12, 14a, 14b, and 21 (Table 4), forty-eight of the original ninety-six icosahedra around Al(7) have been lost (50% occupancy), and eight icosahedra (8a) have been added. There is accordingly a gain of forty-eight icosahedra per unit of structure, and the apparent requirement of having about half the vertices occupied by magnesium atoms and the other half by aluminum atoms is fulfilled through the splitting of the atoms Mg(11) and Al(14) into the pairs Mg(11)–Al(12) and Mg(13)–Al(14) respectively. While the idealized ordered model* contains 280 Friauf polyhedra, 624 icosahedra, and 288 more-or-less irregular polyhedra, the disordered atomic arrangement corresponds to 252 Friauf polyhedra, 672 icosahedra, and 244 more-or-less irregular polyhedra of ligancy 10 to 16, of which 48 are modified Friauf polyhedra.

No definite statement can be made whether the disorder is static or dynamic.

Another interesting feature of this structure is the pronounced tendency towards the formation of five-fold axes, not only those of the icosahedra, but also those of the VF polyhedra. This striving towards pentagonality is also reflected in the Fourier section shown in Fig. 1.

I thank Professor Linus Pauling for his great interest in this work and Dr R. Marsh for valuable sug-

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* The structure of NaCd₂ contains 624 icosahedra instead of 528 as was erroneously stated in the paper of Samson (1962); the atoms 96g₅ in Table 1 of that paper have icosahedral coordination.

gestions in preparing the manuscript. I am grateful to Dr R. Marsh, Dr N. Webb, Mr D. J. Duchamp and Mr A. Kendig for providing the IBM 7094 programs. Mr K. Christiansson and Mrs B. Christiansson carried out most of the experimental work and data collection. I am especially grateful for their successful efforts to prepare the single crystals. Mr K. Christiansson prepared the drawings for Figs. 11 to 17. I also thank Professor Gunnar Hägg (University of Uppsala) for supplying me with detailed drawings of the Guinier–Hägg camera.

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Neutron Diffraction Study of Chemical Order-Disorder in PtMn₃*

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A neutron study of the chemical order-disorder in PtMn₃ was made by utilizing the nuclear properties of Mn and Pt nuclei. The $b_{Mn} = -0.36 \times 10^{-12}$ cm and the $b_{Pt} = 0.95 \times 10^{-12}$ cm. In a disordered crystal structure of the stoichiometric PtMn₃ alloy, the manganese atoms scatter thermal neutrons 180° out of phase with those of platinum. As a result the structure becomes a nuclear null-matrix, and no diffraction peaks appear in its neutron pattern; however, when even a partial ordering takes place in the structure, diffraction peaks do appear in the pattern, and since their intensities depend upon the degree of ordering, they permit a precise determination of the disorder parameter. Numerical values of the disorder parameter of an ordered and a disordered sample of PtMn₃ were determined. The technique of using a nuclear null-matrix to study chemical order-disorder phenomena is described.

Introduction

The crystal structure of the PtMn₃ alloy is cubic with 4 atoms per unit cell and $a_0 = 3.84$ Å. It is similar to

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that of AuCu₃ which has been extensively used to study order-disorder phenomena for this type of structure. The main feature of the X-ray diffraction pattern of the disordered state is that only the all-odd and all-even Miller-index reflections appear, whereas in the ordered state, in addition to the above reflections, mixed Miller indices or the so-called 'super-structure' reflections appear. This follows from the fact that the structure factor for the disordered state is

$$|Fhkl| = \left(\frac{f_{Pt}+3f_{Mn}}{4}\right)\{1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\};$$

$$(1)$$

and for the ordered state, in which, say, 1 Pt is at $(0,0,0)$ and 3 Mn at $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$,

$$|F_{hkl}| = f_{Pt} + f_{Mn}\{e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\}, \quad (2)$$

where f_{Pt} and f_{Mn} are X-ray scattering factors of platinum and manganese respectively. In the case of neutron structure factors f_{Pt} and f_{Mn} are replaced by coherent nuclear scattering amplitudes b_{Pt} and b_{Mn} respectively. The X-ray and neutron structure factors squared are as given in Table 1.

