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Establishment of an ordered phase of composition Au_5Mn_2 in the gold-manganese system.

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The composition range 20–33 at.% Mn in the Au–Mn system is found to be very rich in ordered structures. Thus a phase Au_4Mn was found by Kiessmann & Raub (1956), the ordered structure of which has been determined by Watanabe (1957). Raub, Zwicker & Baur (1953) have studied a phase Au_3Mn, the structure of which has been investigated in more detail by Watanabe (1958, 1960, 1961). Recently Morris, Hughes & Davies (1963) have reported the existence of two other ordered phases in the composition range 21–24 at.% Mn. In a systematic investigation of the Au–Mn system in this laboratory this result of Morris *et al.* has been confirmed, and in addition two new phases have been discovered in the composition range 25–33 at.% Mn. Finally there exists at about 33 at.% Mn an ordered phase Au_2Mn, the structure of which has been studied by Herpin, Mériel & Meyer (1958) and by Hall & Royan (1959). Totally there thus exist 7 phases in the composition range 20–33 at.% Mn of the system. This means that new structures appear for about every 2 at.% change of the manganese concentration in this range. For one of the new phases of the present investigation corresponding to the composition Au_5Mn_2 the atomic arrangement has been evaluated in detail and I give the results here.

Fig. 1 gives examples of X-ray records obtained in this investigation with a Guinier monochromator camera, the radiation used being Cu $K\alpha_1$. Fig. 1(*a*) shows the lines of one of the new structures, here termed X, while (*b*) shows the lines of X together with those of Au_5Mn_2, the lines of which appear practically isolated in (*c*). Fig. 1(*d*) finally shows the lines of Au_5Mn_2 together with those of the phase Au_2Mn.

The evaluated crystal symmetry of Au_5Mn_2 can be derived by a slight monoclinic deformation of the basic f.c.c. lattice which has first acquired an orthorhombic deformation. The monoclinic feature of the structure is clearly apparent, as in the photograms not only reflexions of the form $p00$ but also those of form ppp are being divided up into components. The monoclinic deformation can in this case be described by shearing an orthorhombic cell, in a [100] direction through an angle of magnitude 0·29°. The lattice parameters of the basic f.c. cell are, disregarding the superstructure,

$$a' = 4{\cdot}125,\ b' = 3{\cdot}954,\ c' = 4{\cdot}088\ \text{Å};\ \beta' = 90{\cdot}29°.$$

For the evaluation of the atomic arrangement of the superstructure the axis system of the face-centered fundamental cell with four atoms is not suitable. In fact it would result in quite a large unit cell. The close analysis of the X-ray data has resulted in the structure model shown in Fig. 2. The unit cell of the axis system

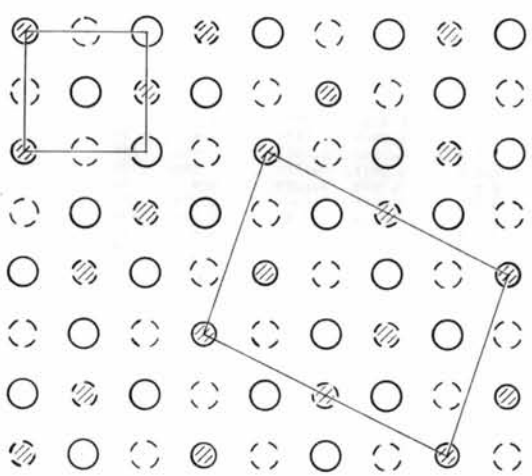

Fig. 2. Projection of the established Au_5Mn_2 structure in a plane perpendicular to the b direction of the lattice. The indicated unit cell with monoclinic symmetry contains 14 atoms.

○ and ● Au and Mn atoms respectively of the first layer.
○ and ● Au and Mn atoms respectively of the second layer.

shown in the Figure contains only 14 atoms. The corresponding lattice parameters are:

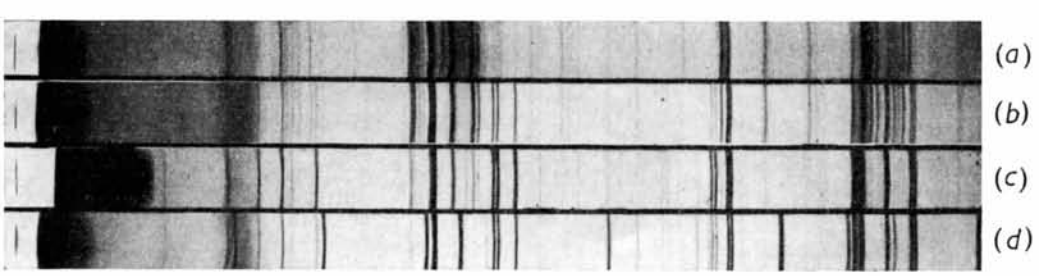

Fig. 1. (*a*) X-ray record of an alloy with 26·7 at.% Mn, showing the lines of phase X. (*b*) Alloy with 28·0 at.% Mn showing the Au_5Mn_2 phase in coexistence with the unknown phase X. (*c*) Alloy with 28·7 at.% Mn, showing practically only the lines of Au_5Mn_2. (*d*) Alloy with 31·5 at.% Mn, showing the coexistence of Au_5Mn_2 and Au_2Mn.

