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# Cubic-Tetragonal Transition and Antiferromagnetism of $\alpha'$-$MnZn_3$

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The low temperature transition of $\alpha'$-$MnZn_3$ alloy of $Cu_3Au$ type structure has been investigated by X-ray and neutron diffraction experiments, dilatometry, magnetization measurements and specific heat measurements. This alloy exhibits antiferromagnetism below 130°K, at which the cubic lattice is transformed to the tetragonal lattice, the axial ratio $c/a$ being 0.95. On heating, both the tetragonality and sublattice magnetization vanish abruptly, indicating that this transition is of the first kind. The integrated value of the anomalous specific heat and the entropy change due to the transition are in rough agreement with those calculated by taking only the magnetic contribution into account. Apart from this transition, the field dependence of susceptibility becomes appreciable below 170°K, and the remanent magnetization appears below 60°K. These behaviours are probably due to the stacking fault in the fcc lattice, since the corresponding hcp lattice of metastable $\varepsilon'$-$MnZn_3$ is ferromagnetic.

## § 1. Introduction

The $\alpha'$ phase in the Mn-Zn system is stable in the composition range between 25 and 30 atomic % Mn at temperatures below 600°K.[1] Recently the following has been found by the present authors and their collaborators.[2-4] The crystal structure of $\alpha'$-$MnZn_3$ at room temperature is of the $Cu_3Au$ type with $a=3.86$ Å.[2] This alloy exhibits the paramagnetism which obeys the Curie-Weiss law. At 130°K it becomes antiferromagnetic and undergoes a transition to a tetragonal structure; the lattice parameters $a=3.90$ Å, $c=3.72$Å and $c/a=0.95$ at 100°K.[3] The magnetic unit cell determined by neutron diffraction experiments is twice as large as the chemical unit cell along the $c$-axis; the magnetic moments in a $c$-plane are parallel to each other and antiparallel to those in adjacent $c$-planes.[4]

In this paper the results of specific heat measurements and dilatometry on the $\alpha'$-phase alloys near the composition of $MnZn_3$ are presented, together with more detailed results of the X-ray and neutron diffraction experiments and the magnetic measurements.

## § 2. Experimental Procedures and Results

### 2.1 *Preparation of samples*

Samples of the $\alpha'$-phase alloys containing 23, 26, 27 and 29 atomic % Mn were prepared by the following procedures. Electrolytic Mn (99.9%) and pure Zn (99.9%) were mixed, sealed in an evacuated quartz tube and heated in an electric furnace at about 900°C. The molten alloy was quenched into water, sealed in a quartz tube again and annealed at 500°C for 48 hours. The product was the $\varepsilon$-phase alloy which is stable at high temperatures. The ingot was powdered by filing and annealed at 250°C for 48 hours to produce the $\alpha'$-phase alloy. The internal stress imposed by filing seems to accelerate the rate of transformation from $\varepsilon$ to $\alpha'$. A portion of the powdered sample was pressed at a pressure of around 100 kg/cm² to obtain a cylindrical sample of 10mm in both diameter and length; the weight was about 5g and the porosity was estimated to be 15%. The cylindrical sample was annealed at 250°C again to remove the stress due to pressing.

The powder sample was used for X-ray and neutron diffraction measurements. The pressed cylindrical sample was used for dilatometry and specific heat measurements. A broken piece of the pressed sample was used for magnetic measurements. The compositions of alloys, examined by chemical analysis, were not significantly different from the mixing ratios.

*2.2 The X-ray diffraction experiments*

The X-ray diffraction experiments were conducted by using an X-ray diffractometer of Geiger-counter type. The Cu $K_\alpha$ radiation was used throughout this work. For the low temperature measurements, a sample holder of copper was placed in a cryostat.