It is apparent from these values that the X-ray diffraction patterns of the disordered and the ordered states of the alloy would give normal reflections for this type of structure. Neutron diffraction patterns, however, would be unique. The coherent nuclear scattering amplitude of elementary manganese for thermal neutrons is $b_{Mn} = -0.36 \times 10^{-12}$ cm, and of platinum, $b_{Pt} = 0.95 \times 10^{-12}$ cm. The structure of the disordered alloy is one of a typical face-centered cubic nuclear null-matrix, in which the nuclei of manganese atoms scatter thermal neutrons 180° out of phase with those

of platinum, and thereby reduce the resultant scattering amplitude,

$$b_n = p_{Pt}b_{Pt} + p_{Mn}b_{Mn}, \quad (3)$$

to a negligible value and the structure factor squared values for all reflections to practically zero. Here p_{Pt} and p_{Mn} are fractions of all sites occupied by platinum and manganese respectively. For an ordered sample the structure factor squared values for all-odd and all-even Miller-index planes are also practically zero. Only the mixed-Miller-index planes give diffraction peaks. Since these reflections result only when ordering takes place in the sample and their intensities depend upon the degree of ordering, these properties were utilized to study order-disorder phenomena in the PtMn₃ alloy.

Experimental procedure

The PtMn₃ samples were prepared from pure platinum and manganese metals in 1 to 3 molar ratio. Pieces of metals were placed at the bottom of a long vertical quartz tube and melted by induction heating under argon gas atmosphere. The melting temperature was approximately 1250–1300 °C. To obtain a homogeneous alloy successive remelting was done at a temperature

Table 1. *Structure factors squared for* PtMn₃

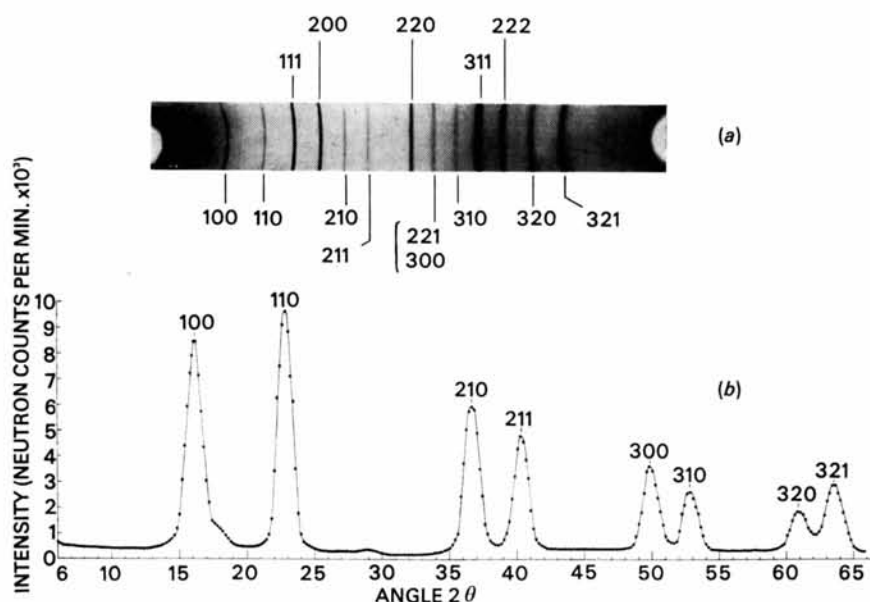| State	Miller indices	For X-rays $\lvert F_{hkl}\rvert^2$	For neutrons $\lvert F_{hkl}\rvert^2 \times 10^{24}$ cm²
Disordered	(a) hkl all odd and all even	$(f_{Pt}+3f_{Mn})^2$	0·017
	(b) hkl mixed	0	0
Ordered	(a) hkl all odd and all even	$(f_{Pt}+3f_{Mn})^2$	0·017
	(b) hkl mixed	$(f_{Pt}-f_{Mn})^2$	1·716

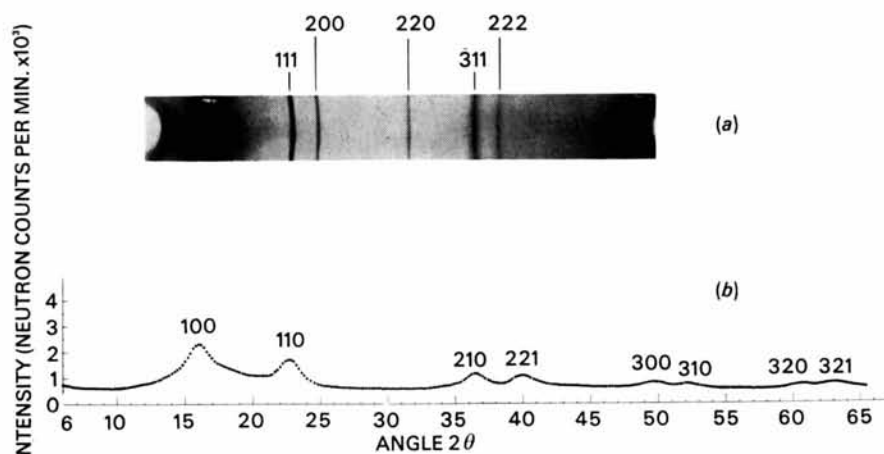Fig. 1. Diffraction patterns of ordered PtMn₃. (a) Filtered Fe radiation, (b) neutron, $\lambda = 1.08$ Å.

