where $G = g(\nu)/4\hbar^2$ and the C's are given by

$$C_{1,2} = \pm D g_\perp^2 \sin^2\theta\, R_\pm((S\pm M-1)(S\mp M+2))^{1/2}/8g^2(g\beta H+2b(M\mp 1)+am) \quad (20)$$

$$C_{3,4} = \pm R_\pm r_+(c\mp B)/4(g\beta H+b(2M\mp 1)+a(m-1\pm M)) \quad (21)$$

$$C_{5,6} = \pm g_\perp g_\parallel \sin\theta\cos\theta R_\pm(m(B-A)-D(2M\mp 1))/2g^2(g\beta H+b(2M\mp 1)+am) \quad (22)$$

$$C_{7,8} = \pm R_\pm r_-(C\pm B)/4(g\beta H+b(2M\mp 1)+a(m+1\mp M)) \quad (23)$$

$$C_{9,10} = \pm g_\perp g_\parallel \sin\theta\cos\theta\, r_\pm(B-A)/2ag^2 \quad (24)$$

where the upper sign out of $\pm$ or $\mp$ goes with the first C and the lower one with the second C. Prime over any of the C's in an expression for $W(M,m \leftrightarrow M+i,m+j)$ indicates a change of M to $M+i$ and m to $m+j$ in the expression for the corresponding unprimed C.

The above results represent a generalisation for arbitrary orientation, of similar results reported earlier[1] in literature and reduce to them in the appropriate limits.

From equations (13) and (17) it can be seen that zerofield splitting does not affect the probabilities of the allowed transitions of the type $|\Delta M| = 1$, $\Delta m = 0$, whereas it is mainly responsible for transitions of the type $|\Delta M| = 2$, $\Delta m = 0$. It can also be seen that

$$W(M,m \leftrightarrow M+2,m)/W(m,m \leftrightarrow M+1,m) \sim (D/g\beta H)^2 \quad (25)$$

$$W(M,m \leftrightarrow M+1,m+1)/W(M,m \leftrightarrow M+1,m) \sim W(M,m \leftrightarrow M+1,m-1)/W(M,m \leftrightarrow M+1,m) \sim (A,B/g\beta H)^2. \quad (26)$$

Thus $|\Delta M| = 2$, $\Delta m = 0$ transitions can be induced at almost the same rate as the first order forbidden transitions in the specimens in which zero-field splitting is comparable with the hyperfine splitting. Saturation of the allowed transitions by microwave pumping (Overhauser effect) has been frequently used to enhance nuclear polarisation and NMR absorption, the general expressions for which in the case of paramagnetic crystals have already been published by the authors[4]. By a similar calculation it has been found that the same degree of dynamic nuclear polarisation is obtained by saturating the $|\Delta M| = 2$, $\Delta m = 0$ transitions. The samples having a large zero-field splitting could therefore also be dynamically polarised by pumping at double the frequencies of the allowed transitions.

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REFERENCES

1. JEFFRIES C. D., *Dynamic Nuclear Orientation*, Chapter 2, Interscience, New York (1963).
2. GUPTA S. K. and NARCHAL M. L., *Phys. Rev. B* **2**, 1405 (1970).
3. GUPTA S. K. and NARCHAL M. K., *Prog. Theor. Phys.* **44**, 1 (1970).
4. SUKHEEJA B. D. and NARCHAL M. L., *J. chem. Phys.* **52**, 5230 (1970).

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New antiferromagnetic intermetallic compound in the Mn-Pd system: $MnPd_2$

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IN THE Mn-Pd system around the $MnPd_3$ composition a one-dimensional long-period superlattice, based on the Cu_3Au type order with periodic antiphase domains, was observed[1–3]. This phase has a simple collinear antiferromagnetic structure[1] with magnetic moment directions depending on concentration and atomic order[3–4]. In the 30–36 at.% Mn interval, on long annealing below 600°C, the X-ray diffraction measurements of Raub and Mahler[5] showed a new phase the crystal structure of which was not determined but which was assumed to be a superstructure based on a face-centred tetragonal unit cell with a probable orthorhombic distortion. The existence of this phase was confirmed by others[2, 6] but no data can be found concerning its magnetic properties.

In order to determine the crystal and magnetic structure of the phase observed by Raub and Mahler[5] in the Mn–Pd system between 30–36 at.% Mn, a neutron diffraction study was carried out on a sample belonging to this concentration interval.

The sample was prepared from 99·9 per cent purity metals by melting in an induction furnace under argon atmosphere. The ingot was powdered then sealed in an evacuated quartz tube. To obtain the superstructure indicated by Raub and Mahler[5] the powder was annealed successively for 1 day each at 900 and 800°C, for 3 days each at 700, 600 and 500°C, for 7 days at 450°C, then slowly cooled down to room temperature. The composition was checked by chemical analysis and the value of 32·1 at.% Mn was obtained.

The neutron diffraction measurements were carried out in the 77–1100°K temperature range. Neutrons with a wavelength of 1·14 Å were used. In addition, an X-ray diffraction Guinier photograph was taken at room temperature.

