

Equiatomic Transition Metal Alloys of Manganese

II. The Tetragonal IrMn Phase

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Lattice parameter, density and magnetic susceptibility measurements are reported for the IrMn phase which has the tetragonal CuAuI type structure, and a range of homogeneity of ~ 15 atomic %. The solid solution is substitutional. The slope of the lattice parameter *versus* composition curves changes sign in the region of equiatomic composition. It is proposed that the IrMn phase exhibits an anti-ferromagnetic arrangement with very high Néel temperature ($> 1150^\circ\text{K}$).

In continuation of our examination of transition metal alloys of manganese occurring in the equiatomic region,¹ we here present data on the tetragonal IrMn phase with the CuAuI type structure. These phases have either the disordered b.c. cubic, the ordered CsCl, or the ordered CuAuI type structure. Sometimes more than one of these structures is found within the same system, depending on the temperature and composition; the disordered phase then occurs at the highest temperatures and the CuAuI type structure at lower temperatures and on the manganese-poor side of the CsCl type structure.

Our particular interest in these phases centres in the different A—A and B—B distances that occur in the ordered CuAuI and CsCl type structures (see Fig. 1) for identical A—B separations when the B atoms, say, are significantly larger than the A atoms.¹ Under these conditions very close B—B approaches are found in the CuAuI type structure, both within the ordered B layers, and between the B and A layers at compositions richer in B than the equiatomic, when there is substitution of B in the A layers. Since the manganese alloys with the CuAuI type structure occur over a range of composition extending on both sides of 50 atomic %, it is interesting to study the effect

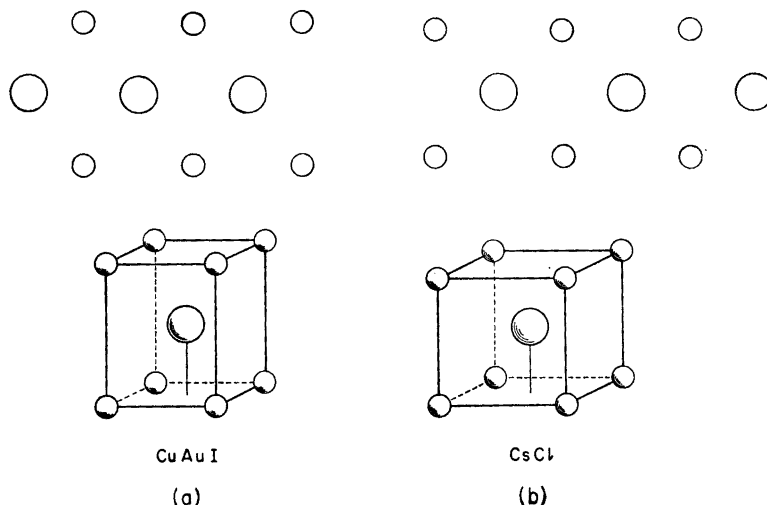


Fig. 1. The structural arrangement of (a) CuAuI (the primitive cell with two atoms is shown) (b) CsCl.

of the intra- and inter-layer, like-neighbour interactions on unit cell dimensions and magnetic properties when the two components have different size.

Raub and Mahler² first reported the structure of the IrMn phase.

EXPERIMENTAL

The alloys, made from 99.9 % pure iridium (Engelhard Industries, Inc.) and deoxidized 99.9+ % pure manganese (Johnson, Matthey & Co., Ltd.), were prepared by heating accurately weighed quantities of the powdered components in evacuated, sealed silica tubes for three days at 800°C. After regrinding, all alloys were annealed at 950°C for three days and finally quenched in water without shattering the enclosing silica capsules.

The compositions of 15 alloys were determined by chemical analysis,* either of both components (first series) or of manganese only (second series). (Two two-phase alloys were not analysed.) The 9 alloys analysed for both components gave analytical totals ranging from 99.84 to 100.13 % with an average deviation of 0.09 % from 100 %. There was no reported insoluble oxide.

X-Ray powder photographs were taken in a 190 mm diameter Unicam camera. Lattice constants, which are expressed in Ångström units on the basis of $\lambda(\text{CuK}\alpha_1) = 1.54050 \text{ \AA}$, were determined from high-angle reflections by a method based on the Nelson-Riley³ extrapolation. Guinier photographs were taken in a camera of 80 mm diameter using strictly monochromatized $\text{CuK}\alpha_1$ -radiation. Potassium chloride (Analar, The British Drug Houses Ltd. $a = 6.2919 \text{ \AA}$) was added to the specimen as an internal standard. Average values of the lattice constants obtained by the two methods were used. The results are less satisfactory than those obtained for the PtMn phase.¹ For example, data collected with the Unicam camera for both series of alloys were self-consistent and closely agreeing when expressed in terms of nominal composition, but differed when expressed in terms of chemically analysed compositions. (This was surprising since both

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series of alloys were prepared in short sealed silica tubes under identical conditions, and there was no apparent loss of manganese due to distillation.)

