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Crystallographic data for DL-thiomalic acid, dihydrositsirikine *p*-bromobenzoate, and a methyl trichloro-trideoxy-hexoside.

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Crystallographic data are given in Table 1 (λ, Cu $K\alpha$ = 1·5418 Å, λ, Mo $K\alpha$ = 0·7107 Å) for the three compounds.

Table 1. *Crystallographic data*

	DL-Thiomalic acid $C_4H_6O_4S$	Dihydrositsirikine *p*-bromobenzoate $C_{28}H_{31}N_2O_4Br$	Methyl trichloro-trideoxy-hexoside $C_7H_{11}O_3Cl_3$
M	150·2	539·5	249·5
Crystal system	Monoclinic	Orthorhombic	Monoclinic
a	5·23 ± 0·01 Å	37·79 ± 0·10 Å	7·87 ± 0·01 Å
b	14·19 ± 0·03	22·88 ± 0·07	5·42 ± 0·01
c	16·98 ± 0·03	16·09 ± 0·05	35·86 ± 0·05
β	96·6 ± 0·1°	—	119·9 ± 0·2°
U	1251 Å^3	13912 Å^3	1326 Å^3
Z	8	~20	4
D_m	~ 1·5 g.cm^{-3}	~ 1·25 g.cm^{-3}	1·25 g.cm^{-3}
D_x	1·59	1·29	1·25
Space group	*Cc* or *C*2/*c*	$P2_12_12_1$	*P*2

The DL-thiomalic acid crystals, $HO_2C.CH(SH).CH_2.CO_2H$, are colourless needles elongated along [100], and frequently twinned. The diffraction pattern exhibited a series of diffuse streaks parallel to c^*, through every reciprocal lattice point, and with occasional maxima of spacing about $\frac{1}{3}c^*$. These streaks probably correspond to a disordered structure with a partially ordered superlattice; no outstanding peaks corresponding to S–S vectors could be located on the *a*-axis Patterson projection. Crystals of dihydrositsirikine *p*-bromobenzoate are fine colourless needles elongated along [100]; the large unit cell, and large number of molecules in the cell, indicate a complex structure. Crystals of the hexoside are colourless needles elongated along [010]. Since the compound is optically active ($[\alpha]_D = +159°$ in methanol), the alternative space groups, *Pm* and *P*2/*m*, are ruled out; there are two molecules in the asymmetric unit, so that structure analysis requires the initial location of six chlorine atoms.

As a result of these various complicating features no further work on these compounds is planned.

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An X-ray powder investigation of ordered Au_3Mn.

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The alloy Au_3Mn has been the subject of several recent investigations. Raub, Zwicker & Baur (1953) originally found that the high-temperature disordered f.c.c. solid solution of Mn in Au suffered a transformation at 645 °C into an ordered structure which was not determined. Resistance and magnetic measurements were made by Giansoldati & Linde (1955) and by Giansoldati, Linde & Borelius (1959). The knee observed in the resistance–temperature curve at 650 °C was characteristic of order–disorder, whilst that at −123 °C was attributed to a Néel point in the ordered alloy. Meyer (1957) carried out detailed magnetic measurements and observed a Néel point at 145 °K (−128 °C), and concluded that the ordered structure was a metamagnetic. The crystal structure has been investigated by Watanabe (1958, 1960) by electron diffraction on thin films and it was deduced that the structure can be thought of as formed from the fundamental face-centred orthorhombic lattice ($a_1 = 4·08$, $a_2 = 4·05$, $a_3 = 4·03$ Å) in which the atoms arrange themselves as in the ordered structure of Cu_3Au, but the two kinds of step-shift, $\pm(a_2 \pm a_3)/2$ and $\pm(a_3 \pm a_1)/2$, occur at every M_1 and M_2 cells along the x and y directions respectively. M_1 and M_2 were found not to be integers but the idealized lattice of the ordered Au_3Mn was considered to have a unit cell of dimensions $2a_1$, $4a_2$, a_3 (or a 2 × 4 × 1 cell). The magnetic behaviour of disordered and ordered Au_3Mn has also been reported by Jacobs, Kouvel & Lawrence (1962) and by Sato, Hirone, Watanabe, Maeda & Adachi (1962). The former authors in their discussion assumed the ordered structure to be the idealized 2 × 4 × 1 superlattice of Watanabe, whilst Sato *et al.* quote a table of observed and calculated lattice spacings and intensities based on a 2 × 4 × 1 superlattice cell, but with a fundamental face-centred orthorhombic cell having $a = 4·08$, $b = 4·04$, $c = 4·01$ Å.

Morris & Hughes (1962) reported that a structure having a fundamental orthorhombic unit cell of dimensions $a = 4·0814$, $b = 4·0599$, $c = 4·0377$ Å, and referred to by them as the α'' phase, existed between about 21·0 and 22·2 at.% Mn after appropriate heat treatment.

