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The Magnetic Phase in Mn-Al-Co, -Cu, -Fe and -Ni Ternary Alloys

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The new magnetic phase, named κ phase, was observed in the ternary alloy systems of Mn-Al with Cu, Ni, Co and Fe. The composition range of the κ phase is from 20 to 45 at. % Mn, from 10 to 30 at. % Ni and from 40 to 52.5 at. % Al for the Mn-Al-Ni system and similar for the other systems. The crystal structure of the κ phase is CsCl type with the lattice parameter from 2.90 to 2.99 Å. The magnetic properties of the κ phase may be interpreated by the ferrimagnetism originated from the antiferromagnetic interactions between Mn atoms occupying different two sublattices in CsCl type crystal.

The new magnetic phase was observed in the ternary alloy systems of Mn-Al with Cu,[1)2)] Ni,[3)] Co[4)] or Fe.[5)] This magnetic phase had not yet been reported, and was named κ phase. The composition range, crystal structure and magnetic properties of these magnetic phases are almost similar to each other.

In this paper, the authors would like to report the crystallographic and magnetic properties of the κ phase and to propose some assumptions to explain their magnetic properties, mainly in the case of the Ni κ phase.

For the preparation of the specimens, the suitable proportions of each elements were mixed and melted in an alumina crucible with a Tamman furnace in air, and cast into rods, 10 mm in diameter. Ingots were annealed for an hour at 900°C in a vacuum to remove the segregation, then cooled to room temperature at the rate of 150°C per hour.

The composition range in which the specimens show ferromagnetism was determined by the magnetic examination; this result is shown in Fig. 1 with the result of X-ray analysis.

According to X-ray analysis, the composition range of the κ phase is from 20 to 45 at. % Mn, from 10 to 30 at. % Ni and from 40 to 52.5 at. % Al for Ni κ phase and almost similar for the other κ phases, and this composition range nearly coincides with the one which is determined by the magnetic examination. The crystal structure of the κ phase is ordered structure of CsCl type. The lattice parameters are from 2.99 to 2.90 Å, changing with the composition and the sort of third elements.

The magnetic properties such as the saturation magnetization, the Curie temperature, and the temperature dependence of saturation magnetization and inverse susceptibility were observed. The temperature dependence of

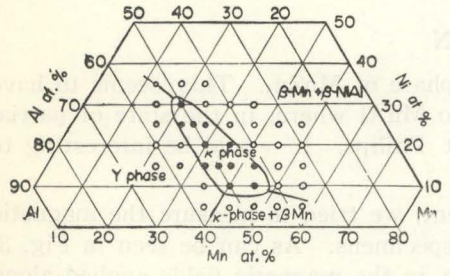

Fig. 1. The results of the magnetic examination and X-ray analysis of the Ni κ phase,
●: ferromagnetic,
○: non-magnetic.

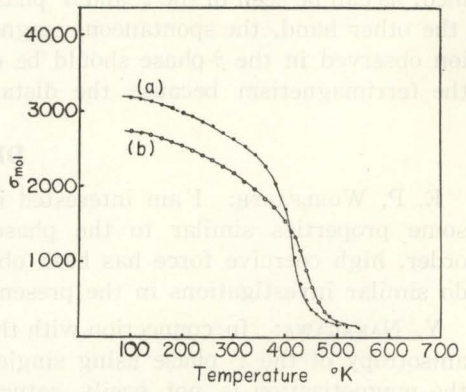

Fig. 2. The temperature dependence of saturation magnetization, in gauss per mole.
(a): 35 at. % Mn, 15 at. % Ni, 50 at. % Al.
(b): 40 at. % Mn, 15 at. % Ni, 45 at. % Al.

saturation magnetization is shown in Fig. 2 for the specimens with the composition of 15 at. % Ni and 35 at. % Mn (a), and of 15 at. % Ni and 40 at. % Mn (b). The saturation magnetization of the specimen (a) is higher than that of (b) but the Curie temperature of (a) is lower than that of (b).

The composition dependence of saturation magnetization, together with the phase boundary of the κ phase is shown in Fig. 3. The maximum value of saturation magnetization is 4000 gauss per mole, and this maximum is observed at the phase boundary of Ni poor side, namely, 40 at. % Mn, 10 at. % Ni and 50 at. % Al. The saturation magnetization decreases along Al-Mn axis with an increase of Mn content and also decreases along Ni-Mn axis with a decrease of Mn content.

