JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-I, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

Magnetic Behavior of Disordered and Ordered Au_3Mn

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Disordered Au_3Mn exhibits a broad susceptibility maximum near 100°K and its hysteresis loop is displaced upon cooling to lower temperatures in a field. It is concluded that this alloy, like disordered alloys of Mn in Cu and in Ag, possesses a spatially inhomogeneous ferromagnetic-antiferromagnetic state; it is not ferromagnetic as previously claimed. The susceptibility of the ordered Au_3Mn alloy is confirmed to have a sharp peak at 150°K, but drops more rapidly with decreasing temperature than reported by Meyer, reaching a low temperature value about one-half that at the peak. At a threshold field of 47 koe, the low temperature susceptibility increases rapidly to twice its initial value; the transition is suggestive of antiferromagnetic spin-flopping. An antiferromagnetic model with orthorhombic anisotropy gives a satisfactory description of the magnetic data and is consistent with the idealized atomic structure proposed by Watanabe.

ntroduction

Interest in the gold-manganese alloy system has been high since the discovery of ordered crystallographic structures at several definite compositions. We report here measurements on disordered and ordered polycrystalline Au_3Mn[1] of susceptibility, hysteresis loops to 10 koe, and pulsed field magnetization to 140 koe, from 4.2°K to 300°K. This work was stimulated by the results of Meyer[2] reporting the disordered alloy as ferromagnetic with a Curie point of about 120°K (based on measurements above 90°K), and the ordered alloy as antiferromagnetic with a Néel point near 145°K. This ferromagnetism of the disordered alloy is unlike the mixed ferro-antiferromagnetic properties shown by disordered, 25 at.% Mn in Cu or Ag,[3] and suggested closer study. The antiferromagnetism of the ordered alloy and its large positive paramagnetic Curie temperature suggested to Meyer a possible metamagnetism analogous to that in Au_2Mn.[4] The threshold field was estimated, following Néel,[5] to be about 60 koe, which is well within the range of our pulsed field apparatus.

Behavior of Disordered Au_3Mn

Polycrystalline specimens were prepared as follows: a master alloy at the eutectic, Au_2Mn, made by induction melting electrolytic Mn and pure Au under argon, was remelted with extra Au to reach Au_3Mn, and homogenized. The composition, by analysis, was 24.3 at.% Mn. Disordering was by water-quenching from 900°C. X-ray diffraction from quenched filings showed some faint superstructure lines. Similar superstructure traces were noted by others[1),6)] on quenched samples.

Fig. 1 presents the magnetization at 10 koe *vs.* temperature for a disordered specimen cooled to 4.2°K in zero field. There is a broad maximum near 100°K. From hysteresis measurements, the magnetization was observed to be nearly proportional to field over this temperature range. As indicated, the

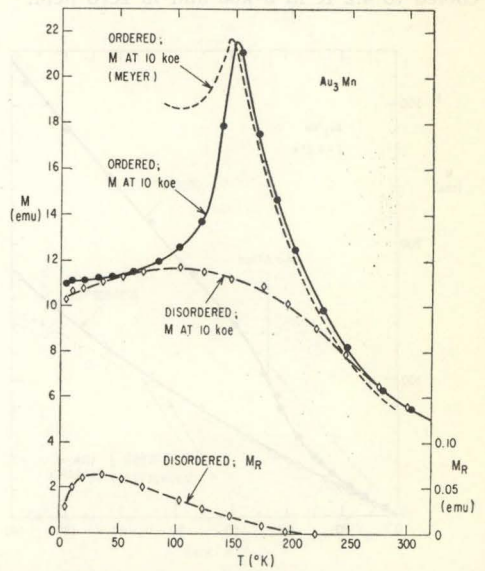

Fig. 1. Magnetization *vs.* temperature in Au_3Mn at moderate fields.

* Read by C. D. Graham.

extremely small remanence, M_R, is largest at about 40°K. The hysteresis loop at 4.2°K is linear with nearly zero area. Upon cooling to 4.2°K in a field of 5 koe, this linear loop is displaced 700 oe toward negative fields, as shown in Fig. 2. This displacement decreases with increasing temperature, vanishing below 100°K. The curve of magnetization *vs.* field to 140 koe, in Fig. 3, shows an upward curvature.

This behavior is markedly similar to that of disordered alloys of Mn in Cu and in Ag. Loop displacement in all these alloys is evidence for the exchange anisotropy discussed previously[3]. Hence, we propose that disordered Au_3Mn has a spatially inhomogeneous ferro-antiferromagnetic state arising from ferromagnetic and antiferromagnetic interactions between Mn atoms of different separation. It is not ferromagnetic, contrary to the earlier report.

