MAGNETIC PROPERTIES OF Mn-Ge SOLID SOLUTIONS

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Alloys of Mn and Ge containing from 8 to 22 at. % Ge are found to have a large coercive force and a magnetization that depends in a very complex way on both the temperature and thermal treatment. All the peculiarities of the temperature dependence of the magnetization of the investigated samples can be explained by refining the phase diagram and assuming that the alloys in this concentration range are formed by ordered replacement of the Mn atoms in the γ-Mn lattice.

INTRODUCTION

IIII UMEROUS investigations of the magnetic properties of Mn-Ge alloys have disclosed a great diversity of magnetic structures realizable in this system. Thus, the compound $Mn_{3.25}Ge$, according to[1], is antiferromagnetic, whereas Mn_3Ge and Mn_5Ge_3 are ferromagnetic.[2,3] In Mn_5Ge_2 there is a compensation point,[4-6] and in Mn_3Ge_2 a transition from antiferromagnetism to weak ferromagnetism is observed.[7] All of these compounds occur in a narrow range of germanium concentration (from 23.8 to 40 at. %), but the change in magnetic properties is quite pronounced. Such diversity of magnetic structures in manganese compounds can be understood by assuming the presence in them of several types of Mn atoms with different magnetic moments, and this is borne out by the experimental facts. The phase α-Mn is antiferromagnetic and consists, according to neutron diffraction data,[8,9] of four types of Mn atoms with different magnetic moments. The presence of a compensation point in Mn_5Ge_2 is also direct evidence that there are in this compound at least two types of nonequivalent Mn atoms having different magnetic moments. The average magnetic moment of the Mn atoms in Mn_5Ge_3 is markedly less than the value 3.5 μ_B characteristic for Mn atoms in a collinear magnetic structure,[10] and therefore it must be assumed that the magnetic structure of Mn_5Ge_3 is ferrimagnetic, the sublattices being composed of nonequivalent Mn atoms. From this point of view, it should be interesting to study the magnetic properties of alloys in the range from α-Mn to $Mn_{3.25}Ge$ (23.8 at. % Ge), since in these alloys the Ge atoms can replace, in ordered fashion, a portion of the Mn atoms of one sort, and this must have a significant effect on the magnetic properties of the alloys. The magnetic properties of this portion of the Mn-Ge system have not been investigated, to our knowledge. Our first experiments have shown that alloys with Ge concentrations from 8 to 22 at. % are ferromagnetic and have a high coercive force and magnetization that depend on thermal treatment. These facts determined the course of the investigations the results of which are reported in this paper.

MEASUREMENT METHOD AND SAMPLES

The samples we investigated were obtained by melting the appropriate quantities of Mn and Ge together in an induction furnace under an Ar atmosphere. For this we used electrolytic Mn (99.94%) and monocrystalline Ge with an impurity concentration of 10^{14} cm^{-3}. A series of samples weighing 30 g each, with concentrations of Ge from 2 to 22 at. %, every 2%, was prepared all at one time.

The magnetic properties were studied in static magnetic fields (to 12 kOe) in the temperature interval 77—1000° K and in strong pulsed fields (to 150 kOe) in the interval 77—400° K. The samples for the static-field measurements were small, weighing from 10 to 100 mg; those for the pulsed-field measurements were cylinders 2.2 mm in diameter and 10 to 12 mm long. The measurements in pulsed fields were made by the induction method described in[11].

The ordering anneal was carried out at 670° K in a crucible furnace, with periodic monitoring of the magnetization and electrical conductivity of the samples, to see if there was any effect of annealing time on these properties.

RESULTS

As already mentioned in the Introduction, the preliminary experiments showed that alloys with 8 to 22 at. % Ge were ferromagnetic, with a magnetization that depended on temperature and length of heat treatment. By trial, it was established that heat treatment at 670 K had the greatest effect. In Fig. 1 are typical hysteresis loops obtained in a sample of $Mn_{0.8}Ge_{0.2}$ at room temperature after several anneals at 670° K. It is
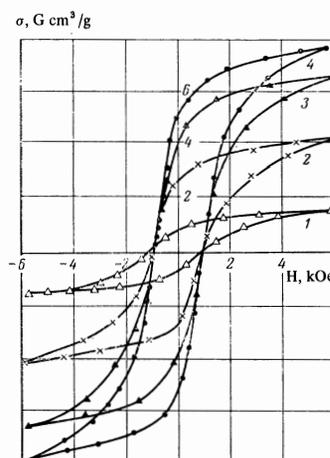