The Curie temperature dominantly depends on the Mn content as shown in Fig. 4, and goes up in Mn rich side (480°K), and down in Mn poor side (350°K).

In Fig. 5 is shown the temperature dependence of inverse susceptibility above Curie temperature of the specimens along Mn-Ni axis with 50 at. % Al that contain 10, 15, 20 and 25 at. % Ni, respectively. In this figure, the slopes of these curves are almost inversely proportional to Mn content. This results suggest that the atoms which contribute to the magnetic moment are Mn atoms.

For the specimens containing less than 50 at. % Al, the relation between inverse susceptibility and temprature generally shows nonlinear, ferrimagnetic behavior, like the curve (a) in Fig. 6. The 50 at. % Al speci-

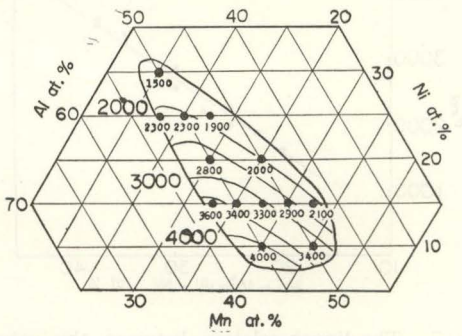

Fig. 3. The composition dependence of saturation magnetization and the phase boundary of the Ni κ phase.

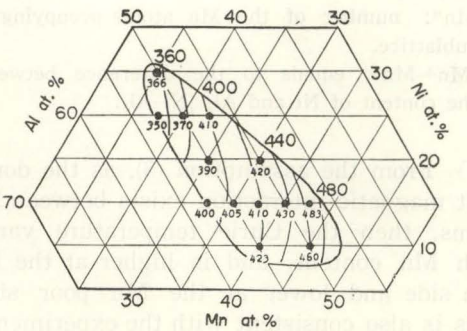

Fig. 4. The composition dependence of the Curie temperature.

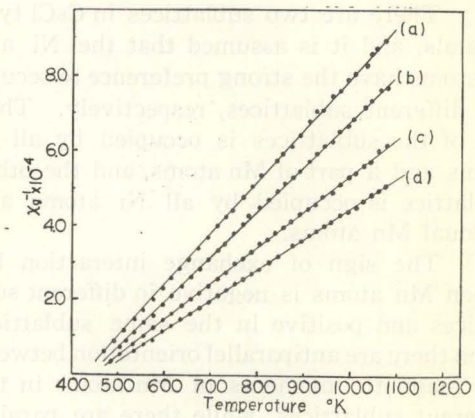

Fig. 5. The temperature dependence of the inverse susceptibility of the specimens along Mn-Ni axis with 50 at% Al.
a) 25 at. % Mn, 25 at. % Ni, 50 at. % Al,
b) 30 at. % Mn, 20 at. % Ni, 50 at. % Al,
c) 35 at. % Mn, 15 at. % Ni, 50 at. % Al,
d) 40 at. % Mn, 10 at. % Ni, 50 at. % Al.

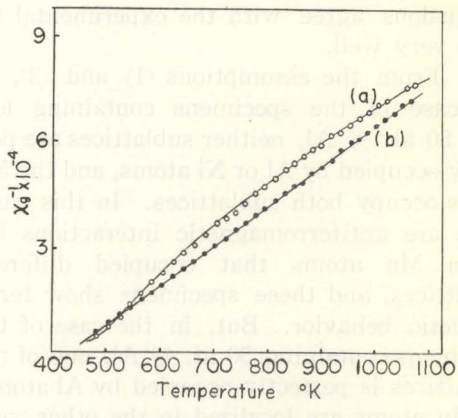

Fig. 6. The temperature dependence of the inverse susceptibility of the specimens along Al-Mn axis with 15 at. % Ni.
a) 40 at. % Mn, 15 at. % Ni, 45 at. % Al,
b) 35 at. % Mn, 15 at. % Ni, 50 at. % Al.

mens are nearly ferromagnetic like the curve (b).

The almost similar results were obtained for the other κ phases. There are some differences in the value of saturation magnetization or Curie temperature among these phases but these disagreements are only a few percent.

Above experimental results suggest that the κ phase is generally ferrimagnetic, but 50 at. % Al specimens are ferromagnetic. Then following assumptions are proposed to explain their magnetic properties.