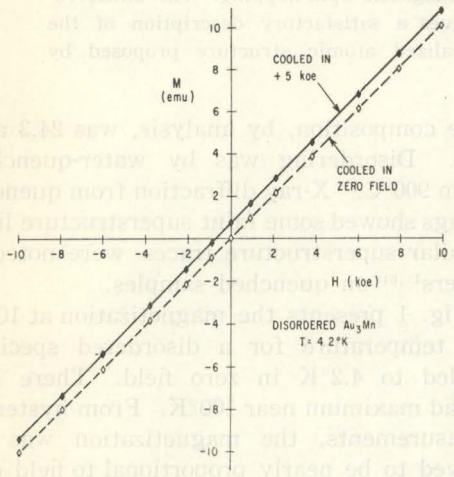

Fig. 2. Hysteresis loops of disordered Au_3Mn cooled to 4.2°K in 5 koe and in zero field.

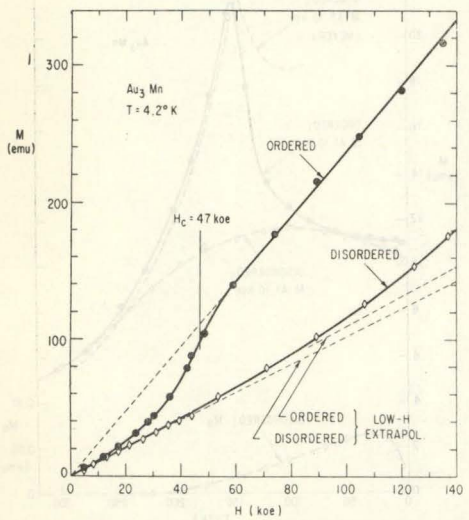

Fig. 3. High magnetic field behavior of Au_3Mn at 4.2°K.

The nearest neighbor Mn-Mn separation in this alloy is 2.87A, which is similar to that of the comparable Ag-Mn alloy, where it has been associated with an antiferromagnetic interaction.[3] Since about 97% of the Mn atoms in disordered Au_3Mn would have a Mn atom as a nearest neighbor, there would be a powerful deterrent to ferromagnetic alignment.

Behavior of Ordered Au_3Mn

Specimens were ordered by annealing for one day each at 600°C, 570°C and 540°C, then furnace-cooling. Annealed filings showed strong x-ray superstructure lines. Fig. 1 shows the magnetization at 10 koe *vs.* temperature. The sharp peak near 150°K is in agreement with Meyer,[2] as shown. At all temperatures, the magnetization is proportional to field, with no detectable remanence. No exchange anisotropy is observed upon field cooling, presumably because atomic ordering results in a spatially homogeneous magnetic state, even though there are both ferromagnetic interactions shown by the positive paramagnetic Curie temperature[2),7)] and antiferromagnetic interactions shown by the susceptibility peak. The decrease in magnetization from the peak at 150°K to 4.2°K is much more rapid than suggested by Meyer's data. We observe that the ratio $\chi(4.2°K)/\chi(150°K)$ is 1/2, which is smaller than the 2/3 expected for a simple polycrystalline uniaxial antiferromagnet. The same anomalous ratio was obtained for a compact of small chips (taken from the same ingot and given the same treatment) and cannot therefore be the result of preferred crystal orientation.

The magnetization to 140 koe at 4.2°K is shown in Fig. 3. A steep increase in magnetization occurs between 20 and 60 koe, such that the differential susceptibility above 60 koe is about twice that at low fields. A linear extrapolation from high fields back to $H=0$, passes through the origin, reminiscent of spin-flopping in MnF_2[8] or $CuCl_2 \cdot 2H_2O$[9], in

contradistinction to the metamagnetic transformation to a ferromagnetic state in Au_2Mn.[4] At 77°K the curve is similar; a smeared-out transition occurs at 135°K, which has disappeared at 155°K. Using Néel's[10] calculations of susceptibility *vs.* orientation for a spin-flopping process, the threshold field in ordered Au_3Mn at 0°K is estimated to be 47 koe. The ratio of low to high field susceptibilities expected for this process in a simple polycrystalline uniaxial antiferromagnet is 2/3, in contrast to the observed value of 1/2. Thus, the quantitative variations of the magnetization of ordered Au_3Mn with field and with temperature are anomalous.

The observed deviations from the simple antiferromagnet suggest an orthorhombic two-sublattice model with uniaxial anisotropy in a strongly preferred plane. All anisotropies are assumed to vanish at 150°K. For an infinite anisotropy out of the plane, this model gives $\chi(0°K)/\chi(150°K)=1/3$ at low fields and $\chi(H=0)/\chi(H>60\text{ koe})=1/2$ at low temperatures. For a finite anisotropy out of the plane, such that the transverse susceptibility out of the plane is one-half that in the preferred plane, these two ratios are 0.5 and 0.6 respectively. This reasonable agreement can be improved with a four-sublattice model, more realistically in accord with a magnetic structure based on the idealized orthorhombic superlattice discussed below.