Fig. 2. Diffraction pattern of disordered PtMn$_3$. (a) Filtered Fe radiation, (b) neutron $\lambda = 1\cdot08$ Å.

a few degrees above the melting point of the alloy and the final melt in each case was allowed to cool in the tube under increased flow of argon. The samples prepared this way were found to be ordered. A sample which appeared to be disordered when examined with X-rays consisted of filings smaller than 120 mesh. The chemical composition of the ordered sample used in this investigation was 74·5 at.% Mn and 25·5 at.% Pt, and of the disordered sample, 73·8 at.% Mn and 26·2 at.% Pt.

Results

The X-ray and neutron diffraction patterns of the ordered state of PtMn$_3$ at room temperature are shown in Fig. 1. The X-ray diffraction pattern consists of reflections from all-odd and all-even Miller-index planes as well as from the mixed-Miller-index planes. In contrast, as mentioned above, the neutron pattern consists primarily of reflections from the mixed-Miller-index planes; the presence of weak intensity peaks at 2θ values of approximately 18° and 29° is due to magnetic ordering which will be treated separately. The neutron pattern of the sample which appeared to be disordered when examined with X-rays (Fig. 2) shows weak intensity reflections of mixed Miller indices planes, indicating that the sample is partly ordered.

The degree of disorder was determined by measuring the disorder parameter, γ, for each sample. If the atomic positions in the unit cell of PtMn$_3$ were occupied as given in Table 2,

Table 2. *Occupancy of positions in unit cell*

	0, 0, 0	$\frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}$	Total
Pt	$1-\gamma$	γ	1
Mn	γ	$3-\gamma$	3

in which γ is the fraction of Pt atoms that change sites, the structure factor for the partly ordered alloy is then:

$$|F_{hkl}| = \{(1-\gamma)b_{\mathrm{Pt}} + \gamma b_{\mathrm{Mn}}\} + \frac{1}{3}\{\gamma b_{\mathrm{Pt}} + (3-\gamma)b_{\mathrm{Mn}}\}$$
$$\{e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\} . \quad (4)$$

For mixed-Miller-index planes the expression (4) becomes:

$$|F_{hkl}| = (1 - \tfrac{4}{3}\gamma)(b_{\mathrm{Pt}} - b_{\mathrm{Mn}}) . \quad (5)$$

For a completely ordered sample, $\gamma = 0$, and

$$|F_{hkl}| = b_{\mathrm{Pt}} - b_{\mathrm{Mn}} \quad (6)$$

and for a completely disordered sample, $\gamma = \frac{3}{4}$, and

$$|F_{hkl}| = 0 . \quad (7)$$

The $|F_{hkl}|$ values as a function of γ are given in Fig. 3.

The experimental values of $|F_{hkl}|$ factors for the disordered and the ordered samples of PtMn$_3$ were obtained from measured integrated intensities of a number of diffraction peaks in the neutron pattern of each sample. The expression used for the integrated intensity, P_{hkl}, for a powdered cylindrical sample was:

$$P_{hkl} = K^2 \left(N_c^2 \frac{\varrho'}{\varrho_0} \right) \left(\frac{A(\theta)}{\sin\theta\,\sin 2\theta} \right) j_{hkl}\, F_{hkl}^2(0)$$
$$\exp.\left[-2\beta \frac{\sin^2\theta}{\lambda^2} \right] \quad (8)$$

(Sidhu, Heaton & Mueller, 1959), where K is a constant of the experiment and includes the geometry of the spectrometer, the intensity of the incident beam,
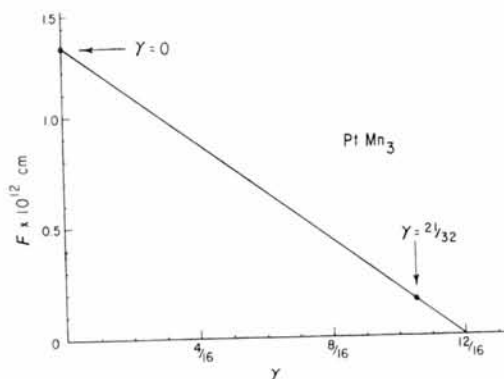

