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Errata in *International Tables for X-ray Crystallography*, Vol. I (2nd edition).

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A corrected electron density expression is given for space groups $P4_122$ (No. 91) and $P4_322$ (No. 95).

The electron density expressions for the enantiomorphous space groups $P4_122$ (No. 91, p. 426) and $P4_322$ (No. 95, p. 429) should read:

$$\varrho(XYZ) = \frac{8}{V_c}\left\{\sum_0^\infty\sum_0^\infty\sum_0^\infty{}^{l=2n}|F(hkl)|\,[\cos 2\pi hX \times \cos 2\pi kY \cos 2\pi lZ \cos\alpha(hkl) - \sin 2\pi hX \sin 2\pi kY \sin 2\pi lZ \sin\alpha(hkl)] + \sum_0^\infty\sum_0^\infty\sum_0^\infty{}^{l=2n+1}|F(hkl)|\,[-\sin 2\pi hX \times \cos 2\pi kY \sin 2\pi lZ \cos\alpha(hkl) + \cos 2\pi hX \sin 2\pi kY \cos 2\pi lZ \sin\alpha(hkl)]\right\}.$$

Corrections to the phase relationships have appeared already (Schultze-Rhonhof, 1966).

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The structure of Mn_2Au and Mn_3Au.

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X-ray and neutron diffraction measurements have shown that Mn_2Au is a compound with a tetragonal unit-cell of dimensions $a=3{\cdot}328$ and $c=8{\cdot}539$ Å and that it can be assigned to the same space group as $MnAu_2$, namely $I4/mmm$ ($D_{4h}{}^{17}$). The neutron diffraction pattern of 74·2 at.% MnAu can be explained only if the ordered structure of this alloy is identical with that of Mn_2Au. Thus the compound Mn_3Au apparently does not exist.

Introduction

In their investigation of the phase diagram of the Mn–Au system, Raub, Zwicker & Baur (1953) proposed the existence of the compound Mn_3Au, and from X-ray diffraction of a 70 at. % Mn alloy they concluded that it had a complex tetragonal structure, and also remarked on the similarity of the diffraction pattern to that obtained from an alloy of composition Mn_2Au.

Gaunt & Eden (1965) proposed a tetragonal structure for Mn_3Au with cell dimensions $a=4{\cdot}706$, $c=8{\cdot}539$ Å and atomic coordinates

Au: 000; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$;
Mn: $00\pm z$; $\frac{1}{2}0\frac{1}{2}\pm z$; $0\frac{1}{2}\frac{1}{2}\pm z$
$\frac{1}{2}\frac{1}{2}\pm z$; $\frac{1}{2}\frac{1}{2}0$

with $z\simeq\frac{1}{3}$.

They also commented on the close similarity of this structure to that determined for $MnAu_2$ by Hall & Royan (1959).

During an investigation of Mn_3Au it was found that the neutron diffraction patterns could not be explained in terms of the above structure, and this prompted the following study.

Experimental

Three ingots, each weighing about 60g, were prepared by melting together manganese (4*N*5) and gold (5*N*) in an argon arc furnace. The ingots were homogenized at 900 °C *in vacuo* for 50 hours and annealed at 500 °C for a further 50 hours. Chemical analysis showed the compositions of the ingots to be 62·6, 67·4 and 74·2 at. % Mn.

X-ray diffraction patterns from flat polished specimens of all three compositions were similar to that reported by

Gaunt & Eden for Mn_3Au. The pattern obtained for the 67·4 at. % Mn specimen using a Philips diffractometer and Cu $K\alpha$ radiation is shown in Fig. 1(*a*).

The other two specimens gave diffraction patterns which showed all of these reflexions, together with extra reflexions from a second phase that was identified as the α-Mn phase ($a = 8{\cdot}93$ Å) in the 74·2 at. % Mn sample and as the β phase ($a = 3{\cdot}19$ Å) in the 62·6 at. % Mn sample.

The neutron diffraction pattern [Fig. 1(*b*)] for the 67·4 at. % Mn alloy was obtained from a cylindrical specimen 5 cm $\times$ 1 cm in diameter, using neutrons of wavelength 1·082 Å. The other two alloys showed the same second phase reflexions as were found in the X-ray diffraction patterns.

Differences in the relative intensities of the X-ray and neutron reflexions result from the difference in sign between the neutron scattering lengths for Mn and Au.

No peaks were detected for $l = 3n$ in the neutron diffraction pattern and none of the weaker lines for mixed odd and even values for the Mn_3Au structure were observed, although they should have been readily detected by neutron diffraction. For example, the intensity of the 001 reflexion should have been 20% of the 111 reflexion. (this 111 reflexion becomes 101 on the new indexing).