FIG. 1. Effect of heat treatment on the magnetic properties of a sample of $Mn_{0.8}Ge_{0.2}$. Temperature of anneal 670° K, time for the different curves: 1—10, 2—30, 3—100, 4—300 h.
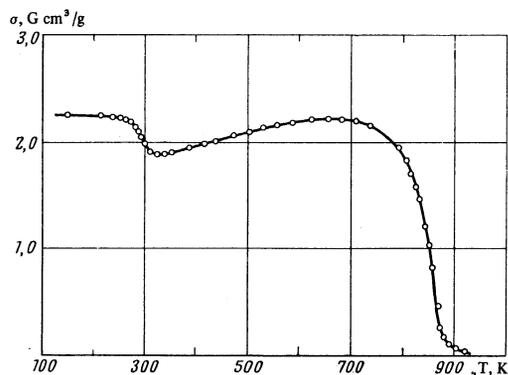
FIG. 2. Temperature dependence of the magnetization of a sample of $Mn_{0.84}Ge_{0.16}$.

FIG. 3. Change of the temperature dependence of magnetization of a sample of $Mn_{0.86}Ge_{0.14}$ for successive measurement cycles: ○—first cycle, ●—subsequent cycles;–○––after heating at 920°K.

seen that the magnetization increases steadily with annealing time. This suggests that the anneal produces ordering in the alloys.

The temperature dependence of the magnetization of these samples, as seen in Fig. 2, is complex. From 150 to 270°K the magnetization changes slightly with temperature; then, up to 350°K, we see a drop in magnetization followed by an increase. Finally, near 870°K the magnetization falls as sharply as in ferromagnetics near the Curie point. The samples with the other Ge concentrations behaved similarly; however, the growth of magnetization on initial heating may be sharper. This is clearly seen in Fig. 3, which gives several cycles of the temperature dependence of magnetization at H = 4 kOe for $Mn_{0.86}Ge_{0.14}$. The initial measurement in this figure is point A. From 370 to 820°K one sees a rapid increase in magnetization, with a subsequent drop-off from 820 to 870°K. Cooling and reheating give practically the same temperature dependence. It can be assumed that during the initial heating there occurs a phase transformation accompanied by an increase in magnetization. The Curie temperature of this phase is close to 870°K. However, a two-hour anneal at 920°K evokes a new phase transformation. The cooling curve for this new phase is labeled dcef in Fig. 3. Note the increase in magnetization at temperatures below 330°K, which is typical of this phase.

Figure 4 demonstrates that all the investigated samples in the 8 to 22 at.% range have similar temperature behavior. The curves in this figure were obtained in a magnetic field of 4 kOe after the samples had been annealed at 670°K for 100 h and then subjected to a two-hour heat treatment at 920°K.

Some idea of the magnetic structure of these alloys is given by the magnetization curves in strong magnetic fields shown in Fig. 5. At 77°K the magnetic structure is evidently collinear, whereas at 313°K the same sample shows a sudden increase in magnetization in strong field, which is characteristic only of a noncollinear structure.

No phase transformations of any kind were observed in alloys containing less than 8 at.% Ge. However, in the 2% alloy near 100°K, we see a maximum in magnetic susceptibility like that observed at these temperatures in α-Mn.[12] Alloys containing 6 at.% Ge are paramagnetic over the entire investigated temperature range.
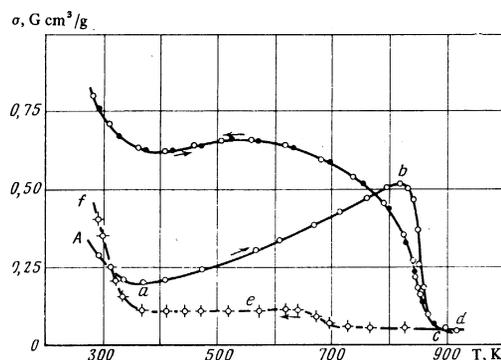
DISCUSSION

The change in the magnetic properties of these samples with temperature can be explained only on the basis of a specific model which in turn is based on the phase diagram for the investigated concentration range. Zwicker[13] was the first to investigate the portion of the diagram of interest to us. According to this phase diagram (see Fig. 6a), at small Ge concentrations the alloys keep the complex lattice of α-Mn, but beginning at 8 at.% Ge and up to the appearance of the compound $Mn_{3.25}Ge$, the alloys must be two-phase, consisting of a solid solution of γ-Mn with Ge and the compound $Mn_{3.25}Ge$. According to[11] this latter compound is antiferromagnetic with Neél temperature $T_N = 139°$ K, so that this phase should not give a significant contribution to the total magnetization of the samples. Hence, the reason for the appearance of ferromagnetism must be sought in the special properties of the solid solution of γ-Mn with Ge. Therefore, we must examine the γ-Mn lattice. The phase γ-Mn is antiferromagnetic with $T_N = 660°$ K.[14] Above T_N this phase has the face-centered cubic lattice (FCC), and below there is a tetragonal distortion of the lattice with c/a = 0.95.[15] In this state, the antiferromagnetic structure pictured in Fig. 7 is realized.