For the alloy containing 26 atomic % Mn, a typical diffraction pattern of fcc structure was obtained at room temperature. An elaborate technique was required to observe the superlattice lines because of little difference in atomic number between Mn and Zn.[2] At low temperatures the (200) line of the cubic structure splits into the two lines, (200) and (002), of the tetragonal structure from which the two parameters $a$ and $c$ can be determined. As shown in Fig. 1, tetra-

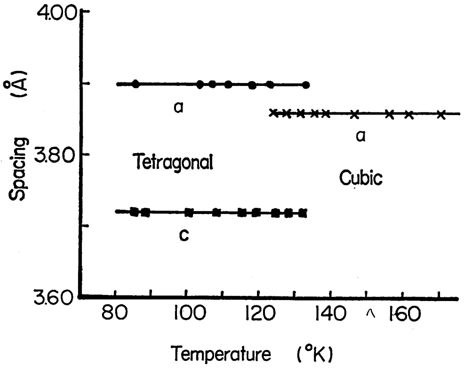


Fig. 1. Variation of lattice spacings $c$, $a$ with temperature for α′-$MnZn_3$ (26 at. % Mn).

gonality $(c/a)-1$ is almost independent of temperature and seems to vanish abruptly at the transition point. The unit cell volume of the tetragonal structure is slightly smaller than that of the cubic structure. Figure 2 shows the temperature variation of peak intensities of the (200) lines.

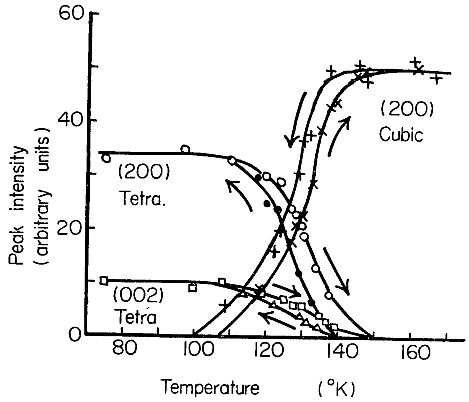


Fig. 2. Temperature dependence of peak intensities of (200) lines of X-ray diffraction for α′-$MnZn_3$ (26 at. % Mn). ○□× heating. ●△+ cooling.

Similar results were obtained for the alloy with 27 atomic % Mn. However, the samples containing 23 or 29 atomic % Mn gave the diffraction patterns contaminated by the γ phase or ε phase, respectively. The tetragonal distortion of the α′ phase was less remarkable in these samples than in the samples containing 26 and 27 atomic % Mn.

The effect of internal stress on the transition was examined for the alloy with 26 atomic % Mn. If the powder sample has been pressed and re-powdered without annealing, the transition proceeds less abruptly in a lower temperature range.

*2.3 Neutron diffraction measurements*

These studies were carried out with a neutron diffractometer of the Institute for Solid State Physics, which had been installed at the reactor JRR-3 of Tokai Laboratories. The powder sample, enclosed in an assembly of aluminum within a cryostat, was placed in the neutron beam of wavelengh 1.08 Å.

Diffraction patterns at room temperature and 96°K are almost the same as those described in our earlier paper.[4] The main magnetic reflection is $(00\frac{1}{2})$, the scattering angle $2\theta$ being about 8.35°. The most intense nuclear reflection (110) is observed near $2\theta=22.58°$. Peak intensities of the $(00\frac{1}{2})$ and (110), measured as a function of temperature, are shown in Fig. 3. The intensity of the $(00\frac{1}{2})$ reflection decreases with increasing temperature and vanishes at the tetragonal transition point $T_0$.* A smooth extrapolation of the

* The transition point $T_0$ observed by neutron diffraction experiments seemed to be about 10° lower than that determined by other experiments. It is unlikely, however, that the discrepancy is essential.

intensity versus temperature curve, indicated by a broken line in Fig. 3, gives the Néel temperature $T_N$. Although the present data are insufficient to give a precise value of $T_N$, it can be concluded that $T_N$ is definitely higher than $T_0$. The intensity of the (110) reflection increases with increasing temperature, corresponding to the increase of the volume fraction of the cubic phase. These results are consistent with those of the X-ray diffraction.

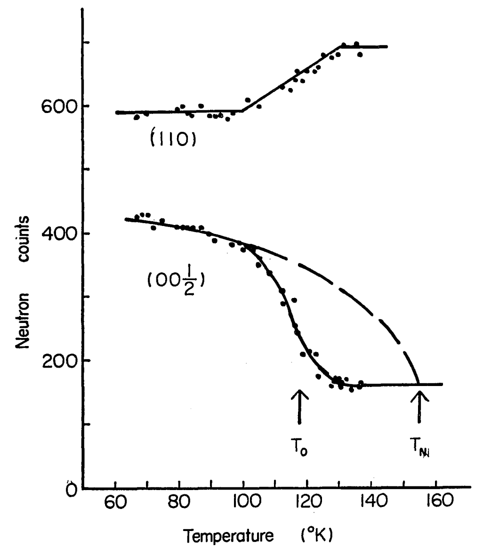


Fig. 3. Temperature variation of peak intensities of (00½) magnetic line and (110) nuclear line for α′-$MnZn_3$ (26 at. % Mn). Diffracted neutrons were counted for about 2.9 minutes at each temperature.