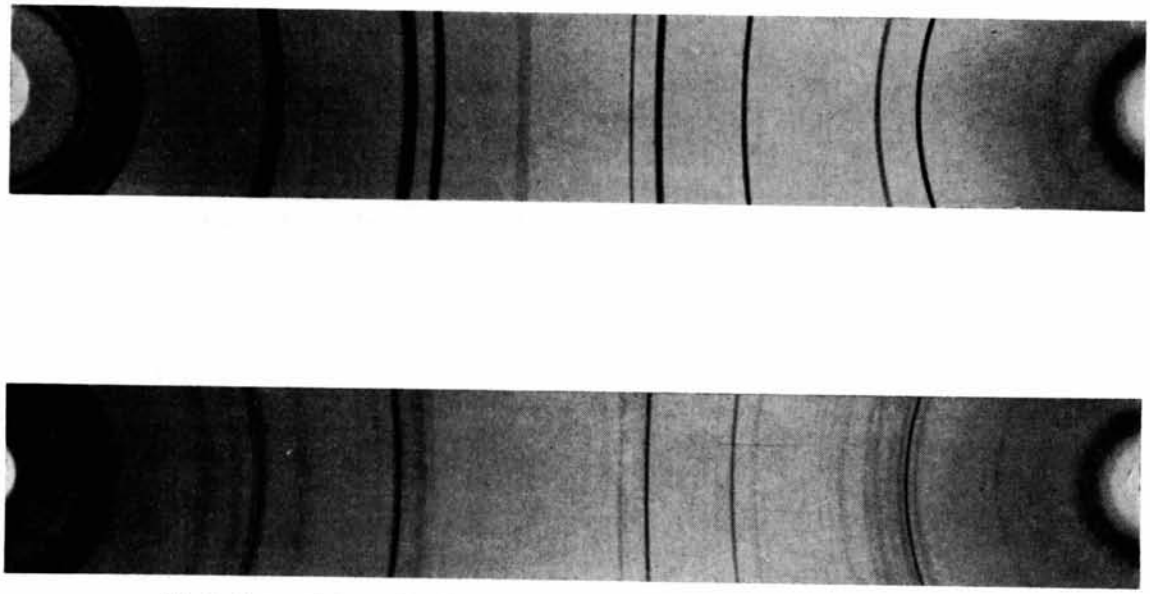

Fig. 1. X-ray photographs of the α'' phase (top) and the Au_3Mn phase (bottom).

Between this and the Au_3Mn composition occurred a hexagonal η phase, whilst in alloy 24·0 η coexisted with a complex structure. Further investigation has now shown that this latter structure corresponds to the composition Au_3Mn and that it differs from the so called 'Au_3Mn' of Watanabe. The present note describes the determination of the fundamental cell dimensions by X-ray powder methods. The full structure is an example of the periodic anti-phase domain structures and it is hoped to examine this in more detail by single-crystal methods.

Fig. 1 shows X-ray powder photographs taken at room temperature with Cu $K\alpha$ radiation of the α'' and the Au_3Mn phases. The α'' photograph was obtained from a powder sample containing 21·7 at.% Mn quenched after three days at 360 °C, and that of Au_3Mn from a sample containing 25·0 at.% Mn quenched after 24 hr at 550 °C, both samples having been initially annealed in the cubic region to remove internal strain. It is seen that the deformation of the original cubic lattice is much less in Au_3Mn than in α''. Further studies of each structure were made with a diffractometer. In the case of Au_3Mn the intensity distribution in the fundamental (422) reflexion is shown in Fig. 2 and corresponds to a tetragonal distortion with $c/a > 1$. The reflexions are thus indexed in the sequence (224), (422, 242) with increasing θ, with almost exact superposition of $(224)\alpha_2$ and $(422,\ 242)\alpha_1$. There is also very near superposition of $(115)\alpha_2$ and $(333,\ 511)\alpha_1$. The reflexions chosen to determine the fundamental cell dimensions were $(224)\alpha_1$, $(422)\alpha_2$ (corrected to the α_1 position), and $(115)\alpha_1$, thus avoiding errors due to the assumption of exact α_1 and α_2 superposition. Both the film and the diffractometer trace were used, and taking $\lambda\, K\alpha_1 = 1{\cdot}54051$ Å and $\lambda\, K\alpha_2 = 1{\cdot}54433$ Å, the mean values of the fundamental cell dimensions of Au_3Mn at 22 °C are: $a = 4{\cdot}041_8 \pm 0{\cdot}001$, $c = 4{\cdot}064_5 \pm 0{\cdot}001$ Å, $c/a = 1{\cdot}005_5 \pm 0{\cdot}0005$.

The fundamental cell of α'' is orthorhombic, and in alloy 21·7 at.% Mn, the dimensions at 22 °C are:

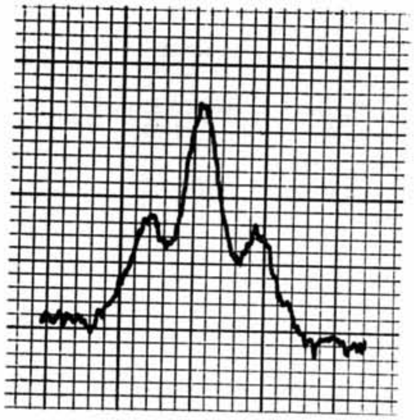

Fig. 2. Intensity distribution of the fundamental 422 reflexion of the Au_3Mn phase.

$$a = 4{\cdot}081_6 \pm 0{\cdot}0005,\ b = 4{\cdot}059_5 \pm 0{\cdot}0005,$$
$$c = 4{\cdot}038_5 \pm 0{\cdot}0005\ \text{Å}\ .$$

These are in good agreement with those previously reported (Morris & Hughes, 1962) for alloy 21·0 at.% Mn.

