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DISCUSSION

D. S. RODBELL: There is a Mn-Ge alloy that exhibits a 1st order transition. Is that alloy one that you have studied?

K. YASUKŌCHI: $Mn_{2.65}Ge$ undergoes a phase transition. A 1st order transition was noted for Mn_3Ge_2 by Fakidov *et al.* We also have made a study on its magnetism; the results will be reported later.

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Magnetic Properties of Mn-Zn Alloys

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Crystal structures and magnetic properties of various phases in the Mn-Zn system have been investigated. The ε phase (15–35 at. % Mn, h.c.p. structure) shows the paramagnetism which obeys the Curie-Weiss law. The 25% Mn alloy becomes ferromagnetic if the superlattice of Ni_3Sn type is formed by annealing at about 100°C. The γ phase (20% Mn, γ-brass type) and the α' phase (27% Mn, f.c.c. Cu_3Au type) are also paramagnetic, the extrapolated Curie temperatures being 70° and 100°K, respectively. The latter phase is transformed to the f.c.t. structure at 150°K probably owing to the Jahn-Teller effect. This transformation gives rise to a marked decrease in magnetic susceptibility. The β phase (60% Mn, b.c.c. CsCl type) has the spontaneous magnetization at room temperature, which may be due to the ferrimagnetism.

1. Introduction

Although a number of alloys and compounds of Mn have been observed to be ferromagnetic or antiferromagnetic, only a few reports on the magnetic properties of Mn-Zn alloys have appeared. Nowotny and Bittner[1] reported briefly that the alloys containing about 30 at. % Mn were ferromagnetic at room temperature. The ferromagnetism was proved by the present authors[2] to be due to a metastable phase which has an ordered h.c.p. structure.

The phase diagram of this system was fully investigated by Schramm[3] and by Potter and Huber[4], and summarized in Hansen's book[5], as is reproduced in Fig. 1. The present report deals with the ε, α', γ, and β phases.

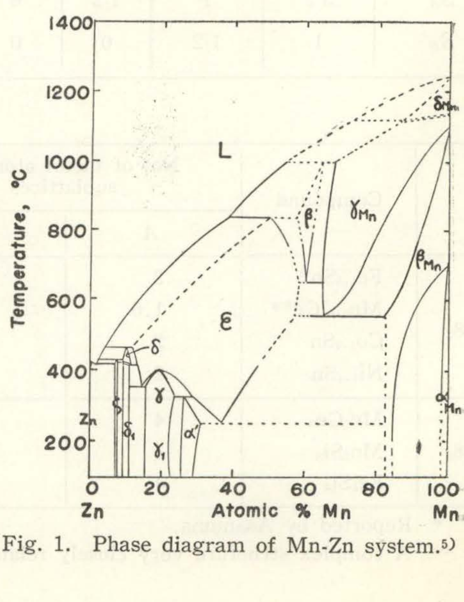

Fig. 1. Phase diagram of Mn-Zn system.[5]

2. Experimental Methods

The specimens were prepared by melting electrolytic Mn and pure Zn sealed together in evacuated quartz tubes. In some cases the single crystals were grown by a slow solidification technique. Magnetizations were measured by means of Faraday's method using an automatic chemical balance. Crystal structures were determined by using an X-ray diffractometer of Geiger-counter type.

3. Experimental Results

(1) **ε phase** This phase is stable at high temperatures in a wide range of composition, and can be retained at room temperature by quenching the specimen into water. The crystal structure is h.c.p., and the lattice constants at room temperature depend linearly on the compasition; a=2.767 Å, c=4.448 Å at 15% Mn, and a=2.746 Å, c=4.457 Å at 35% Mn.

The magnetic susceptibilities at high temperatures obey the Curie-Weiss law. The paramagnetic Curie temperature, θ_p, and the effective Bohr magneton numbers per Mn atom, $p_{\rm eff}$, are shown in Table I. These values obtained are not so accurate because the temperature ranges of the susceptibility measurements are rather limited: the accuracies of $p_{\rm eff}$ and θ_p are $\pm$0.1 and $\pm$40°, respectively.

Table I. Paramagnetism of the ε-phase alloys.

Composition (at. % Mn)	Temperature range (°K)	θ_p (°K)	p_{eff}
15	660-770	150	3.6
20	670-830	50	4.0
25	650-870	-50	4.3
30	590-930	-120	4.3
35	570-960	-190	4.3

The susceptibilities of the quenched specimens at room temperature are, in general, larger than those obtained by the extrapolation of the high-temperature values. If the quenched specimens are powdered by filing, the susceptibilities decrease and coincide with the extrapolated values. On the other hand, if the quenched specimens are annealed at about 100°C, the susceptibilities increase apparently. In all cases the X-ray diffraction patterns indicate only the h.c.p. lattice. Therefore, the difference in the magnetic properties should be due to the short-range order in the atomic arrangement. The short-range order may exist even in the quenched specimens, and may be developed by annealing whereas destroyed by filing the specimens. The quenched specimen of 15% Mn alloy becomes ferromagnetic at low temperatures, as shown in Fig. 2. The magnetic moment per Mn atom at 100°K is 1.8 μ_B. If the specimen is powdered by filing, the magnetization is markedly reduced.

