Fig. 2. Typical standard curve for amounts of ascorbic acid between 0.4 and 4 μg, obtained with a 5 cm cell.

Equiatomic Transition Metal Alloys of Manganese

VII. A Neutron Diffraction Study of Magnetic Ordering in the IrMn Phase

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vitamin C in dried feed stuffs down to approximately 0.1 μg/g.[5]

The modifications described in the present paper make it possible for one person to determine readily the ascorbic acid content of some 50 — 60 samples (150 — 180 tubes) per day.

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The purpose of the protracted research program of which the work described in this paper forms a part is to elucidate the structural and magnetic properties of transition metal phases with the CsCl and CuAu(I) types of crystal structures, especially in relation to the sizes and valences of the component atoms. The investigations [1-6] have hitherto been limited to alloys of manganese in combination with another transition element (Rh, Ir, Ni, Pd, Pt, or Au), since essentially ordered arrangements of the CsCl and CuAu(I) types are found to be stable over considerable ranges of composition and temperature in the equiatomic regions of these alloy systems. An advantage of studying these phases is that the second component has generally a very small or zero moment, which simplifies the interpretation of the magnetic data and has allowed a tentative bonding scheme to be suggested [4-6] for the phases NiMn, PdMn, and PtMn. The RhMn and IrMn phases provide further possibilities for testing and adjusting the proposed model, but most of the previous data [2,7-11] are unsuitable for this purpose. In order to obtain a partial remedy to this situation the neutron diffraction study of the IrMn phase reported here was undertaken, and the results of a detailed study of the cubic and tetragonal RhMn phases will be presented in a forthcoming paper.

Three alloys with intended compositions 45, 49, and 53 atomic % Ir were prepared from 99.9 % pure Ir (Johnson, Matthey & Co., Ltd.) and electrolytic 99.9+ % pure Mn (Johnson,

Table 1. Comparison of observed and calculated neutron diffraction data (at room temperature).

Reflection		$Ir_{44}Mn_{56}$		$Ir_{49}Mn_{51}$	
hkl	Type	$jF_o{}^2$	$jF_c{}^2$	$jF_o{}^2$	$jF_c{}^2$
100	Magn.	3.5	3.60	4.3	4.28
001	Nucl.	12.5	12.50	15.5	15.46
110	Nucl.	23.5	25.00	29.8	30.92
101	Magn.	7.3	7.30	8.3	8.64
111	Nucl.	8.6	8.96	15.4	14.40
200	Nucl.	4.2	4.48	7.8	7.20
002	Nucl.	2.4	2.24	3.8	3.60
210	Magn.	49.3	{ 1.56	59.6	{ 1.85
201	Nucl.		{ 50.00		{ 61.84
102	Magn.	2.5	2.49	3.5	2.94
211	Magn.	2.8	2.78	3.8	3.28
112	Nucl.	49.1	50.00	59.7	61.84
220	Nucl.	4.9	4.48	8.0	7.20
202	Nucl.	8.9	8.96	15.9	14.40
300	Magn.	46.7	{ 0.23	55.4	{ 0.27
221	Nucl.		{ 50.00		{ 61.84
212	Magn.	0.0	1.12	0.0	1.36
310	Nucl.		{ 50.00		{ 61.84
003	Nucl.	58.9*	{ 12.50	67.5*	{ 15.46
301	Magn.		{ 0.35		{ 0.42
103	Magn.	23.2*	{ 0.50	29.5*	{ 0.55
311	Nucl.		{ 17.92		{ 28.80
113	Nucl.	9.6	8.96	12.4	14.40
222	Nucl.	9.4	8.96	13.9	14.40
320	Magn.	0.0	0.19	0.0	0.23
302	Magn.	0.0	0.26	0.0	0.31
203	Nucl.	43.6	{ 50.00	58.8	{ 61.84
321	Magn.		{ 0.36		{ 0.43
312	Nucl.	99.4	100.00	117.6	123.68

* The contribution from the empty sample holder is subtracted.