Table 1. *Observed and calculated* $\sin^2\theta$ *and line intensities of* Au_5Mn_2

Specimen: Filed powder of 28·7 at.% Mn annealed at 400 °C, 60 hr

Radiation: Monochromatized Cu $K\alpha_1$, $\lambda = 1{\cdot}54050$ Å

h k l	$\sin^2\theta$ observed	$\sin^2\theta$ calculated	Intensity observed	Intensity calculated ($\propto \lvert F\rvert^2 \cdot n$)
0 0 1	0.0142	0.0144	v v w	4
$\bar{2}$ 0 0	0.0286	0.0286	v w	33
2 0 1	0.0377	0.0377	w	71
1 1 0	0.0452	0.0451	n	138
$\bar{2}$ 0 1	0.0483	0.0483	v w	31
$\bar{1}$ 1 1	0.0569	0.0568	w	60
0 0 2	0.0575	0.0575	w	67
$\bar{2}$ 0 2	0.0967	0.0968	w	61
$\bar{1}$ 1 2	0.0975	0.0973	w	54
$\bar{1}$ 1 2	0.1077	0.1080	v v str	2088
$\bar{3}$ 1 1	0.1092	0.1087	v v str	2084
4 0 1	0.1180	0.1181	w	58
3 1 1	0.1247	0.1247	n	115
0 0 3	0.1286	0.1294	v v w	25
$\bar{4}$ 0 1	0.1397	0.1395	v str	962
2 0 3	0.1421	0.1420	v str	958
0 2 0	0.1523	0.1518	v str	936
$\bar{1}$ 1 3	0.1667	0.1665	w	107
3 1 2	0.1757	0.1758	v w	47
$\bar{2}$ 2 0	0.1809	0.1804	v w	47
2 2 1	0.1899	0.1895	w	103
$\bar{2}$ 2 1	0.2006	0.2001	v w	45
$\bar{3}$ 1 3	0.2076	0.2077	w	100
0 2 2	0.2099	0.2093	w	100
$\bar{5}$ 1 0	0.2171	0.2168	v w	44
$\bar{5}$ 1 1		0.2178		44
$\bar{5}$ 1 1	0.2450	0.2445	w	95
5 1 2	0.2480	0.2476	w	94
2 2 2	0.2491	0.2486	w	94
3 1 3	0.2556	0.2558	v w	42
$\bar{6}$ 0 0	0.2580	0.2575	v w	47
$\bar{4}$ 2 1	0.2704	0.2699	w	92
$\bar{2}$ 0 4	0.2802	0.2801	str	738
6 0 2	0.2834	0.2830	str	736
6 0 1	0.2878	0.2879	v w	20
$\bar{4}$ 2 1	0.2921	0.2913	v str	1452
$\bar{2}$ 2 3	0.2946	0.2938	v str	1444
$\bar{3}$ 1 4	0.3005	0.3004	v w	41
$\bar{4}$ 0 4	0.3020	0.3018	v w	44
4 2 2		0.3024		40
1 3 0	0.3495	0.3487	v w	83
0 0 5	0.3597	0.3595	v w	41
$\bar{1}$ 3 1		0.3604		37
$\bar{2}$ 0 5	0.3613	0.3614	v v w	41
4 2 3	0.3644	0.3636	v w	36
3 1 4		0.3645		82
0 2 4	0.3822	0.3819	v w	36
5 1 3	0.3862	0.3862	str	1276
$\bar{7}$ 1 0	0.3884	0.3884	str	1272
$\bar{1}$ 1 5	0.3913	0.3913	str	1264
$\bar{5}$ 1 4	0.3934	0.3935	str	1260
$\bar{1}$ 3 2	0.4006	0.4009	v v w	35
$\bar{7}$ 1 2	0.4089	0.4085	v w	78
6 2 0		0.4093		78
$\bar{1}$ 3 2	0.4125	0.4116	v str	1236
$\bar{2}$ 3 1		0.4123		1236
3 1 5	0.4178	0.4156	v w	34
$\bar{1}$ 1 5		0.4180		34
6 0 4	0.4230	0.4235	v w	41
4 2 3	0.4262	0.4277	v w	78
3 3 1	0.4286	0.4283	v w	78
$\bar{2}$ 2 4	0.4318	0.4319	str	1208
6 2 2	0.4349	0.4348	str	1204

$a = 9{\cdot}188$, $b = 3{\cdot}954$, $c = 6{\cdot}479$ Å; $\beta = 97{\cdot}56°$.

The structure apparently belongs to the space group $C2$ (C_2^3). From Fig. 2 the following coordinates of the basic atoms of the cell are obtained

Au: 3/7, 0, 2/7; 6/7, 0, 4/7; 2/7, 0, 6/7; 5/7, 0, 1/7; 4/7, 0, 5/7; 13/14, 1/2, 2/7; 5/14, 1/2, 4/7; 11/14, 1/2, 6/7; 3/14, 1/2, 1/7; 1/14, 1/2, 5/7.

Mn: 0, 0, 0; 1/7, 0, 3/7; 1/2, 1/2, 0; 9/14, 1/2, 3/7.

Table 1 gives the observed and calculated $\sin^2\theta$ and line intensities of the X-ray record (*c*) of Fig. 1. It appears from this that especially as regards the $\sin^2\theta$ values the agreement between observed and calculated data is excellent.

The new structure reported here has been found in alloys annealed below about 500 °C within a composition range of approximately 27–32·5 at.% manganese. The homogeneity range of Au_5Mn_2 seems to be very narrow. Practically single-phase records have been obtained only for an alloy with 28·7 at.% Mn, thus corresponding almost exactly to the formula Au_5Mn_2. The investigation will be continued.

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