38
1 1 8	30.25	29.88	3 2 0	54.51	57.74	6 0 1	154.80	156.68
1 2 0	24.60	26.78	3 2 1	33.46	32.83	6 0 2	39.28	36.56
1 2 1	76.24	71.03	3 2 2	55.33	53.45	6 0 3	130.58	135.56
1 2 2	28.93	24.53	3 2 3	30.41	28.60	6 0 4	33.42	29.71
1 2 3	58.97	60.85	3 2 4	48.07	42.90	6 0 5	95.17	103.91
1 2 4	20.42	19.42	3 2 5	21.53	21.76	6 0 6	26.45	21.54
1 2 5	46.11	45.65	3 2 6	30.32	30.45	6 1 0	23.88	23.78
1 2 6	14.28	13.62	3 2 7	14.24	14.80	6 1 1	42.79	44.39
1 2 7	27.90	30.50	3 3 0	124.91	137.20	6 1 2	21.35	22.13
1 3 0	65.31	62.11	3 3 1	104.08	105.85	6 1 3	37.40	38.69
1 3 1	203.13	195.40	3 3 2	130.72	126.73	6 1 4	17.67	18.02
1 3 2	53.91	56.85	3 3 3	96.00	90.81	6 1 5	27.81	29.77
1 3 3	160.51	164.99	3 3 4	105.17	101.95	6 2 0	39.62	31.72
1 3 4	44.81	44.84	3 3 5	66.46	69.07	6 2 1	125.58	127.21
1 3 5	126.81	123.12	3 3 6	71.97	73.59	6 2 2	33.19	29.63
1 3 6	31.67	31.86	3 4 0	25.30	25.89	6 2 3	113.27	111.31
1 3 7	80.97	83.64	3 4 1	14.58	14.31	6 2 4	27.98	24.29
1 4 0	18.16	11.67	3 4 2	27.39	24.22	6 2 5	89.30	86.23
1 4 1	30.68	30.85	3 4 3	14.06	12.60	6 3 0	12.80	15.09
1 4 2	13.43	10.89	3 4 4	20.69	19.93	6 3 1	24.87	26.46
1 4 3	25.81	26.99	3 4 5	12.32	9.91	6 3 2	17.06	14.12
1 4 4	12.11	8.91	3 5 0	71.86	61.43	6 3 3	24.20	23.32
1 4 5	21.02	20.88	3 5 1	52.54	47.96	7 0 0	29.52	30.13
1 5 0	26.51	26.56	3 5 2	59.55	57.72	7 0 1	29.59	31.22
1 5 1	82.27	84.50	4 0 0	96.35	93.03	7 0 2	26.14	28.20
1 5 2	26.25	24.95	4 0 1	244.49	237.84	7 0 3	26.19	27.30
1 5 3	69.33	74.57	4 0 2	87.21	83.88	7 0 4	23.80	23.25

Table 4 continued

$h k l$	F_o	F_c	$h k l$	F_o	F_c	$h k l$	F_o	F_c
2 0 0	331.47	326.75	4 0 3	195.19	196.65	7 1 0	100.85	104.51
2 0 1	219.36	214.98	4 0 4	64.11	64.59	7 1 1	61.78	62.14
2 0 2	280.14	278.01	4 0 5	134.28	143.69	7 1 2	93.44	97.78
2 0 3	162.20	162.95	4 0 6	45.22	45.21	7 1 3	54.45	54.42
2 0 4	192.61	196.62	4 0 7	88.95	96.50	7 1 4	75.46	80.69
2 0 5	111.43	111.24	4 1 0	17.07	13.72	7 2 0	23.21	23.26
2 0 6	130.55	130.74	4 1 1	70.44	69.85	7 2 1	22.92	24.73
2 0 7	72.11	72.23	4 1 2	17.15	12.98	7 2 2	21.06	21.83
2 0 8	80.98	82.40	4 1 3	60.02	60.02	7 2 3	22.43	21.76
2 1 0	72.79	70.48	4 1 4	11.63	10.81	7 3 0	69.22	71.51
2 1 1	58.68	58.53	4 1 5	45.35	45.14	7 3 1	41.29	42.16
2 1 2	66.02	64.35	4 1 6	10.44	7.88	8 0 0	71.62	73.69
2 1 3	52.65	48.67	4 1 7	28.08	30.44	8 0 1	62.50	64.15
2 1 4	52.71	51.07	4 2 0	75.99	71.52	8 0 2	66.38	69.20
2 1 5	38.94	35.81	4 2 1	181.15	183.55	8 0 3	52.69	56.63
2 1 6	33.95	35.87	4 2 2	71.30	65.67	8 1 0	27.18	29.51
2 1 7	23.26	23.67	4 2 3	163.48	156.05	8 1 1	12.79	13.39
2 1 8	20.36	22.78	4 2 4	54.69	52.23	8 1 2	25.26	27.70
2 2 0	205.21	225.67	4 2 5	132.12	117.48	8 2 0	60.74	60.99
2 2 1	141.80	150.90	4 2 6	34.64	37.39			