*2.4 Dilatometry*

The dilatation was measured by a differential method using strain gauges, one of which were cemented on a sample of Mn-Zn and another on a standard of brass. They were inserted in a copper block with two holes and placed in a cryostat.

The difference in dilatation between the sample and the standard could be measured as the change in resistivity of the strain gauges detected by a bridge balance method. A linear dimension of the polycrystalline sample is decreased by about 0.04% by the transition from cubic to tetragonal structure. The thermal hysteresis was also found in this measurement; the transition temperatures in heating and cooling processes were 131°K and 122°K, respectively.

*2.5 Magnetization measurements*

Magnetizations at temperatures down to 6°K were measured using a vibrating sample magnetometer of the Institute for Solid State Physics. An automatic magnetic balance was also used for the measurements of magnetization at higher temperatures.

The magnetization of the alloy containing 26 atomic % Mn at $H$=10.9 kOe is plotted as a function of temperature in Fig. 4. The existence

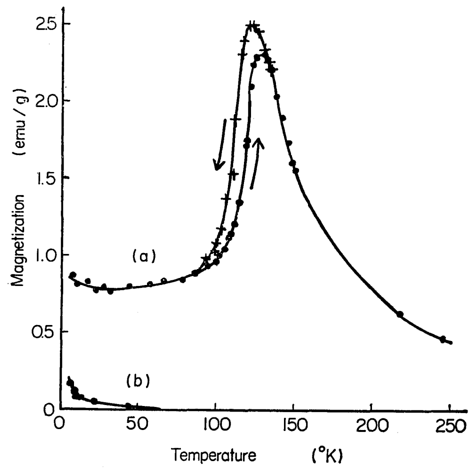


Fig. 4. Magnetization vs. temperature curves for α′-$MnZn_3$ (26 at. % Mn). (a) Magnetization at $H$= 10.9 kOe, (b) Remanent magnetization.

of a peak point on the curve may be regarded as an evidence of antiferromagnetism. The peak point, however, does not correspond to the Néel point $T_N$ but to the tetragonal transition point $T_0$ (cf. Fig. 3). Complete magnetization curves from −20 kOe to +20 kOe are shown in Fig. 5. The curve (b) at 77°K is bent toward the field axis; this "S"-shaped curve passing through the

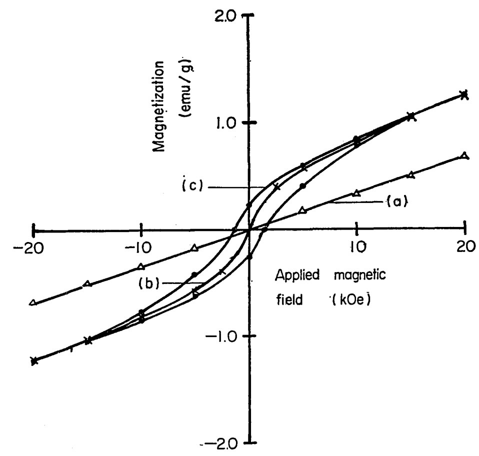


Fig. 5. Magnetization curves for α′-$MnZn_3$ (26 at. % Mn). (a) 300°K, (b) 77°K, (c) 7°K.

origin is characteristic of superparamagnetic material. The higher the temperature the less remarkable becomes this behaviour, but it can be seen even at 170°K which is much higher than $T_0$. In the temperature range below 60°K, weak remanent magnetization appears, as shown by the curve (c) in Fig. 5 and also by the curve (b) in Fig. 4.

In order to test the relation between the weak ferromagnetism and the antiferromagnetic transition, the thermo-remanent magnetization, produced by cooling the specimen from room temperature down to 77°K in a magnetic field of 7 kOe, was measured at 77°K by means of torque method,[5] the measuring field being 0.3 kOe. The remanence observed was only $1.6\times10^{-3}$ emu/g, suggesting that the superparamagnetic behaviour is not influenced by the antiferromagnetic transition.