The distortion of the FCC lattice below the Neél temperature is due to the fact that with the appearance of order, that state in which 4 of the 12 nearest Mn atoms belong to the second coordination sphere corresponds to the energy minimum. This condition is satis-
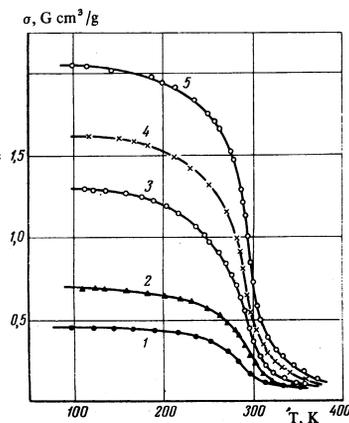

FIG. 4. Temperature dependence of the magnetization of a sample of $Mn_{1-x}Ge_x$ after a two-hour anneal at 920°K: 1—x = 0.1; 2—x = 0.14; 3—x = 0.16; 4—x = 0.18; 5—x = 0.20.
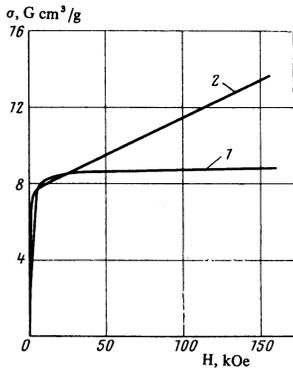
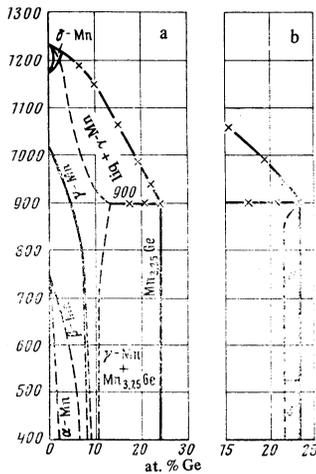FIG. 5. Magnetization curves for a sample of $Mn_{0.8}Ge_{0.2}$ in a high magnetic field: $1-77°K$; $2-313°K$.

FIG. 6. Phase diagrams of the Mn-Ge system: a—according to [13]; b—according to [16].

FIG. 7. Magnetic structure of γ-Mn.

ordered sample steadily increase with increasing concentration. However, along with this, increasing the Ge concentration ought to increase the relative content of the second phase $Mn_{3.25}Ge$, which is paramagnetic above 139°K. This means that the greatest magnetization should, according to the phase diagram be observed at some intermediate Ge concentration. Thus, the experimental results within the framework of our proposed model cannot be made to agree with the phase diagram obtained in[13], so that it is necessary either to reject the model or admit that this diagram is wrong.

An unambiguous conclusion was arrived at after analysis of the results of Ohoyama's work,[16] in which the phase diagram of the Mn-Ge system in the concentration range from 21.8 to 35.7 at.% was investigated. The phase diagram obtained in this work is shown partially in Fig. 6b. Ohoyama denies the existence of a compound $Mn_{3.25}Ge$ and says that there is a compound $Mn_{3.4}Ge$ (22.7 at.% Ge) which can have two modifications: a low-temperature one ϵ' and a high-temperature phase ϵ. The high-temperature phase is hexagonal and the other tetragonal. The parameters of the tetragonal phase ϵ' found in[16] are so close to the parameters of the tetragonal γ-Mn lattice that one automatically thinks they might be identical. The phase ϵ evidently actually corresponds to the compound $Mn_{3.4}Ge$. The supposition that ϵ' and γ-Mn are identical also is not contradicted by the experimental fact that the Curie temperature of solid solutions of γ-Mn with Ge and the shape of the magnetization vs. temperature curves, under comparable conditions, practically coincide with the results given by Ohoyama for ϵ'. If one introduces these correlations into the phase diagram (Fig. 8), then the complex

fied by a tetragonal distortion, when four Mn atoms whose spins are parallel are at a greater separation from each other than the remaining eight atoms with antiparallel spins.