Table 5 Final atomic parameters.

(a) positional parameters

Site	Composition	x	y	z
I (2e)	Au	0.2003(1)	0	1/4
II (2f)	Cd _{0.95} Au _{0.05}	0.7050(3)	1/2	1/4

(b) anisotropic temperature factors

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I (2e)	0.0128(3)	0.0182(4)	0.0109(3)	0	0	0
II (2f)	0.0139(6)	0.0133(7)	0.0111(5)	0	0	0

NO (Number of reflections)=257

NV (Number of variables)=9

 $R=4.78\%$ $wR=5.10\%$ U_{ij} 's are defined in the temperature factor T as follows:

$$T = \exp \{ -2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13}) \}$$

IV. Discussion

The atomic parameters reported by Ölander were $X_{Au}=3/16(=0.1875)$ and $X_{Cd}=11/16(=0.6875)$, while our results are $X_{Au}=0.2003(1)$ and $X_{Cd}=0.7050(3)$. The R factors were calculated for the previous positional parameters by Ölander and are compared in Table 3. It is clear that the positional parameters have been greatly improved by the present work.

Tadaki and Shimizu⁽¹³⁾ predicted positional parameters using a hard sphere model. Positional parameters on the second layer were $(a/2.524, 0, c/2)$, which were converted to $X_{Au}=0.1981$ and $X_{Cd}=0.6981$ with the coordinates in the International Tables for X-ray

Fig. 2. The crystal structure of the γ_2' phase of a Au-47.5 at%Cd alloy. The origin is shifted to the position of Cd atom from the coordinate in International Table for X-ray Crystallography I. Arrows in the figure indicate the direction of deviation from the ideal positions which form hcp structure. The lengths of arrows are exaggerated. Atoms of Au and Cd are drawn with radii of 0.144 and 0.151 nm, respectively.

Crystallography I⁽¹⁷⁾. Atoms in the same layer are arranged symmetric. The R factors were also calculated from their parameters and are shown in Table 3.

The crystal structure determined is shown in Fig. 2, where the origin is shifted to the position of Cd atom of site II for convenience. If two kinds of atoms were not distinguished, the structure would be a hcp structure. In the hcp structure, triangular nets are formed and the interatomic distance in the layer is all the same, i.e. atoms are arranged centro-symmetric in one layer. Atoms on the second layer is located at the center of gravity of the triangle formed by atoms in the first layer, i.e. $x=1/6$ and $2/3$ at $z=1/2$ for conventional coordinate in Fig. 2. However, in this alloy, the radii of Au and Cd atoms are not equal, i.e. 0.144 and 0.151 nm, respectively⁽²⁰⁾, so Cd atoms are not arranged centro-symmetric in the layer as shown in Fig. 2(a). The deviation from the centro-symmetric position is shown by the arrow with the value. Atoms on the second layer (in Fig. 2(b)) are also shifted from an ideal position in the hcp structure because of the difference of the atomic radii, i.e. $x=0.0947$ and 0.5900 instead of $0.1667(=1/6)$ and $0.6667(=2/3)$ in the coordinate of the figure. The deviations from the ideal posi-

Table 6 Interatomic distances.