As reported previously[2)], the ε-phase alloys containing about 25% Mn become strongly ferromagnetic at room temperature if annealed at 100°C for several days. The ferromagnetism may be due to the formation of the long-range order of Ni_3Sn type; this phase has been named the ε' phase. Since the ε' phase is merely metastable, more prolonged annealing gives rise to the transformation to the

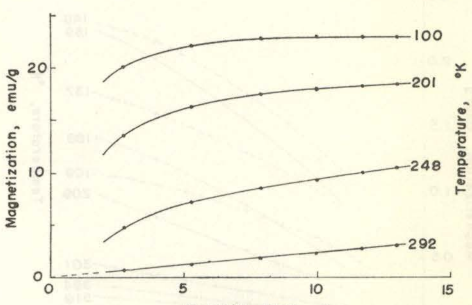

Fig. 2. Magnetization curves for the quenched ε-phase specimen of 15% Mn.

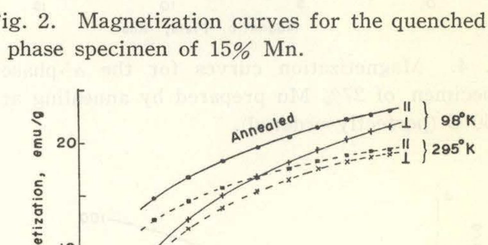

Fig. 3. Magnetization curves for the h. c. p. single crystal of 25% Mn quenched from 500°C and then annealed at 100°C for 50 hrs. The measurements were made for both annealed and not-annealed states. The magnetic fields are parallel (||) or perpendicular ($\perp$) to the c-axis; the temperatures are 98° or 295°K.

α' phase which is not ferromagnetic at room temperature. Recently, the investigations were made on single crystals of 25% Mn alloy; the results are shown in Fig. 3. The specimen was quenched from 500°C and then annealed at 100°C for 50 hrs. The annealed specimen shows a uniaxial magnetic anisotropy, which may be partly due to the non-spherical shape of the ferromagnetic particles of the ε' phase distributed in the paramagnetic matrix of the ε phase.

(2) α' **phase** This phase has the ordered f.c.c. structure of Cu_3Au type (a=3.860 Å for 27% Mn at room temperature). The superlattice lines in the X-ray diffraction pattern were detected firstly by the present authors using a fixed-counting technique.[2] The α'-phase specimen was prepared by annealing the ε-phase specimen at 250°C or below. If the specimen had been powdered by filing before the annealing, the rate of transformation to the α' phase was markedly accelerated; the annealing at 100°C for 44 hrs. was proved to be sufficient for the complete transformation. However, the superlattice lines observed for this specimen were less distinct than those for the specimen annealed at 250°C.

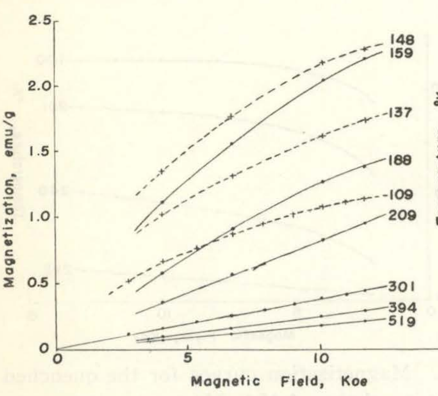

Fig. 4. Magnetization curves for the α'-phase specimen of 27% Mn prepared by annealing at 250°C (perfectly ordered).

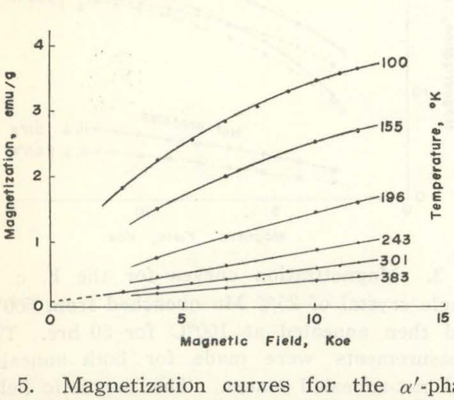

Fig. 5. Magnetization curves for the α'-phase specimen of 27% Mn prepared by annealing at 100°C (imperfectly ordered).