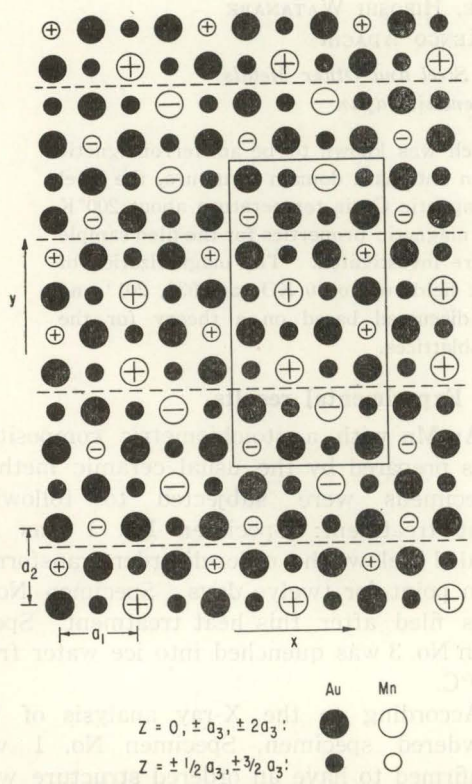

Fig. 4. Idealized orthorhombic superlattice of ordered Au_3Mn after D. Watanabe, with the moment directions assigned as described in text.

Applying the *two*-sublattice approximation to our data, we find that the ratio of ferromagnetic exchange within a sublattice to antiferromagnetic exchange between sublattices is about 9. The antiferromagnetic exchange field H_E deduced from $\chi(150°K)$ is 131 koe. Thus, from the threshold field H_c, we estimate an in-plane anisotropy field of 9 koe, using[9-12] $H_c^2=2H_EH_A$.

In an electron diffraction study of monocrystalline films of ordered Au_3Mn, Watanabe[6] noted a slight orthorhombic distortion of the elementary face-centered cell ($a_1=4.08$A, $a_2=4.05$A, $a_3=4.03$A). He observed a superlattice which can be idealized as in Fig. 4, showing the two planes needed for a complete description. The idealized superlattice cell, outlined by the solid lines, is $2a_1\times4a_2\times a_3$ in size. Moment directions have been assigned by aligning nearest neighbor Mn pairs antiferromagnetically and next nearest neighbor pairs ferromagnetically. A kinked chain of four non-equivalent Mn atoms appears along the *y*-direction, propagating indefinitely along the *z*-axis to form double bands with intra-band ferromagnetic coupling and inter-band antiferromagnetic coupling. If the third nearest neighbor coupling is also assumed ferromagnetic, then the full structure of Fig. 4 is generated. The ferromagnetic bands are now coupled to form ferromagnetic layers, parallel to the *x*-*z* plane and $2a_2$ thick. These anisotropic layers are outlined by the dashed lines, across which all the antiferromagnetic bonds occur. If the opposite though less likely assumption regarding third nearest neighbor coupling were made, thinner ferromagnetic layers would be found parallel to the *y*-*z* plane. The preferred planes and directions of the magnetic model described earlier are consistent with the orthorhombic symmetry of either structure.

Acknowledgments

We are most grateful to J. S. Kasper for

many enlightening discussions concerning the crystal structure of ordered Au_3Mn, and to H. N. Treaftis for his able assistance in some of these measurements.

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Magnetic Properties of Au_3Mn Alloys

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The magnetic properties of Au_3Mn alloy, which was known to be antiferromagnetic were investigated. In the ordered state with an antiphase domain structure, the Néel temperature was found to be 140°K, the paramagnetic Curie temperature about 200°K and effective Bohr magneton 4.06 μ_B. Also the magnetic properties for the filed sample of the ordered alloy and the quenched alloy were investigated. The magnetization of ordered alloy was measured in static magnetic fields up to 80 KOe at 293°, 201° and 83°K. The observed magnetic behaviors were discussed based on a theory for the antiferromagnetic crystal with non-equivalent sublattices.

1. Introduction

It was known by many workers[1,2,3] that the ordered Au_3Mn alloy was an antiferromagnetic with the Néel temperature at 145°K. The behavior of magnetization at strong magnetic field was predicted by Meyer[4]. On the other hand, an antiphase domain structure in the ordered Au_3Mn was recently studied in detail by Watanabe[5]. In this paper the antiferromagnetic properties of Au_3Mn alloy in the ordered and disordered states, and the magnetizations in strong magnetic fields of this alloy are studied, and the origin of the magnetic properties is discussed in connection with the special atomic arrangement in this alloy.

2. Experimental results

Au_3Mn with a stoichiometric composition was prepared by the usual ceramic method. Specimens were subjected to following heat treatment: Specimen No. 1 was annealed below the order-disorder transformation point for twelve days. Specimen No. 2 was filed after this heat treatment. Specimen No. 3 was quenched into ice water from 700°C.

According to the X-ray analysis of the powdered specimen, Specimen No. 1 was confirmed to have an ordered structure with two-dimensional antiphase domain. The results of analysis are shown in Table I. Lattice parameters corresponding to the original