1) There are two sublattices in CsCl type crystals, and it is assumed that the Ni and Al atoms have the strong preference to occupy the different sublattices, respectively. Then one of the sublattices is occupied by all Al atoms and a part of Mn atoms, and the other sublattice is occupied by all Ni atoms and residual Mn atoms.

2) The sign of exchange interaction between Mn atoms is negative in different sublattices and positive in the same sublattice. Then there are antiparallel orientation between the magnetic moments of Mn atoms in the different sublattices, while there are parallel orientation between ones in the same sublattice.

3) The magnetic atoms which dominantly contribute to magnetic properties are Mn atoms.

According to these assumptions, following three conclusions can be deduced about the magnetic properties of the κ phase, and these conclusions agree with the experimental results very well.

1) From the assumptions (1) and (2), in the case of the specimens containing less than 50 at. % Al, neither sublattices are perfectly occupied by Al or Ni atoms, and the Mn atoms occupy both sublattices. In this case, there are antiferromagnetic interactions between Mn atoms that occupied different sublattices, and these specimens show ferrimagnetic behavior. But, in the case of the specimens containing 50 at. % Al, one of the sublattices is perfectly occupied by Al atoms, all Mn atoms are localized in the other sublattice and there is no antiferromagnetic interaction among Mn atoms, and these specimens show ferromagnetic behavior. However, this is an exceptional case. This conclusion agrees with the experimental results.

2) From the assumptions (2) and (3), the saturation magnetization is proportional to the difference between the numbers of Mn atoms which occupied each sublattices. Then the saturation magnetization is increased with an increase of Mn content along Mn-Ni axis, because the additional Mn atoms substitute to Ni atoms; this makes the saturation magnetization increased. On the other hand, it is decreased with an increase of Mn content along Mn-Al axis, because in this case, the additional Mn atoms substitute for Al atoms; this makes the saturation magnetization decreased.

In Fig. 7 are shown the experimental results of the relation of the saturation magnetization to the difference between the numbers of Mn atoms which occupy two sublattices; the relation is almost linear and this result also supports the conclusion (2).

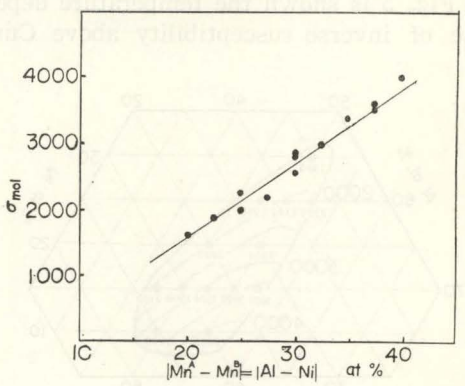

Fig. 7. The linear relation between the saturation magnetization and difference between the numbers of Mn atoms in two sublattices.
Mn^A: number of the Mn atoms occupying A sublattice.
Mn^B: number of the Mn atoms occupying B sublattice.
$|Mn^A - Mn^B|$ equals to the difference between the content of Ni and Al, |Ni-Al|.

3) From the assumption (3), as the dominant magnetic interaction exists between Mn atoms, then the Curie temperature varies with Mn content, and is higher at the Mn rich side and lower at the Mn poor side. This is also consistent with the experimental results.

According to the consistence of the above

conclusions with the experimental results, it can be understood that the assumptions are justified. Then the magnetic properties of the κ phase can be explained by the ferrimagnetism originated from the antiferromagnetic interactions between Mn atoms occupying two different sublattices in the CsCl type crystal.

References

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DISCUSSION

S. Iida: I think that, in your limiting case of 50% Al, a Curie temperature of 400°K is too high to be accounted for by direct exchange for a distance of 2.9 Å. How could you explain this fact?

I. Tsuboya: I can not explain this high Curie temperature.

J. B. Goodenough: If only *d* electrons are involved in the magnetic interactions, one would anticipate a Curie temperature that is quite sensitive to lattice parameter. I believe that this is not the case in these alloys. This suggests, therefore, that the *s-p* electrons play an important role. In an ionic structure, one anticipates antiferromagnetic superexchange through the intermediary, but in a covalent structure a ferromagnetic superexchange. The b.c.c. symmetry of this alloy has antiparallel spin correlations between simple-cubic sublattices, and ferromagnetic coupling in these sublattices, so that a ferromagnetic superexchange through the Al atoms appears feasible.