The films and diffractometer traces showed many superlattice reflexions for both structures, but they were very faint for α''. The observed d values and the visually estimated intensities are listed in Table 1, for comparison with the d values of Sato *et al.*, and those of Watanabe for so called 'Au_3Mn'. The latter were obtained by electron diffraction of single crystal-like film, a technique which gave many more superlattice reflexions than were observed by the X-ray powder method. Table 1 contains only those reflexions common to both methods of observation. It is seen that the 'Au_3Mn' phase of Watanabe corresponds closely to our α'' phase.

Our observations on Au_3Mn are in good agreement with those of Sato *et al.*, but they deduced an ortho-

Table 1. *Observed lattice spacings and intensities for* $\mathrm{Au_3Mn}$ *and* α''

	$\mathrm{Au_3Mn}$		
	Morris & Hughes (present work)		Sato *et al.*
*hkl**	I_0	d_0	d_0
—	*vvw*	3·680	3·67
—	*mw*	3·605	3·59
—	*w*	2·884	2·84
—	—	—	2·67
—	—	—	2·50
—	*vvw*	2·465	2·46
—	*ms*	2·425	2·41
111	*s*	2·337	2·33
—	*ms*	2·280	2·27
—	*w*	2·180	2·18
—	*mw*	2·088	2·09
{200}	*mw*	2·023	2·02
—	—	—	1·91
—	*w*	1·878	1·86
—	*vw*	1·807	1·80
—	*w*	1·766	1·76
—	—	—	1·70
—	*vvw*	1·656	1·65
—	—	—	1·57
—	—	—	1·53
—	*mw*	1·504	1·50
{220}	*s*	1·431	1·43
—	*vvw*	1·386	1·39
—	*vvw*	1·352	1·34
—	—	—	1·32
—	—	—	1·29
—	*vvw*	1·259	1·26
—	*vvw*	1·232	1·23
{311}	*s*	1·226	1·22
—	*vw*	1·212	1·21
—	*vvw*	1·198	1·19
—	*vvw*	1·184	1·18
222	*ms*	1·172	1·17

rhombic and not a tetragonal fundamental cell. They also list the *d* values and intensities calculated on the basis of a 2 × 4 × 1 combination of their fundamental cell, the former agreeing well with the observed values except for the reflexion of largest spacing. Our results are also very similar with a 2 × 4 × 1 unit cell, but equally good agreement between calculated and observed values is obtained on the basis of a 1 × 1 × 10 unit cell. It has not been possible to distinguish between these possibilities by the powder method. The low intensities of the fundamental (200) and (331) reflexions are not accounted for by the calculations of Sato *et al.*, and it appears that the atoms are displaced from the corner and centre sites of the fundamental cell.

With regard to the α'' phase, only 20 reflexions having *d* values greater than 1·224 Å were observed by the powder method, as compared with 60 recorded in this range by Watanabe. The true unit cell has thus not been determined, but good agreement between observed and calculated *d* values has been obtained for both a 2 × 4 × 1 and a 6 × 6 × 4 unit cell.

Further work is in progress.

Table 1 (*cont.*)

	α''		
	Morris & Hughes (present work)		W. '$\mathrm{Au_3Mn}$'†
*hkl**	I_0	d_0	d_0
—	*vvw*	8·96	9·15
—	*vw*	4·19	4·21
—	*w*	3·98	3·99
—	*w*	3·74	3·74
—	*w*	3·64	3·63
—	*w*	3·51	3·54
—	*vw*	3·19	3·20
—	*vw*	2 59	2·61
—	*vw*	2·56	2·57
111	*vs*	2·340	2·34
200	*s*	2·036	2·040
020	*s*	2·024	2·025
002	*s*	2·015	2·015
—	*vvw*	1·800	1·799
—	*vvw*	1·776	1·774
—	*vvw*	1·756	1·754
220	*s*	1·437	1·437
202	*s*	1·434	1·434
022	*s*	1·430	1·428
311	*s*	1·228	1·228
131	*s*	1·224	1·220
113	*s*	1·220	1·218
222	*ms*	1·171	—

* Fundamental reflexions.

† Watanabe's values for '$\mathrm{Au_3Mn}$' (see text).

Note added in proof.— It has since been shown (Morris, Hughes & Davies, 1963) that a metastable transition structure occurs between disordered and fully ordered $\mathrm{Au_3Mn}$, its fundamental cell being orthorhombic with lattice parameters $a = 4{\cdot}107$, $b = 4{\cdot}051$, $c = 4{\cdot}011$ Å at 22 °C in a sample quenched from 445 °C.

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