Matthey & Co., Ltd.; H_2 treated at 950°C for 5 h) by heating weighed quantities of the mixed components in evacuated silica tubes for 3 days at 800°C. The sintered powders were ground and reannealed at 950°C for another 3 days and then quenched in water without shattering the enclosing silica capsules. The X-ray and neutron diffraction data for the two Ir-poor alloys confirmed that they were homogeneous, and of the desired CuAu(I) type structure, whereas the Ir-rich alloy proved to contain the Ir and $IrMn_3$ phases in addition to various compositions of the IrMn phase. It was found to be impossible to homogenize this and a subsequent 53 atomic % Ir sample, despite the use of a variety of heat treatments (500—1000°C). In view of the previous success [2] in synthesizing small amounts of corresponding

Ir-rich alloys, the present difficulties are attributed to the increased sample size. Chemical analysis of both components established the compositions of the two usable alloys as 44.2 and 48.8 atomic % Ir; no insoluble oxide was found and the analytical totals were 99.93 and 99.99 %.

The X-ray diffraction data showed that the structures of the two alloys are of the CuAu(I) type with essentially complete primary interlayer order and without any secondary intralayer order on the mixed Ir/Mn sites. The dimensions of the primitive chemical unit cells at room temperature are $a_C = 2.720 \pm 0.001$ Å, $c_C = 3.666 \pm 0.002$ Å and $a_C = 2.726 \pm 0.001$ Å, $c_C = 3.644 \pm 0.002$ Å for $Ir_{44}Mn_{56}$ and $Ir_{49}Mn_{51}$, respectively, consistent with the data previously published.[2]

Neutron diffraction diagrams were obtained using neutrons of wavelength $\lambda = 1.186$ Å from the JEEP II reactor. Due to the high absorption cross-section of iridium [12] for thermal neutrons a rectangular shaped, 3 mm thick sample holder of thin-walled aluminium was used. (The use of a flat sample holder was found to give considerable improvement in intensity and resolution over a cylindrical one.) The transmission through the samples was determined to be $\exp(-\mu t) = 0.44$ for both alloys. The integrated intensities were corrected for absorption and converted to jF_0^2 by multiplication with L^{-1}.

The neutron diffraction patterns were readily indexed in terms of C-centred cells with $a_M = \sqrt{2}a_C$, $c_M = c_C$, the nuclear $(h+k=2n)$ and magnetic $(h+k=2n+1)$ reflections being generally well separated (Table 1). This is consistent with the corresponding data [4-6,11,13-19] for the chemically isostructural RhMn, NiMn, PdMn, and PtMn phases. Since rather few compounds and alloys containing iridium have been studied with neutron diffraction and the published values for its scattering length show great variation, it was considered of interest to derive a value for b_{Ir} from the present data. Using the commonly accepted $b_{Mn} = -0.36 \times 10^{-12}$ cm [12,20] and assuming perfect primary CuAu(I) type ordering the value $b_{Ir} = (1.10 \pm 0.05) \times 10^{-12}$ cm was obtained. This value is in violent disagreement with the original figure $(b_{Ir} = 0.36 \times 10^{-12}$ cm) of Sidhu et al.[21] listed in Bacon [12] and International Tables,[20] but within the error limits in agreement with the revised value 1.06×10^{-12} cm.[22] The calculated structure factor data in Table 1 are based on the latter value. The form factor for Mn^{2+} given by Hastings et al.[23] was used to calculate jF_c^2-values for the magnetic reflections.

The magnetic structures of the two alloys are of orthorhombic or lower symmetry, the moments being aligned antiferromagnetically within (001) planes. The spin quantum numbers $2S_{Mn} = 3.4 \pm 0.2$ and $2S_{Mn} = 3.1 \pm 0.2$ were deduced for $Ir_{49}Mn_{51}$ and $Ir_{44}Mn_{56}$, respectively, whereas the Ir atoms were found to be nonmagnetic within the experimental accuracy $(2S_{Ir} < 0.2)$ in both alloys.