*2.6 Specific heat measurements*

The specific heat was measured with an adiabatic vacuum calorimeter of standard design.[6] Since the specific heat measurement was possible only in the heating process, a differential thermal analysis was also made to examine the thermal hysteresis; the results were consistent with those obtained by the dilatometry and the magnetic measurements.

The observed curve of the specific heat $c_p$ vs. temperature $T$ for well-annealed specimen containing 26 atomic % Mn is given in Fig. 6(a).

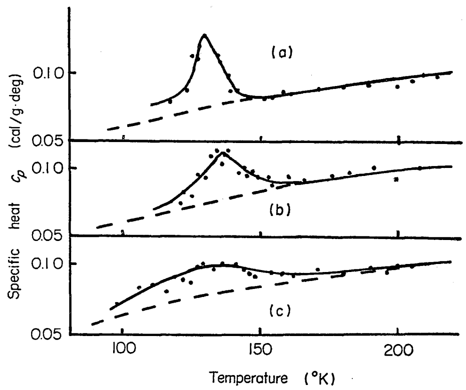


Fig. 6. Temperature dependence of specific heats of $\alpha'$-$MnZn_3$ (26 at. % Mn). (a) well-annealed, (b) pressed lightly, (c) pressed heavily.

The integrated value of the specific heat anomaly, $\Delta q=\int\Delta c_p\,dT$, is about 1.0 cal/g, and the change in entropy, $\Delta s=\int(\Delta c_p/T)\,dT$, is about 0.01 cal/g·deg. If the sample has not been annealed after pressing, the anomaly of the specific heat becomes less remarkable, as shown by curves (b) and (c) in Fig. 6.

## § 3. Discussion and Conclusions

It is confirmed by neutron diffraction that the antiferromagnetic transition of the $\alpha'$ phase in the Mn-Zn system is accompanied by the tetragonal distortion of the cubic lattice. This is very similar to the transition of $\gamma$-Mn.[7] Because both the tetragonality and the antiferromagnetic moment vanish abruptly at the transition point, the transition must be of the first kind. However, the susceptibility and the specific heat curves exhibit no discontinuity, probably because there is a distribution of the transition points due to segregation or internal stress in the sample.

The specific heat anomaly at the transition temperature may consist of both the magnetic contribution and the contribution from lattice transition. Although the latter has been discussed in terms of the Jahn-Teller effect,[8] a quantitative analysis of this effect seems to be difficult. The magnetic contribution to the specific heat anomaly, on the other hand, can easily be calculated on the basis of a localized-moment model;[9] the integrated value of the specific heat anomaly $\Delta q_m$ and the entropy change $\Delta s_m$ are expressed as

$$\Delta q_m=(3/2)\cdot N\cdot k\cdot T_N\cdot\frac{S}{S+1}\,, \qquad (1)$$

$$\Delta s_m=N\cdot k\cdot\ln(2S+1)\,, \qquad (2)$$

where $k$ is the Boltzmann constant, $S$ the spin quantum number, $N$ the number of Mn atoms per unit mass and $T_N$ the Néel temperature.

As it has been determined from the neutron diffraction measurements[4] that the magnetic moment of Mn is about $3\mu_B$ (Bohr magnetons), the value of $S$ can be chosen as 3/2. Although $T_N$ is higher than $T_0$, it is tentatively assumed that $T_N=T_0$ (130°K) to calculate the value of $\Delta q_m$. The calculated values are $\Delta q_m=0.93$ cal/g and $\Delta s_m=0.011$ cal/g·deg. If these are compared with the experimental values $\Delta q=1.0$ cal/g and $\Delta s=0.01$ cal/g·deg, it seems that the energy change and the entropy change due to the tetragonal transition are mostly attributed to the onset of antiferromagnetism.

The weak ferromagnetism or superparamagnetism in $\alpha'$-$MnZn_3$ is not directly related to the antiferromagnetism, but seems to be due to small ferromagnetic regions. If the superparamagnetic behaviour is analyzed on the basis of a spherical particle model,[10] a mean value of the particle diameter is estimated to be about 60Å. The ferromagnetic regions may possibly be stacking faults in the fcc lattice of $Cu_3Au$ type; the corresponding hcp lattice of $Ni_3Sn$ type also exists in the Mn-Zn system, called the $\varepsilon'$ phase.[2,3] Since $\varepsilon'$-$MnZn_3$ is ferromagnetic at room temperature, the stacking faults in the fcc matrix can exhibit superparamagnetism or weak ferromagnetism even at temperatures above $T_0$.


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