Densities of the alloys were determined pycnometrically with kerosene as displacement liquid (at 25.00°C). To remove gases adsorbed by the sample, the pycnometer was filled under vacuum with kerosene. The samples weighed 1–1.5 g.

Magnetic susceptibilities of all alloys were measured by the Gouy method (at $H_{\max} = 4015, 4700, \text{ and } 5110 \text{ O}$) between 90 and 725°K. The samples were enclosed in thin-walled silica tubes of about 2 mm internal diameter. These were filled to a height of 85 mm. Magnetic susceptibilities of four representative alloys were also measured by the Faraday method (maximum field used $\sim 7000 \text{ O}$) between 300 and 1150°K on 20–40 mg samples.

RESULTS

The X-ray photographs of the IrMn phase were indexed on tetragonal axes. (The primitive cell (Fig. 1) containing two atoms is used.) The variation in the unit cell dimensions shown in Fig. 2 suggests that this phase has a range of

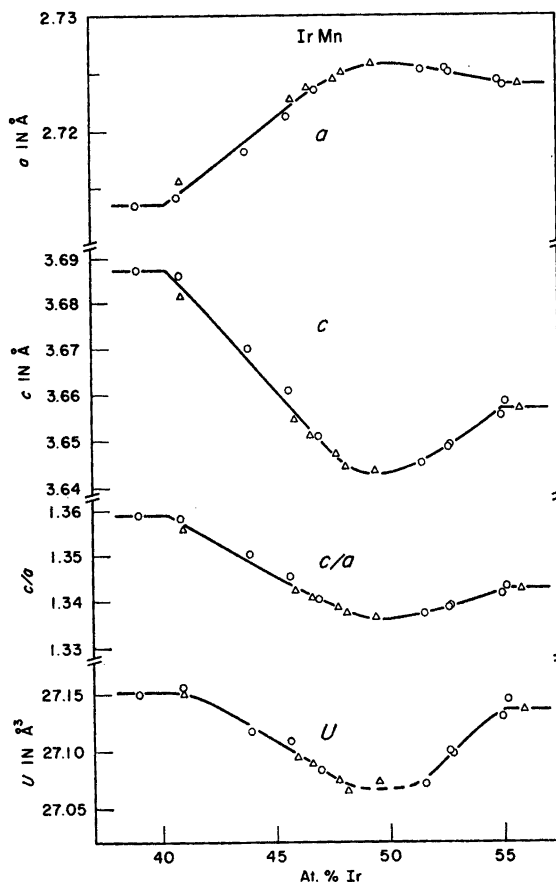


Fig. 2. Variation in lattice constants, axial ratio, and unit cell volume of the IrMn phase as a function of composition. Series I (O), series II (Δ).

homogeneity from ~ 40 to ~ 55 atomic % Ir. As seen from Fig. 2 there is a striking change of slope of the lattice parameters with composition in the equiatomic region. There is a maximum in a and minima in c , c/a , and U at this composition.

The Ir atom is larger than the Mn atom in the IrMn phase, but the difference in sizes is less than that of Pt and Mn in the PtMn phase. (The shortest interatomic distances in the pure metals are (*cf.* Pearson ⁵): $d_{\text{Ir}} = 2.7145 \text{ \AA}$, $d_{\text{Pt}} = 2.7746 \text{ \AA}$.) It is not surprising therefore to find that the unit cell dimensions of the IrMn phase (Fig. 2) change with composition in a manner similar to those of the PtMn phase, but that the relative rates of change with composition are smaller. Only the unit cell volume, U , in the Mn-rich alloys differs, since it decreases with increasing Ir content in the IrMn phase, whereas it increases with increasing content in the PtMn phase.

The solid solution of the IrMn phase is strictly substitutional on both sides of the equiatomic composition as indicated by the comparison (Fig. 3) of

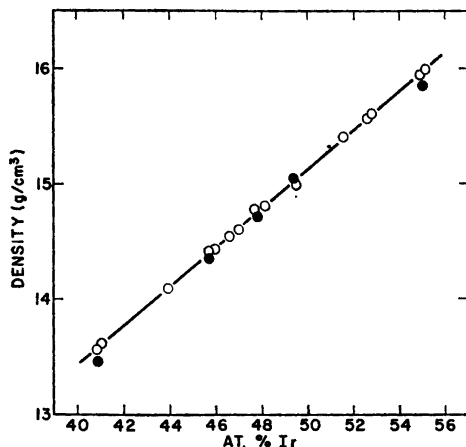


Fig. 3. Observed (●) densities of the IrMn phase and those calculated on the basis of substitutional solid solution (○), both as a function of composition.