If it is assumed that the Ge atoms are arranged in ordered fashion in the γ-Mn lattice, i.e., they occupy sites in one of the sublattices, then it becomes understandable that the antiferromagnetism of γ-Mn should be replaced by ferrimagnetism in solid solutions of γ-Mn with Ge. The change in properties shown in Fig. 1, as well as the change in electrical conductivity of the samples with degree of heat treatment (which is characteristic for ordered alloys and therefore not presented here), permits us to assert that the assumption of an ordered arrangement of Ge atoms in the γ-Mn lattice does not engender any doubt whatsoever and qualitatively explains the experimentally observed ferromagnetism. The relatively small magnetization of these samples can be explained only by assuming that inequivalently located Mn atoms have different magnetic moments.

The temperature dependence of magnetization observed in the initial heating for ordered samples (Fig. 3) is in general characteristic for a ferrimagnetic having a different temperature dependence of magnetization of the sublattices. But since upon cooling and subsequent heating the temperature dependence is again different, the growth of magnetization on the first heating must be associated with an irreversible phase transition. The phase diagram presented in Fig. 6a does not allow for such a transformation. The model we have introduced does not agree with this phase diagram as far as the concentration dependence of magnetization is concerned, either. The model requires that the magnetization of an
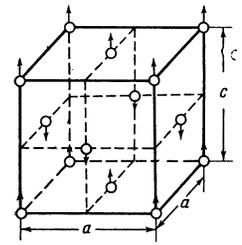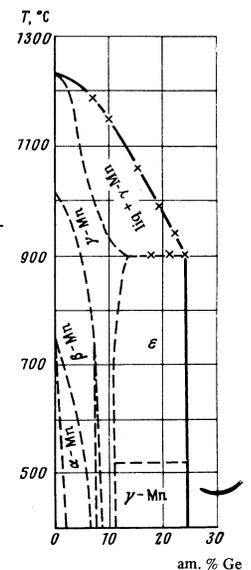

FIG. 8. Possible phase diagram for the Mn-Ge system.

temperature dependence of the magnetization of the investigated samples can be completely explained.

The high temperature phase ϵ is stabilized at high temperatures. Hence, immediately after melting and even after the ordering anneal there is a certain amount of high-temperature phase present in the samples. On the basis of the magnetic investigations of Mn$_3$Ge, Ohoyama[16] supposes that it contains a noncollinear magnetic structure with a Curie temperature of 350°K. This was confirmed by neutronographic investigations by Kouvell and Kasper,[17] who found a triangular magnetic structure at room temperature in Mn$_3$Ge. But since the phase ϵ corresponds to the compound Mn$_{3.4}$Ge or Mn$_3$Ge, the drop in magnetization seen in Fig. 2 between 270 and 350°K is occasioned by the decreasing magnetization of phase ϵ as it approaches its Curie temperature. If a transition from phase ϵ to γ-Mn is observed in the investigated samples, the magnetization ought to increase. This transition, most likely, is irreversible and so the increase in magnetization due to it ought to be observed only during the initial heating, which is clearly visible in Fig. 3 (curve ab). The possibility of the transition $\epsilon \rightarrow \epsilon'$ is pointed out in[18].

The effect of heat treatment at 920°K on the magnetic properties of these samples is a logical consequence of the phase transition γ-Mn $\rightarrow \epsilon$. After this transformation, which is observed during high-temperature heating, the samples should contain only the phase ϵ. At high temperatures, this phase is paramagnetic, and a sharp increase in magnetization should be observed only at temperatures below 350°K, when an ordered magnetic structure appears. Such a change in magnetization, as is seen in Fig. 4, is observed after heat treatment at 920°K in all the investigated samples. To completely justify our proposed model for the appearance and change of the magnetic properties of these samples it is necessary to show that the phase ϵ really has a noncollinear magnetic structure below the Curie temperature. For this we made measurements of the magnetization of several samples of different composition in intense pulsed magnetic fields. As is seen in Fig. 5, at 313°K the magnetization curves have a steep slope in strong fields, characteristic for the triangular structure. To explain so steep a slope by a paraprocess is hardly possible, since the increase of susceptibility of a paraprocess is observed ordinarily in the immediate vicinity of the Curie point and is diminished as the intensity of the magnetic field is increased, which we did not observe. At the same time, note that at 77°K complete saturation is observed in the same samples, so that a decrease in temperature must be accompanied by

a change in the magnetic structure of the phase ϵ. We are presently investigating the magnetic properties of this phase over a wide range of magnetic fields, and the results we have obtained thus far do not contradict the model we propose here.

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