However the diffraction patterns can be explained by replacing the manganese atom at $\frac{1}{2}\frac{1}{2}0$ in the Mn_3Au structure by a gold atom. This allows the unit cell to be reduced in size, to contain only 6 atoms per unit cell. This unit cell has dimensions $a = 3{\cdot}328$, $c = 8{\cdot}539$ Å and the structure is now that of Mn_2Au with atom coordinates:

$$\text{Au: } 000;\ \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2};$$
$$\text{Mn: } 00\pm z;\ \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\pm z\,.$$

Table 1 shows the calculated and observed intensities for Mn_2Au using the results from the 67·4 at. % Mn alloy and putting $z = \frac{1}{3}$. The qualitative agreement between observed and calculated intensities is clearly apparent, but the necessity of using bulk specimens with the possibility of preferred orientation precludes a more accurate determination of z.

Thus Mn_2Au is a compound which has a structure identical with that of $MnAu_2$, space group $I4/mmm$ (D_{4h}^{17}), with the atomic species interchanged, and the compound Mn_3Au apparently does not exist.

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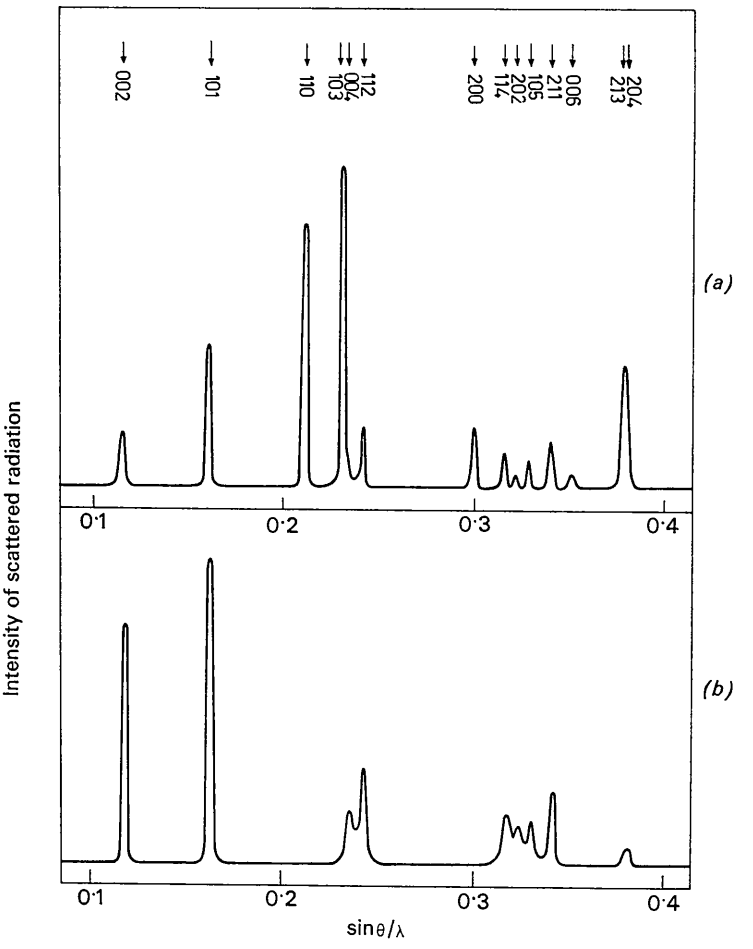

Fig. 1. (*a*) X-ray and (*b*) neutron diffraction patterns of Mn_2Au measured at room temperature.

Table 1. *Observed and calculated intensities from both neutron and X-ray diffraction patterns of* Mn_2Au

$z=\frac{1}{3}$, normalized to 100 for the most intense reflexion in each case.

Reflexion	Neutron I_{calc}	Neutron I_{obs}	X-ray I_{calc}	X-ray I_{obs}
002	47	78	16	16
101	100	100	29	45
110	0	0	63	80
103	0	0	100	100
004	12	18	3	4
112	45	38	10	18
200	0	0	22	22
114	27	18	5	11
202	26	15	4	5
105	25	17	4	9
211	47	28	7	16
006	0	0	6	7
213	0	10	37	47
204	19		3	

lian Atomic Energy Commission. One of us (P.W.) held a Commonwealth Postgraduate Scholarship.

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A note on the greatest value of the Bijvoet ratio.