Magnetic measurements were made on the above-mentioned two specimens; the results are shown in Figs. 4-6. The imperfectly ordered specimen annealed at 100°C becomes gradually ferromagnetic according as the temperature is lowered; a small ferromagnetic moment is superimposed even at room temperature. On the other hand, the perfectly ordered specimen annealed at 250°C shows a maximum in the susceptibility *vs* temperature curve at 150°K; above 200°K the susceptibility is independent of the magnetic field and follows the Curie-Weiss law: θ_p=110°K and p_{eff} =3.7.

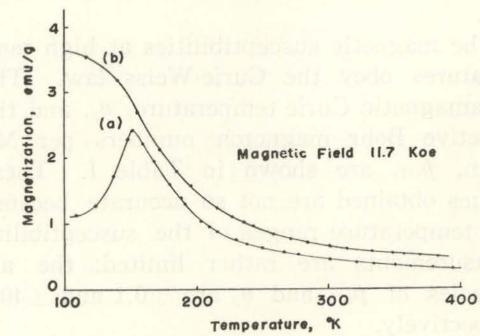

Fig. 6. Magnetization *vs* temperature curves for the α'-phase specimens of 27% Mn prepared by annealing at (a) 250°C and (b) 100°C.

It was proved by the X-ray diffraction experiments at low temperatures that the anomalous magnetic properties of the perfectly ordered specimen are associated with the crystal distortion from the cubic to tetragonal structure. Lattice parameters of the f.c.t. unit cell were found to be as follows: a=3.90 Å, c=3.71 Å, and c/a=0.95 at 100°K. This f.c.t. phase will be referred to as the α_1' phase. It should be noted that the field dependence of magnetization of the α_1' phase is similar to that of ferromagnetics, although the magnetic moment per Mn atom is only less than 0.05 μ_B. On the other hand, the imperfectly ordered specimen annealed at 100°C is not transformed to the α_1' phase, corresponding to the fact that it does not exhibit the anomalous magnetic behaviour at low temperatures.

It is unlikely that the tetragonal distortion results from a magnetic ordering, because an applied field during cooling through the transition point produces no appreciable effect upon the magnetic properties below the transition point.

(3) γ **phase** The crystal structure is similar to that of γ-brass. The 20% Mn alloy shows the Curie-Weiss paramagnetism in the temperature range 100–300°K; $\theta_p=70$°K and $p_{eff}=5.4$.

(4) β **phase** This phase is stable only at high temperatures; the crystal structure is ordered b.c.c. of CsCl type. The quenched specimen is strongly ferromagnetic at room temperature; the magnetization of the 60% Mn alloy is about 40 emu/g (0.7 μ_B per Mn atom) at the field of 10 koe, and the ferromagnetic Curie temperature is higher than 500°K. If the quenched specimen is powdered by filing, the ferromagnetism disappears and the crystal structure is transformed to the f.c.c. structure.

4. Discussion

The experimental results mentioned above are roughly explained on the basis of a usual assumption that magnetic interactions between Mn atoms are antiferromagnetic at shorter distances and ferromagnetic at longer distances. It can be concluded from the susceptibility measurements on the ε-phase alloys that there is a general tendency towards ferromagnetism in the Mn-poor alloys. This tendency is developed if the superlattice is formed, as can be seen in the ε' and α' phases. On the other hand, the spontaneous magnetization observed in the β phase should be due to the ferrimagnetism because the distance between neighbouring Mn atoms is rather short.

The anomalous magnetic properties of the α_1' phase is rather difficult to be accounted for. The transformation from the α' phase to the α_1' phase may be due to the Jahn-Teller effect, and so the covalent bonding between the atoms may result in a marked decrease in magnetic moment. However, another explanation may be possible on the basis of the antiferromagnetism. In the tetragonal lattice with $c/a<1$, it may be reasonable to assume that the spins in the same c-plane are parallel while those in the adjacent c-planes are antiparallel to each other. In order to solve this problem, more detailed investigations are now in progress.

Acknowledgments

The authors are indebted to Mr. S. Tezuka for the preliminary studies, to Mr. K. Fujimaki for the assistance in the magnetic measurements, and to Mr. M. Katase for the preparation of the single crystals. The authors wish to thank also to Prof. K. Yasukōchi of Nihon University and Dr. K. Ohta of Kobayashi Institute of Physical Research for granting the use of X-ray diffractometers.

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DISCUSSION

E. P. WOHLFARTH: I am interested in the ε' phase of $MnZn_3$. This seems to have some properties similar to the phase close to MnAl where, in the state of partial order, high coercive force has been observed at Philips. It would be interesting to do similar investigations in the present system.

Y. NAKAGAWA: In connection with this comment, we tried to measure the magnetic anisotropy of the ε' phase using single crystal specimens. As can be seen in Fig. 3, the magnetization is not easily saturated even in the magnetic fields applied along the direction of easy magnetization, and so the high coercivity due to the crystalline anisotropy might not be expected in this phase.