The powder neutron diffraction technique leaves the direction of the moments undetermined within the (001) planes. On the basis of the Landau theory for second-order transformations Krén and Sólyom [15] point out that only two possible directions of the moments, i.e. [100] and [110] and equivalent directions of the magnetic cell, can arise from a single second-order transi-

tion between a paramagnetic and an antiferromagnetic state. However, in the case of IrMn transformation to the paramagnetic state occurs above 1200°K, which represents the present limit of our magnetic susceptibility equipment. We have therefore not been able to ascertain whether only a single second-order transition takes place. No limitation can accordingly be set on the direction of the moments within (001). Despite the latter ambiguity it should be noted that the type of first kind of antiferromagnetic ordering in the IrMn phase is very nearly the same as that found for the RhMn,[11] NiMn,[13,17,18] and PdMn,[6,14,15,18] phases and also for the PtMn [4,5,16,18,19] phase depending on composition and temperature.

No evidence for the weak ferromagnetism observed in the magnetic susceptibility measurements [2] or Ir-poor IrMn alloys has been detected in the neutron diffraction data. Thus, this may be attributed either to a so small canting of the antiferromagnetically aligned moments that it cannot be detected with the available experimental accuracy, or to the presence of traces of ferromagnetic impurities, e.g. the IrMn$_3$ phase.

Lacking magnetic susceptibility data at and above T_N it is impossible to carry out a detailed analysis of the exchange interactions in the IrMn phase. However, in consideration of the higher Néel temperatures and smaller spin quantum numbers of the IrMn alloys compared with the NiMn, PdMn, and PtMn phases it seems that the dominant exchange parameter (the direct exchange between nearest-neighbour Mn atoms) has considerably higher numerical values in the IrMn phase than in the three other phases. Pál et al.[18] have suggested that T_N for the equiatomic alloys should decrease with increasing interatomic distance between the nearest-neighbour Mn atoms. The IrMn phase obviously falls outside this scheme since T_N decreases in the sequence IrMn, NiMn, PtMn, and PdMn, whereas the shortest Mn-Mn distance increases in the sequence NiMn, IrMn, PtMn, and PdMn. However, the major discrepancy in their proposal is that it neglects the contributions of the indirect exchange interactions, the importance of which appears from the difference between the PdMn and PtMn phases.[4-6]

The ~ 3.5 unpaired electrons per Mn atom at the equiatomic composition of the IrMn phase and the decreasing number of

unpaired electrons with increasing Mn concentration indicate that the overall features of the simple chemical bond scheme previously proposed [4-6] are essentially correct. The reduction from 4.0 unpaired electrons per Mn atom in the equiatomic NiMn, PdMn, and PtMn alloys to $\sim$ 3.5 in the case of IrMn presumably reflects the lowering of the Fermi level resulting from Ir having one valence electron less than Ni, Pd, and Pt.

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N,N'-Diphenyldithiocarbazic Acid and Some Derived Compounds

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Dithiocarbazates may generally be prepared from hydrazine or substituted hydrazines and carbon disulfide. This method fails, however, when the basicities of both nitrogen atoms in the hydrazine have been lowered by aromatic substituents. We now wish to report on the preparation of sodium *N,N'*-diphenyldithiocarbazate (I) by way of a synthetic method originally devised for the preparation of dithioic acids from carbon disulfide and CH-acidic compounds.[1] In addition, the properties of (I) and of some derived compounds have been investigated.

Compound (I) was obtained in good yield by the joint action of carbon disulfide and sodium hydride on hydrazobenzene in dimethyl sulfoxide solution.

$$C_6H_5NHNHC_6H_5 + CS_2 + NaH \xrightarrow{\text{DMSO}}$$
$$C_6H_5NHN(C_6H_5)CS_2Na + H_2 \quad \text{(I)}$$
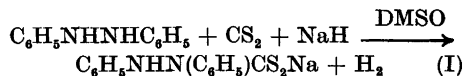
As the reaction between hydrazobenzene and sodium hydride was slow and incomplete, it was found convenient to add carbon disulfide at a rate such that the hydrazobenzene anion which formed was immediately consumed. The progress