The strongest reflections in the X-ray diffraction photograph are associated with a slightly distorted face-centred tetragonal unit cell with $a_0 \simeq 3{\cdot}84$ Å, $c_0 \simeq 4{\cdot}03$ Å and $c_0/a_0 = 1{\cdot}05$. The very weak super-reflections correspond to an orthorhombic cell with $a = 5{\cdot}460\ \text{Å} \simeq (2/\sqrt{2})a_0$, $b = 4{\cdot}029\ \text{Å} = c_0$ and $c = 8{\cdot}127\ \text{Å} \simeq (3/\sqrt{2})a_0$. This orthorhombic unit cell contains three tetragonal cells and thus 12 atomic sites.

All neutron diffraction reflections at 77°K can be indexed in the orthorhombic unit cell. The temperature dependence of the reflections indicates that part of the reflections are magnetic in origin and it yields $T_N = 415 \pm 10$°K. Consequently, the crystal structure was determined from a neutron diffraction pattern taken in the paramagnetic phase at 450°K.

Several extinction rules, the most striking of which is the absence of reflections ($h00$), ($0k0$), ($00l$) and $0kl$) when h, k, l or $k+l$ are odd, were observed in the X-ray and nuclear neutron diffraction patterns. Considering that this structure occurs between 30 and 36 at.% Mn, a crystal structure model with $MnPd_2$ composition, shown in Fig. 1, can be constructed consistently with the observed extinction rules. The study of the symmetry shows this model to belong to the orthorhombic space group *Pnma* with atoms occupying the 4(c) positions. The 4(c) positions in the space group *Pnma* have the coordinates

$$x, \tfrac{1}{4}, z; \bar{x}, \tfrac{3}{4}, \bar{z}; \tfrac{1}{2}-x, \tfrac{3}{4}, \tfrac{1}{2}+z; \tfrac{1}{2}+x, \tfrac{1}{4}, \tfrac{1}{2}-z.$$

In the model of Fig. 1, based on the face-centred tetragonal unit cell, the values of the position parameters are $x = \frac{1}{8}$, $z = \frac{1}{12}$ for the Mn atoms, $x = \frac{1}{8}$, $z = \frac{5}{12}$ for one kind of Pd atoms, and $x = \frac{1}{8}$, $z = \frac{3}{4}$ for the other Pd atoms.

Calculating the neutron intensities for the model of Fig. 1 and comparing them with those measured at 450°K, there is no satisfactory agreement, as seen in columns A of Table 1. However, on changing slightly some of the atomic position parameters, a good agreement can be obtained between the calculated and measured intensities using $x = 0{\cdot}150$, $z = 0{\cdot}095$ for the Mn sites, $x = 0{\cdot}150$, $z = 0{\cdot}417$ for Pd_I and $x = 0{\cdot}150$, $z = 0{\cdot}750$ for Pd_{II} sites, as seen in columns B of Table 1. We assumed in the calculation that the excess Pd atoms which are present at this non-stoichiometric composition occupy the Mn

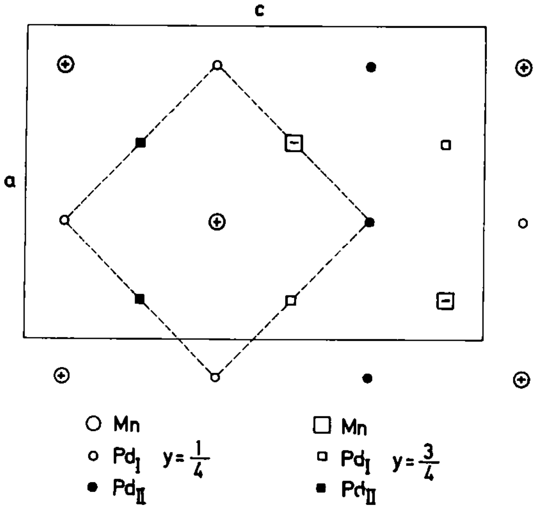

Fig. 1. Crystal and magnetic structure of the $MnPd_2$ phase, projected on the plane (010). The nearly tetragonal subunit is shown by the dashed line.

sites at random. For the scattering amplitudes $b_{Mn} = -0{\cdot}36$ and $b_{Pd} = 0{\cdot}59$ were used. The realiability factor is 5 per cent. The above data suggest that the values of the atomic position parameters (or at least some of them) must differ from those for an 'ideal' cell based on the face-centered tetragonal unit cell. However, the accuracy of the powder neutron diffraction measurements does not permit to establish a unique set of the six atomic position parameters. The values given above represent a possible solution in which all atoms are equally displaced from the 'ideal' position to the x direction and there is a small additional shift of the Mn atoms to the z direction.