Atoms	Distance(nm)	Relation of two atoms
Au-Au ($\times 2$)	0.3077(3)	neighboring layer
($\times 2$)	0.3151(1)	same layer
($\times 2$)	0.3763(5)	neighboring layer
-Cd ($\times 2$)	0.2877(5)	same layer
($\times 4$)	0.2894(1)	neighboring layer
($\times 2$)	0.2915(5)	same layer
Cd-Cd ($\times 2$)	0.3106(3)	neighboring layer
($\times 2$)	0.3151(1)	same layer
($\times 2$)	0.3728(5)	neighboring layer
-Au ($\times 2$)	0.2877(5)	same layer
($\times 4$)	0.2894(1)	neighboring layer
($\times 2$)	0.2915(5)	same layer

Au: site I (2e) {Au}

Cd: site II (2f) {Cd_{0.95}Au_{0.05}}

tions on the second layer are also represented by the arrows with the values. Interatomic distances in this alloy are shown in Table 6.

In conclusion, the crystal structure of the γ_2' phase of a Au-47.5 at%Cd was determined by a single crystal X-ray diffraction experiment. The final R factor with the full-matrix least squares method is 4.8%, which is improved very much from the previous work.

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REFERENCES

- (1) L. C. Chang and T. A. Read: Trans. AIME, **189** (1951), 47.
- (2) D. S. Lieberman, M. S. Wechsler and T. A. Read: J. Appl. Phys., **26** (1955), 473.
- (3) A. Ölander: J. Am. Chem. Soc., **54** (1932), 3819.
- (4) H. K. Birnbaum and T. A. Read: Trans. Met. Soc. AIME, **218** (1960), 662.
- (5) D. S. Lieberman, M. A. Schmerling and R. S. Karz: *Shape Memory Effects in Alloys*, Ed. by J. Perkins, Plenum Press, New York, (1975), p. 203.
- (6) J. Janssen, J. Van Humbeeck, M. Chandrasekaran, N. Mwamba and L. Delaey: J. de Phys., **43** (1982), C4-715.
- (7) G. Scarsbrook, J. Cook and W. M. Stobbs: J. de Phys., **43** (1982), C4-703.
- (8) A. Abu Arab and M. Ahlers: J. de Phys., **43** (1982), C4-709.
- (9) Y. Emura, T. Ohba, S. Miyazaki and K. Otsuka: unpublished work (1989).
- (10) N. Nakanishi, T. Mori, S. Miura Y. Murakami and S. Kachi: Phil. Mag., **28** (1973), 277.
- (11) S. Vatanayon and R. F. Hehmann: *Shape Memory Effects in Alloys*, Ed. by J. Perkins, Plenum Press, New York, (1975), p. 115.
- (12) A. Ölander: Z. Krist., **83A** (1932), 145.
- (13) T. Tadaki and K. Shimizu: Trans. JIM, **18** (1977), 735.
- (14) Z. Nishiyama: *Martensitic Transformations*, Academic Press, New York, (1977).
- (15) *International Tables for X-ray Crystallography* Vol III, Kynoch Press, Birmingham (1968).

- (16) *International Tables for X-ray Crystallography* Vol IV, Kynoch Press, Birmingham (1974).
- (17) *International Tables for X-ray Crystallography* Vol I, Kynoch Press, Birmingham (1969).
- (18) P. Coppens, T. N. Gurn, P. Lenng, E. D. Stevens, P. D. Beeker and Y. W. Yang: *Acta Cryst.*, **A35** (1979), 63.
- (19) T. Tadaki, S. Hamada and K. Shimizu: *Trans. JIM*, **18** (1977), 135.
- (20) L. Pauling: *The Nature of the Chemical Bond*, 3rd ed, Cornell University press, New York, (1960), p. 403.
- (21) A. Bystrom and K. E. Almin: *Acta Chem. Scand.*, **1** (1947), 76.
- (22) R. Chang: *Acta Cryst.*, **4** (1951), 320.
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