pycnometrically determined densities with those calculated from the X-ray data. The relative changes of the lattice parameters with composition therefore appear to result, as in the PtMn phase, from the geometrical requirements of ordered packing of atoms of different size. Thus the increase of a with increasing Ir content in alloys rich in Mn results from the compulsory expansion of the Ir layers as further Mn atoms are replaced by the larger Ir atoms, the Ir—Ir intra-layer contacts at 50 atomic % Ir being 2.725 \AA , only slightly longer than in iridium metal. Substitution of Ir in the Mn layer in Ir-rich alloys results in an expansion of c with increasing Ir content, presumably because of the influence of inter-layer Ir—Ir contacts of 2.65_{-8} \AA . Comparison with the PtMn phase leads to the conclusion that the observed contraction of c in Mn-rich alloys with increasing Ir content, and of a in Mn-poor alloys, are at least in part respectively complimentary to the compulsory expansions of a and c described above, so that the unit cell volume and energy does not increase excessively. However, the overall decrease of cell volume in the

Mn-rich region of the IrMn phase, despite the increasing content of the larger Ir atoms, indicates a dominant influence of cohesive inter-layer Ir—Mn interactions. This difference from the PtMn phase (U increases with increasing Pt content in the Mn-rich region) may be due to either

(i) Ir—Mn cohesive interactions being stronger than the corresponding Pt—Mn interactions, or

(ii) the expansion due to Pt—Pt inter-layer interactions in the PtMn phase dominating the contraction expected from Pt—Mn inter-layer cohesive forces, since Pt atoms are more than 2 % larger than Ir atoms, or to a combination of both.

The results of the magnetic susceptibility measurements by the Gouy method are shown in Fig. 4. With knowledge gained from neutron diffraction studies of the NiMn,⁶ AuMn,⁷ and PtMn⁸ phases and magnetic susceptibility measurements of the NiMn,⁹ PdMn,¹⁰ and PtMn^{1,8} phases the following interpretation of the magnetic susceptibility data of the IrMn phase is suggested:

(i) All Ir—Mn alloys studied (Fig. 4) are essentially in an antiferromagnetic state. (Consequently the magnetic unit cell is different from the primitive chemical cell shown in Fig. 1a. It must be larger and/or have lower symmetry.)

(ii) The weak ferromagnetism observed in alloys containing less than 45 atomic % Ir may be explained on the basis of canted spins *cf.* (Moriya¹¹). The positive slope of the $1/\chi_g$ versus T curves at "low" temperatures for alloys containing more than 45 atomic % Ir may have a similar origin. (The weak

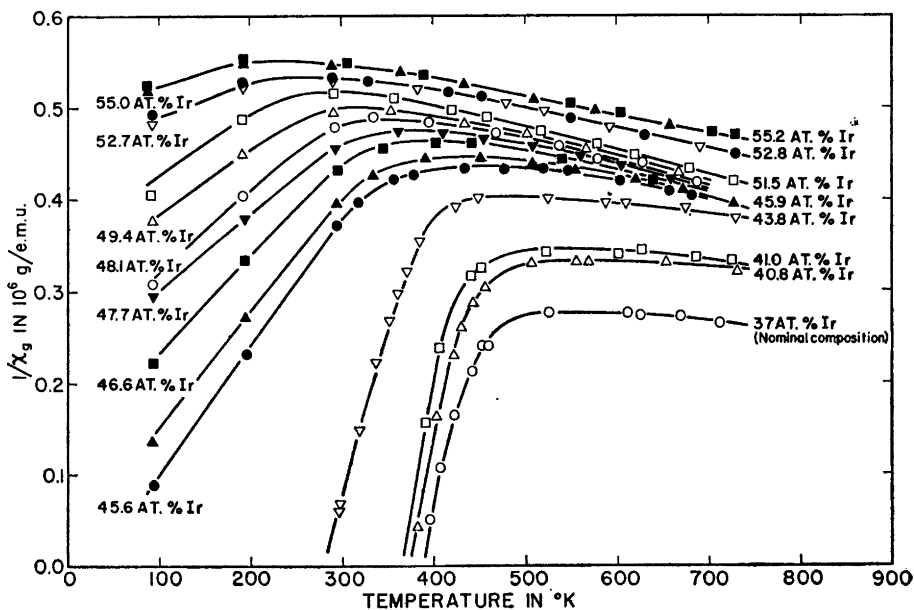


Fig. 4. The reciprocal magnetic susceptibility of the IrMn phase as a function of temperature for alloys of different composition.

ferromagnetism observed for the PtMn phase is also explained similarly; cf. Andresen *et al.*⁸⁾

(iii) Extended magnetic susceptibility measurements (by the Faraday method) on four representative alloys showed that their Néel temperatures are above 1150°K.

(iv) Speculations based on molecular-field considerations (assuming that only the Mn atoms have $S \neq 0$) suggest a spin quantum number S of 4/2 or 5/2 for manganese. Comparison with the NiMn,⁶ AuMn,⁷ and PtMn⁸ phases predicts $S = 4/2$ as the most probable value.

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