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The greatest value of the Bijvoet ratio $\Delta I/I$, has been studied as a function of I. It is shown that the maximum value of $\Delta I/I$ is 2 which occurs only when $I \le I_c$; $I_c = 2\delta(\Sigma f_A)^2$ if $\Sigma f_A \langle \Sigma f_N \rangle \sqrt{1+\delta^2} \Sigma f_A$, otherwise $I_c = 2\delta^2/(1+\delta^2)\,(\Sigma f_N)^2$ (f_N is the scattering factor of the normal scatterers and f_A the real part of scattering factor of the anomalous scatterers); $\delta = \Delta f''/f_A$. For $I > I_c$, the greatest value decreases approximately as the inverse of I and rapidly approaches zero as the maximum possible value of I is reached.

For comparison with theory of the observed anomalous dispersion data from a non-centrosymmetric structure, it is convenient to use a quantity $\Delta I/I = |[|F(H)|^2 - |F(\bar{H})|^2]| / \frac{1}{2}[|F(H)|^2 + |F(\bar{H})|^2]$ (H and $\bar{H}$ indicate indices hkl and $\bar{h}\bar{k}\bar{l}$) as a measure of the anomalous dispersion effect exhibited by a crystal (Zachariasen, 1965). In the present communication the greatest value of $\Delta I/I$ as a function of I has been studied. This analysis is of interest because it makes possible the calculation of the upper limits of $\Delta I/I$ in a given structure. It must be emphasized that these limits are inherent in the function $\Delta I/I$. Though there is no assumption in the theory, its practical application does require a knowledge of the scattering factors of the atoms in the crystal. Any uncertainty in the scattering factors will lead to some practical difficulties which are discussed of the end at this paper.

Maximum of $\Delta I/I$

Let us consider a noncentrosymmetric structure with n_A identical anomalous scatterers having a scattering factor of the form $(f_{0A} + \Delta f'_A + i\Delta f''_A)$ and n_N normal scatterers. It can be easily shown that

$$\Delta I/I = |[|F(H)|^2 - |F(\bar{H})|^2]| / \tfrac{1}{2}[|F(H)|^2 + |F(\bar{H})|^2] = 4k'\delta \sin\varphi(1+\delta^2+k'^2+2k'\cos\varphi)\,, \quad (1)$$

where $k' = |F_N(H)|/|F_A(H)|$. $|F_N(H)|$ is the contribution to the structure factor from the normal scatterers while $|F_A(H)|$ is due to the real part of the scattering by the anomalous scatterers. $\delta = \Delta f''_A/(f_{0A} + \Delta f'_A)$. φ is the angle between vectors $\mathbf{F}_N(H)$ and $\mathbf{F}_A(H)$ in the complex plane. For convenience $|F_N(H)|$ and $|F_A(H)|$ will be denoted by x and y. The limits of x and y are $0 \le x \le x_{max}$ and $0 \le y \le y_{max}$ where $x_{max} = \sum_1^{\eta_N} f_i$ and $y_{max} = n_A(f_{A0} + \Delta f'_A)$. Further $0 \le \varphi \le \pi$.

By definition it is obvious that the maximum value of $(\Delta I/I)$ is 2 and that it occurs when $|F(\bar{H})|^2 = 0$. The following analysis provides additional information. Considering $(\Delta I/I)$ as a function of two variables k' and φ [equation (1)], it can be easily shown that maximum occurs when $k' = \sqrt{1+\delta^2}$. Since δ is in general small, $k' \simeq 1$ and $\varphi \simeq \pi$. For these values of k' and φ it can be shown that

$$|F(H)|^2 = 4\delta^2 |F_A(H)|^2$$

and $|F(\bar{H})|^2 = 0$.

From this, it can be easily deduced that I_c, the maximum value of I for which $\Delta I/I = 2$ can occur, is given by

$$I_c = 2\delta^2 y_{max}^2\,,$$

if $y_{max} < x_{max} > \sqrt{1+\delta^2}\, y_{max}$, and

$$I_c = 2\delta^2 x_{max}^2/(1+\delta^2)$$

if $x_{max} \le y_{max}$ or $y_{max} < x_{max} \le \sqrt{1+\delta^2}\, y_{max}$.

It is seen that I_c is small compared with the average value of I.

Greatest value of $\Delta I/I$

For $I > I_c$, $(\Delta I/I)$ does not possess a maximum and in this we shall investigate the greatest value taken by $(\Delta I/I)$ when x, y and φ are varied continuously over the entire range of permissible values such that

$$I = \tfrac{1}{2}[|F(H)|^2 + |F(\bar{H})|^2] = (1+\delta^2)y^2 + x^2 + 2xy\cos\varphi$$

is a chosen constant.

Let us first consider the case $y_{max} < x_{max} > \sqrt{1+\delta^2}\, y_{max}$. The reason for considering this condition will become clear later. (1) can be rewritten as follows: