Magnetic state of iron-nickel-manganese alloys

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The magnetic diagram of ternary Fe-Ni-Mn alloys is determined. Regions of existence of long-range ferro- and antiferromagnetic ordering are demonstrated. A transition region is shown to exist in which there is no long-range magnetic order but in which strong short-range ferro- and antiferromagnetic order occurs. This is due to the mixed nature of exchange interaction between atoms in the alloys. This leads to various types of short-range magnetic order in the statistical fluctuations of the atoms as functions of the immediate environment. The principal magnetic state of alloys with randomly distributed regions of short-range ferro- and antiferromagnetic order which interact via the disoriented spin zone may be called mixomagnetic, in contrast to spin glasses and mictomagnets.

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The considerable interest shown recently in the iron-nickel-manganese system is due, on the one hand, to the search for new alloys with anomalous linear-expansion coefficients (Invar alloys) and on the other hand to a desire to determine their magnetic state. The earliest investigations of this state were made by Kasper and Kouvel,[1] who investigated the magnetic properties and the magnetic structure of the alloys $(Ni_xFe_{1-x})_3Mn$. The magnetic state of the systems $Ni_3(Fe_xMn_{1-x})$,[2,3] $Ni(Fe_xMn_{1-x})$[4] and $Fe(Ni_xMn_{1-x})$[5] was also investigated. A Japanese group[6–8] has carried out a large set of physical investigations of alloys corresponding to the "Invar composition" $Fe_{0.65}(Ni_{1-x}Mn_x)_{0.35}$. Antonov *et al.*[9] investigated the magnetic properties of this system under pressure. Alloys with fixed ratios of the iron and manganese contents but with different nickel concentrations were investigated by Colling and Carr.[10]

All these investigations, however, were of sporadic character, and the amount of available experimental data did not make it possible to construct a complete diagram of the magnetic state of Fe-Ni-Mn alloys. A more systematic investigation was needed. This was precisely the purpose of the present study, in which we investigated about 80 alloys described by the formula $(Fe_cNi_{1-c-m})Mn_m$ and constituting a series of quasi-binary compositions with transitions from Fe-Ni to Ni-Mn and Fe-Mn via prescribed additions of manganese.

EXPERIMENTAL PROCEDURE

For the investigations we smelted, using pure components, seven systems of iron-nickel alloys with the following fixed manganese additives: 3.0, 5.0, 6.5, 9.0, 10.0, 15.0, and 20.0 at.%. The iron and nickel contents were varied in a wide range, as is seen from Fig. 1. Altogether we investigated about 100 alloys. Chemical analysis has shown that the composition deviations did not exceed 0.4 at.%. Ingots of the alloys were subjected to homogenizing annealing at 1100 °C for ~100 hours, followed by the preparation of the various samples. For the magnetic and neutron-diffraction measurements we used samples in the form of cylinders, with respective diameters 3 and 7 mm and heights 3 and 40 mm. For the Mössbauer investigations the alloys were rolled into foils 20–30 μ thick.

All the investigated alloys had in the initial state, quenched from 1050 °C, a face-centered cubic structure as determined by x-ray diffraction. The principal measurements of the Curie temperature were made with the aid of the Mössbauer effect by observing the vanishing of the paramagnetic absorption line in the course of temperature scanning, and the Néel points were determined by neutron diffraction with the aid of the temperature dependence of the antiferromagnetic reflection (110). The neutron-diffraction investigations were made with a diffractometer installed in one of the horizontal channels of the IVV-2 reactor. The sample temperature was varied with the aid of a specially prepared low-temperature cryostat, which made it possible to vary the temperature from that of liquid nitrogen to 800 °K. In the temperature range 4.2–80 °K the measurements were made in a helium dewar in helium vapor.

The magnetization of the alloys was measured with a vibration magnetometer and a pendulum balance from the temperature of liquid helium to room temperature in fields up to 16.5 kOe. The sample temperature was measured with a copper-iron thermocouple, with accuracy 1°. The magnetic susceptibility was measured with a Faraday balance from the temperature of liquid nitrogen to 1200 °K in a field ~10 kOe.

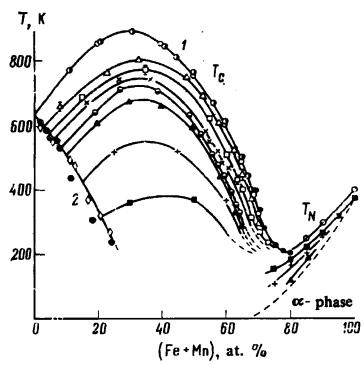

FIG. 1. Concentration dependence of the Curie and Néel points of $(Fe_cNi_{1-c-m})Mn_m$ alloys. 1—Fe-Ni[15]; 2—Ni-Mn[12]; Δ—3Mn, □—5Mn; ×—6.5 Mn, ●—9Mn; ▲—10Mn; +—15Mn; ■—20Mn; ∅—25Mn.[1]

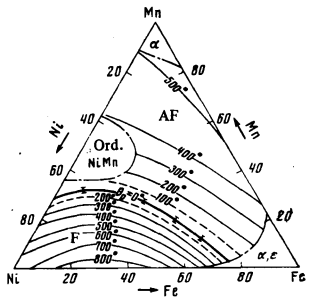

FIG. 2. Projection of the magnetic phase diagram of the ternary Fe-Ni-Mn system. The alloys between the dashed lines are those of the transition region.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Magnetic phase diagram

Figure 1 shows the concentration dependence of the Curie and Néel points of the investigated Fe-Ni-Mn alloys. The abscissas represent the sums of the concentrations of the iron and manganese, to make it possible to trace on one figure the variation of the magnetic state of alloys of different systems with fixed manganese contents. Attention is called to the lowering of the Curie points of iron-nickel alloys when manganese is added to them, and to the analogous lowering of the Néel points when the nickel content of the iron-manganese alloys is increased.

These peculiarities are due to the mixed character of the exchange interaction in Fe-Ni-Mn alloys, as was demonstrated by us experimentally by using inelastic scattering of neutrons by spin waves.[11,12] The following values were obtained for the exchange integrals between different pairs of atoms:

$$J_{Ni-Ni}=(52\mp3)\text{meV},\quad J_{Fe-Ni}=(38\mp2)\text{meV},\quad J_{Mn-Ni}=(44\mp3)\text{meV},$$
$$J_{Fe-Fe}=-(8\mp1)\text{meV},\quad J_{Fe-Mn}=(17\mp2)\text{meV},\quad J_{Mn-Mn}=-(285\mp30)\text{meV}.$$

We see that two out of the six interactions (iron–iron and manganese–manganese) are negative and differ greatly in absolute magnitude. Therefore the contributions of the corresponding interactions to the combined exchange energy depend to a considerable degree on the concentrations of the components.

Indeed, the lowering of the Curie points of Fe-Ni alloys following addition of manganese is due to the increased antiferromagnetic contribution to the summary exchange energy, while the lowering of the Néel points of the iron-manganese alloys following addition of nickel is due to the increased ferromagnetic contribution. In alloys with ferromagnetic and antiferromagnetic long-range order, however, the exchange contributions of opposite sign are small enough and lead only to magnetic inhomogeneities (spin fluctuations), just as in the case of Invar iron-nickel alloys.[13,14] In a certain range of compositions, however, the contributions become equalized, and the competition between the negative and positive interactions causes the system to lose its long-range magnetic order.

On the basis of the results of the present experiments and the data on the binary systems Fe-Ni,[15] Fe-Mn[16–18] and Ni-Mn[19] we plotted the magnetic phase diagram of ternary Fe-Ni-Mn alloys, a projection of which is shown in Fig. 2. In the left (nickel) corner of the diagram there is a larger region of ferromagnetic alloys, while in the upper (manganese) corner there are many antiferromagnetic alloys. Between them there exists a transition region, bounded by the isotherms $T_2=200$ °K on the ferromagnetic-alloy side and $T_n=100$ °K on the antiferromagnetic side. We were unable to determine reliably the temperatures of the phase transitions for the transition-region alloys, since the temperature dependences of the magnetization and of the amplitude of the γ-resonance paramagnetic line were strongly smeared out near the assumed Curie points, and no sufficiently well pronounced maxima were observed on the curves of the magnetostriction of the paraprocess and of the critical scattering of the neutrons. In addition, we observed no antiferromagnetic reflections, within the limits of experimental error (~10%), on the neutron diffraction patterns of the transition-region alloys, at liquid-helium temperatures, an indication of the absence of long-range magnetic order. However, the observed large magnetic small-angle scattering of the neutrons indicated a strong magnetic inhomogeneity of the system and the presence of regions of short-range magnetic order with dimensions (~10–30) Å.

It seems to us that in these regions there is predominantly either antiferromagnetic or a ferromagnetic short-range order. On the one hand, this is due to the fact that in completely disordered alloys there are realized statistical fluctuations such that the manganese or iron atom have in their nearest environment a certain critical number X_{Mn} or X_{Fe} of atoms of the same sort, at which predominantly antiferromagnetic order sets in, by virtue of the conditions $J_{Mn-Mn}<0$ and $J_{Fe-Fe}<0$. As shown in[12], $X_{Mn}=3$ and $X_{Fe}=12$. On the other hand, in the statistical fluctuations of nickel surrounded predominantly by nickel, or iron, or manganese, when the number of atoms is smaller than the critical value, ferromagnetic order is predominantly established. Spanning several coordination spheres, one type of order can go over into the other via intermediate states.

The equality of the positive and negative contributions to the total exchange energy leads to a special state of the alloy in the intermediate region, which is characterized by the vanishing of the paramagnetic Curie point. On the triple magnetic phase diagram of Fe-Ni-Mn alloys (Fig. 2), the series of these alloys is marked by the thick line $\theta_p=0$. Deviation from this line in one direction or another leads to an increase of the number and dimensions of the corresponding regions of the short-range ferromagnetic or antiferromagnetic order, which in essence are nuclei of phases with long-range magnetic order.

2. Magnetic properties of transition-region alloys

The most characteristic properties of alloys of this region are illustrated by an example with three compositions with iron contents $50(\theta_p>0)$, $55(\theta_p=0)$ and $60(\theta_p<0)$ at.% and a constant manganese content 15 at.%. We note that all the statements made below will pertain equally well to alloys of any analogous composition on the triple diagram.

First, the alloys of the transition region have charac-

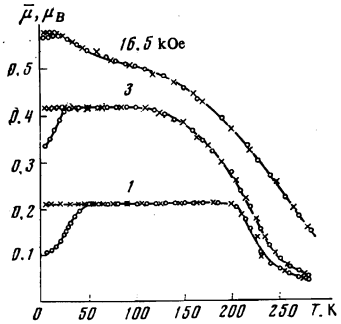

FIG. 3. Temperature dependence of the average magnetic moment per alloy atom, measured in different magnetic fields for the alloy 50Fe35Ni15Mn; o—cooling of the sample without a magnetic field; ×—cooling in a magnetic field of the corresponding strength.

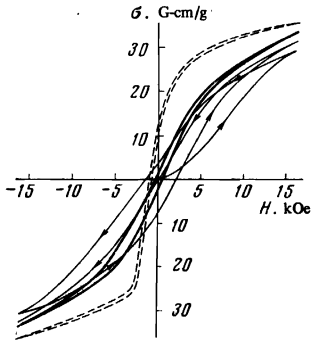

FIG. 5. Magnetization-reversal curves for the alloy 55Fe30Ni15Mn at 4.2 °K. The thick line shows the hysteresis loop obtained after ten additional smooth cycles of magnetization reversal from a 15.7 kOe field. The dashed hysteresis loop was obtained for the alloy at 4.2 °K after cooling in a magnetic field of 15.7 kOe.

teristic temperature dependences of magnetization, measured in different magnetic fields. Their main feature is the presence of a clearly pronounced low-temperature anomaly, which vanishes either with increasing measurement field, or after preliminary cooling of the sample to 4.2 °K in a magnetic field (Figs. 3 and 4). This characteristic temperature dependence of the magnetization curve for alloys of the transition region can be attributed to the coexistence of ferromagnetic and antiferromagnetic short-range order regions. For example, for the alloy 55 Fe($\theta_p = 0$) at 0 °K, the magnetic system is characterized by zero magnetization, inasmuch as any selected direction has no spontaneous moment, because of the random distribution of the magnetic regions in the crystal. With increasing temperature, the exchange energy of the antiferromagnetically interacting pairs of atoms becomes comparable with kT_N^* (at 20–40 °K), and the regions of the antiferromagnetic short-range order go over into the paramagnetic state. The temperature, however, is still too low to upset the positive coupling in the ferromagnetic clusters, which are the ones which induce the magnetization in the magnetic measurement field. Further increase of the temperature disrupts also the ferromagnetic short-range order.

When the sample is cooled in a sufficiently strong magnetic field, the mimimum gives way to a maximum of the magnetization, the largest value of which can be reached as a result of multiple gradual sample magnetization reversal from a field $+H_{max}$ to $-H_{max}$. This is accompanied by the phenomenon of magnetic accomodation, which is illustrated in Fig. 5. The thin line in this figure shows the magnetization-reversal curves of three cycles, while the thick line shows the hysteresis loop after additional application of ten cycles of smooth magnetization reversal in a maximum field 15.7 kOe. The obtained hysteresis loop is symmetrical enough and is not shifted relative to the origin. An entirely different type of hysteresis loop is obtained after cooling the alloy to 4.2 °K in a magnetic field. It becomes much narrower and is shifted by 1.5 kOe (shown dashed in Fig. 5). In this case there is no low-temperature anomaly on the $\sigma(T)$ curves plotted in a magnetic field (Figs. 3 and 4).

Thus, at 4.2 °K, depending on the cooling method, two different types of hysteresis loops are observed for one and the same alloy. To the contrary, at liquid-nitrogen temperature the $\sigma(T)$ and $\sigma(H)$ curves do not depend on the cooling method (Fig. 6). In the latter case, the shapes of the $\sigma(H)$ curves in the absence of a hysteresis loop (Fig. 6, curve 1) suggests that the superparamagnetic state is realized in the alloy, as is evidenced also by the Mössbauer spectra shown in Fig. 7. For alloys with 55 and 60% Fe at 77 °K there is a single line, which is slightly broadened in comparison with the paramagnetic state, and a weakly pronounced hyperfine splitting is observed only for the alloy 50 Fe($\theta_p > 0$).

The alloy state characterized by a displaced hysteresis loop (unidirectional anisotropy phenomenon) is due, as is well known, [20] to the coexistence of systems with ferromagnetic and antiferromagnetic order. On the other hand, a thermodynamic analysis of a magnetic state characterized simultaneously by ferromagnetic and antiferromagnetic vectors, carried out by Vlasov and

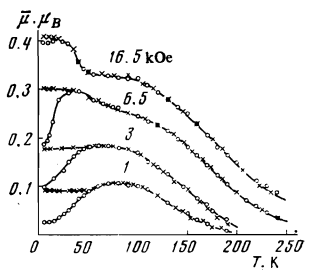

FIG. 4. The same as in Fig. 3, but for the alloy 55Fe30Ni15Mn.

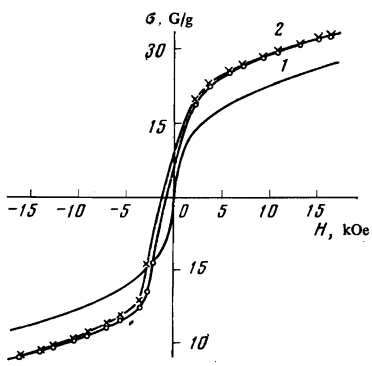

FIG. 6. Magnetization-reversal curves for the alloys 55Fe30Ni15Mn, cooled in a magnetic field 15.7 kOe, obtained at different temperatures: 1—77 °K, 2—4.2 °K.

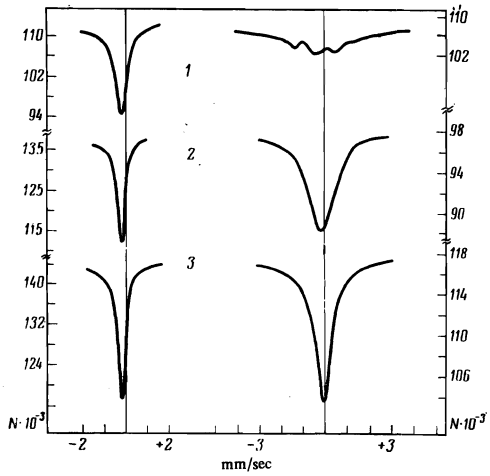

FIG. 7. Mössbauer spectra of alloys obtained at different temperatures: a) room, b) liquid nitrogen. 1) 50Fe35Ni15Mn; 2) 55Fe30Ni15Mn; 3) 60Fe25Ni15Mn.

Mitsek,[21] shows that a displacement of the hysteresis loop should be observed in such a system. In order for a displaced hysteresis loop to appear, however, the necessary condition is the presence of a relatively sharp boundary between the ferromagnetic and antiferromagnetic ordering in the clusters. When the alloys are cooled without a magnetic field there is apparently no such boundary, which appears when the alloy is cooled in the presence of a field. It is probable that the magnetic field contributes, during the course of cooling the system, to the formation of stable ferromagnetic and antiferromagnetic clusters with a sharply pronounced boundary.

3. Principal magnetic state

In alloys of the Fe-Ni-Mn system one can separate three principal types of magnetic state: 1) ferromagnetic, 2) antiferromagnetic, and 3) amorphous. In the first two, the principal state is essentially collinear; however, when the alloys approach the transition region, there appear spin fluctuations (of the paramagnetic type), the number of which increases with increasing iron and manganese concentration in the ferromagnetic region and with increasing nickel concentration in the antiferromagnetic region. In the transition region, the long-range magnetic order vanishes and amorphous magnetism is realized in the alloys.

Two concepts are used at the present time to decribe the principal magnetic state of amorphous magnets, spin glass[22] and mictomagnetism.[23] In spin glass, each individual spin is in a random molecular field H_i, and the system as a whole is characterized by a certain field distribution $\rho(H_i)$. As $T \to 0$ °K the spin system of this state, in contrast to the ordinary paramagnetic state, is more rigid with respect to an external magnetic field, as is manifest in the deviation of the reciprocal susceptibility from the linear law at low temperatures. Spin glass is observed in dilute alloys, and its cause is the oscillatory character of the exchange interaction, described by the Ruderman-Kittel-Kasuya-Yosida mechanism. The term "mictomagnetism" was coined by Beck[23] to define a larger class of amorphous magnets that contain in the principal magnetic state "frozen" ferromagnetic clusters that are randomly distributed in a maximum of spin glass. The mictomagnetic state has by now been observed in the alloys Cu-Mn, Au-Fe, and Mn-Pd.[24]

The principal magnetic state of the Fe-Ni-Mn alloys of the transition region investigated here cannot be described in the framework of either the spin glass or the mictomagnetism approaches. Indeed, according to Edward and Anderson,[25] for the spin-glass state ($\theta_p = 0$) we have the following conditions:

$$\left(\frac{1}{\chi}\right)_{cc} > \left(\frac{1}{\chi}\right)_{p} \quad \text{at} \quad T<T_c \quad \text{and} \quad \left(\frac{1}{\chi}\right)_{cc} = \left(\frac{1}{\chi}\right)_{p} \quad \text{at} \quad T \geqslant T_c.$$

As seen from Fig. 8, in our case we have in a large temperature range $\chi^{-1} < (\chi^{-1})_p$. Moreover, this situation is observed not only for alloys with $\theta_p = 0$, but also for alloys with $\theta_p < 0$. Nor do they agree with the definition of mictomagnets, since the latter have only ferromagnetic clusters. It seems to us that Fe-Ni-Mn alloys of the transition region have a magnetic principal state which can be called "mixomagnetic" (from the word mixed).[26] This state is characterized by the presence of frozen ferromagnetic and antiferromagnetic short-range order regions that interact with one another via a zone of disoriented spins. The main cause of this state is the mixed character of the exchange interaction between the individual pairs of atoms, which is direct and short-range, and is typical of concentrated alloys, differing by the same token from spin glasses, which are observed mainly in sufficiently diluted alloys in which indirect long-range exchange interaction is present.

Even though the terms "micto" and "mixo" equally stem from "mixed," nonetheless they describe different magnetic states of amorphous magnets. In the former case is meant the state of mixing of ferromagnetic clusters with a spin-glass matrix, and in the latter case the presence of a mixed exchange interaction between the atoms in concentrated alloys, which leads to coexistence of mixed regions short-range ferromagnetic and antiferromagnetic order.

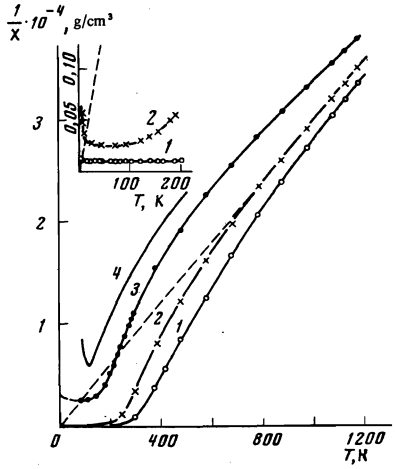

FIG. 8. Temperature dependence of the reciprocal susceptibility for the following alloys: 1) 50Fe35Ni15Mn, 2) 55Fe30Ni15Mn, 3) 60Fe25Ni15Mn, 4) 65Fe20Ni15Mn.[6] The dashed lines is the extrapolated section of the reciprocal susceptibility satisfying the Curie law ($\theta_p = 0$).

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Cross section for recombination of an electron with a positively charged center in a semiconductor

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A formula for the total cross section for the recombination of a conduction electron with positively charged center in a semiconductor is derived under the assumption that the excess electron energy is transferred to acoustic phonons. The cross section is $2kT/ms^2$ times greater than that obtained in the widely cited paper by M. Lax [Phys. Rev. 119, 1502 (1969)] and has a different power-law dependence on the temperature. In contrast to Lax's conclusion that capture of electrons with energies $\sim kT$ by highly excited levels of the center with a binding energy $U \sim kT$ is predominant in the recombination process, it is shown that the main contribution to the total recombination cross section is made by capture of electrons with an energy near ms^2 by levels with a binding energy close to ms^2.

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INTRODUCTION

When a conduction electron is captured by a positively charged center, it should transfer a large energy (on the order of the binding energy) to the lattice. In many cases, the principal channel through which energy is lost is the interaction with acoustic phonons, wherein the electron loses in each collision only a small fraction of its kinetic energy $\sim \varepsilon (8ms^2/\varepsilon)^{1/2}$ (ε is the electron kinetic energy, m is its effective mass, and s is the speed of sound in the crystal). In a well known paper, Lax[1] proposed a "cascade capture" model: the electron is captured by one of the highly-excited levels of the recombination center, which are quasi-continuously arranged, and "rolls down" over them, emitting acoustic phonons. For the case of a gas-discharge plasma, a similar problem concerning the capture of an electron by a positive ion in the presence of neutral atoms was solved by Pitaevskiĭ by another method.[2] We have adapted Pitaevskiĭ's procedure to the case of recombination of a conduction electron in a semiconductor by a charged center, with emission of acoustic phonons, and