The neutron diffraction pattern at 77°K indicates an ordered magnetic structure in which the unit cells of the crystal and magnetic structures coincide. The observed magnetic reflections are compatible with the model shown in Fig. 1 in which the magnetic moments of the Mn atoms are parallel in the (010) planes and the successive planes are coupled antiferromagnetically. As inferred from the absence of the magnetic reflection (010), the magnetic moments are parallel to axis **b**. The comparison of the measured and calculated intensities in columns B of Table 1 shows a good agreement for 77°K, too. For

Table 1. Neutron intensities as measured at 77 and 450°K and as calculated for the crystal and magnetic structures of Fig. 1(A) with the 'ideal' atomic position parameters and (B) with the parameters given in the text. The values are given in barns

	F^2_{hkl} (calculated)						F^2_{hkl} (measured)	
	magnetic		nuclear		total			
hkl	A	B	A	B	A	B	77°K	450°K
001	3·97	5·02	—	—	3·97	5·02	5·3±0·4	< 0·4
101	4·86	5·80	4·97	3·33	9·83	9·13	9·3±0·6	3·1±0·3
002	—	—	3·31	2·70	3·31	2·70	2·3±0·5	2·6±0·5
010	—	—	—	—	—	—	< 0·5	< 0·5
011	—	—	3·31	3·62	3·31	3·62	3·8±0·3	3·8±0·3
102	3·83	3·05	4·97	6·82	8·80	9·87	9·6±0·5	7·0±0·4
111	1·51	0·95	4·97	6·31	6·48	7·26	6·7±0·6	6·2±0·4
012	1·08	0·59	—	—	1·08	0·59	2·0±1	< 0·5
003	8·18	7·79	—	—	16·36	16·32	15·8±1	< 1·7
200	8·18	7·40	—	1·13				
201	—	0·22	3·31	3·28	3·31	3·50	2·8±1	3·5±0·5
112	1·67	2·52	4·97	3·60	6·64	6·12	6·3±0·5	4·0±0·6
103	—	0·21	—	0·02	—	0·23	< 0·8	< 0·8
202	1·48	0·73	—	0·26	25·14	24·12	24·2±2	23·4±3
210	—	0·38	11·83	10·70				
013	—	—	11·83	12·05				

the calculated intensities $\mu_{\mathrm{Mn}} = 4{\cdot}0\,\mu_B$ and the experimental form factor of Mn[7] was used; the magnetic moment on the Pd atoms was assumed to be negligible.

During heating of the sample in a neutron diffraction furnace, the $\mathrm{MnPd_2}$ phase can be observed up to 980°K. Above this temperature the reflections of the $\mathrm{MnPd_2}$ phase rapidly disappear. The neutron diffraction pattern taken at 77°K on the sample quenched from 1100°K corresponds to the antiphase domain structure observed earlier in the 23–30 at.% Mn concentration interval[1–3].

The intermetallic compounds $\mathrm{APd_2}$ with A = Ga, Al, In, Sn, Zn also have an orthorhombic crystal structure with space group *Pnma*[8]. In this structure, denoted as C23, the atoms occupy the 4(c) positions, like in $\mathrm{MnPd_2}$. The values of the atomic position parameters, however, differ considerably from those established for $\mathrm{MnPd_2}$, thus the nearly tetragonal subunit becomes unrecognizable.

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REFERENCES

1. CABLE J. W., WOLLAN E. O., KOEHLER W. C. and CHILD H. R., *Phys. Rev.* **128**, 2118 (1962).
2. SATO H. and TOTH R. S., *Phys. Rev.* **139**, A1581 (1965).
3. KRÉN E. and KÁDÁR G., *Phys. Lett.* **29A**, 340 (1969).
4. KRÉN E., KÁDÁR G. and PÁL L., *J. appl. Phys.* **41**, 941 (1970).
5. RAUB E. and MAHLER W., *Z. Metallk.* **45**, 430 (1954).
6. KJEKSHUS A., MØLLERUD R., ANDRESEN A. F. and PEARSON W. B., *Phil. Mag.* **16**, 1063 (1967).
7. CORLISS L. M., ELLIOTT N. and HASTINGS J. M., *Phys. Rev.* **104**, 924 (1956).
8. PEARSON W. B., *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 2, Pergamon Press, Oxford, London and New York (1967).

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Hydrogen bond studies.

51. Dynamics of the methylammonium ion in solid methylammonium chloride. A proton magnetic relaxation study*

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1. INTRODUCTION

SOLID methylammonium chloride exists in at least three different forms as shown by thermal [1] and i.r. spectroscopic[2–4] data. The α-form is stable above 264°K and has a tetragonal structure[5] with the four-fold symmetry axis coinciding with the *C-N* bond axis. This symmetry is obviously incompatible with the geometry of the methylammonium ion, unless the structure is disordered or otherwise the methylammonium ion reorients rapidly about the *C-N* axis. The γ-phase, stable in the temperature range 264–220°K and the β-phase, stable below 220°K, both have unknown crystal structures. Some aspects of the dynamic behaviour of the methylammonium ion in this compound have recently been investigated by Tsau and Gilson[6] using proton magnetic resonance line-width data. However, the line width is only sensitive to molecular reorientations within a narrow frequency range. For this reason the line-broadening observed on cooling occurs almost entirely in the β-phase, and very little information concerning the α- and γ-phases is provided by the line-width data. In order to learn more about the nature of the molecular reorientations in the various phases of methylammonium chloride, the present authors have measured the temperature dependence of the proton spin-lattice relaxation time in

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