Fig. 3. Structure factor $|F|$ as a function of disorder parameter (γ).

the neutron wavelength and the volume of the specimen in the beam. The term $[N_c^2\,(\varrho'/\varrho_0)]$ is a constant for a particular specimen, N_c being the number of unit cells per cubic centimeter and ϱ'/ϱ_0 the ratio of the measured density, ϱ', of the specimen to the density ϱ_0 which was calculated from the atomic weights of the elements composing the crystal and its known crystal structure. In the term $[A(\theta)/\sin\theta\sin 2\theta]$, θ is the Bragg angle and $A(\theta)$ is the absorption correction factor, and is a function of μr, where μ is the linear absorption coefficient of the substance and r the radius of the sample. A value for μr was obtained for each sample by measuring the decrease in intensity of the nickel 111 reflection in passing through the sample. This beam was defined by placing a small, narrow cadmium slit, 1×20 mm in front of the detector. The μr was then evaluated according to the expression:

$$N'/N_0 = e^{-2^u}r \qquad (9)$$

where N' and N_0 are the number of counts with and without the sample in the beam. Corresponding to the values of μr thus determined, the values of $A(\theta)$ were taken from *International Tables for Determination of Crystal Structures* (1935). The other factors are j_{hkl}, the multiplicity factor, $F_{hkl}(0)$, the structure factor when $\sin\theta/\lambda = 0$ and $\exp(-2\beta\sin^2\theta/\lambda^2)$, the Debye–Waller temperature factor.

The measured integrated intensity was put on an absolute basis by rewriting the expression (8) as follows:

$$M_{hkl}^2 = \frac{\varrho_0}{\varrho'}\,\frac{\sin\theta\sin 2\theta\,P_{hkl}}{N_c^2 j_{hkl}A(\theta)}$$
$$= K^2 F_{hkl}^2\,(0)\exp(-2\beta\sin^2\theta/\lambda^2) \qquad (10)$$

or

$$M_{hkl} = KF_{hkl}(0)\exp\,(-\beta\sin^2\theta/\lambda^2)$$

and

$$\ln M_{hkl} = \ln KF_{hkl}(0) - \beta\sin^2\theta/\lambda^2 \,.$$

K was determined for the standard nickel sample by substituting the measured values of the factors included in M_{hkl}, and then determining the value of $\ln KF(0)$ by both the graphical and the least-squares methods. The experimental value of $KF(0)$ thus obtained was equated to $K \times 4b_{Ni}$ where b_{Ni} is the known value, 1.03×10^{-12} cm, and the numerical value for K was thus obtained. The numerical values of the structure factors for the

disordered and the ordered alloys of PtMn₃ were obtained by dividing the experimental values of $KF(0)$ by the K value obtained from the standard sample. The measured factors used in determining γ and its numerical values are given in Table 3.

Table 3. *Measured factors used in determining γ*

	Ni	PtMn₃	
		Ordered	Disordered
$a_0(\text{Å}^{-1})$	3·52	3·84	3·85
ϱ_0/ϱ'	2·639	1·798	3·183
$N_c(10^{-22})$	2·285	1·766	1·752
μr	0·229	0·162	0·096
$K(10^{12})$	514·5	514·5	514·5
$F(0)$ $(10^{12}\,\text{cm}^{-1})$	4·12	1·31	0·15
γ	—	0	0·667

The Debye-Waller temperature factor was taken as unity for $F(0)$.

Summary

The use of a nuclear null-matrix to study order-disorder phenomena is a unique technique. As long as the atoms which make up the null-matrix remain randomly distributed on lattice sites, no coherent diffraction peaks appear in its diffraction pattern. But when even a partial ordering of the atoms takes place, diffraction peaks characteristic of the ordering in a given null-matrix material begin to appear. For example, when a face-centered cubic nuclear null-matrix orders, reflections only from the mixed-Miller-index planes appear. Another interesting feature of this investigation is *that for crystal structures in which the null-matrix atoms occupy face-centered cubic sites, i.e. (0, 0, 0), $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$, $(0,\frac{1}{2},\frac{1}{2})$, that part of the structure factor which results from the distribution of these atoms is zero for all-odd and all-even Miller-index reflections whether these atoms occupy ordered sites or are randomly distributed.*

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International Tables for Determination of Crystal Structures (1935). Berlin: Gebrüder Borntraeger.