Magnetic phase diagram and features of the spin-glass state in $Fe_{65}Ni_{35-x}Cr_x$ alloys

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The static magnetic properties and differential magnetic susceptibilities of alloys of the quasibinary tie-line of $Fe_{65}Ni_{35-x}Cr_x$ are investigated at temperatures between 4.2 and 500 K. It is shown the spin-glass state is not a property of the classical Invar $Fe_{65}Ni_{35}$, and occurs in $Fe_{65}Ni_{35-x}Cr_x$ systems only if $x \geqslant 5$. It is indicated that near the critical density $x_c = 14$, at which the long-range magnetic order vanishes, the low-temperature magnetic properties of the investigated alloys, on the one hand, have much in common with the properties of dilute spin glasses, and on the other they exhibit a number of substantial differences. A more accurate magnetic phase diagram is obtained for the $Fe_{65}Ni_{35-x}Cr_x$ system.

1. INTRODUCTION

The magnetic state of the classical "Invar" $Fe_{65}Ni_{35}$ has been attracting the interest of many investigators during the last two decades. It was noted in Ref. 1 that the intensity I_{sas} of small-angle scattering by the alloy $Fe_{65}Ni_{35}$ increases anomalously at temperatures lower than 50 K. This was attributed by the authors to a transition of certain regions of the alloy to the spin-glass state. Mokhov,[2] however, did not observe this effect. On the other hand, the high-field susceptibility χ_p and the longitudinal magnetoresistance $1/R\,(\Delta R/\Delta H)$ of Invar have a weak maximum at approximately 35 K.[3,4] It is not clear whether the anomalies of I_{sas}, χ_p, and $1/R\,(\Delta R/\Delta H)$ are connected with the onset of the spin-glass state or are determined by other factors. Important information on this subject can be obtained by investigating the differential reversible susceptibility and the low-field static magnetic properties. These procedures are usually employed to identify the spin-glass state in dilute alloys.

Besides $Fe_{65}Ni_{35}$, we investigated in the present study other alloys (with nickel contents 5, 10, and 15 at. %) that enter in the quasibinary tie-line of $Fe_{65}Ni_{35-x}Cr_x$. When the chromium concentration in this system is increased, the ground state of the alloys (at 0 K) changes from ferromagnetic to that of "cluster" spin glass (at $x > x_c = 14$, Refs. 2 and 5). Comparing the magnetic properties of $Fe_{65}Ni_{35-x}Cr_x$ alloys of various compositions (going in succession from $x \geqslant x_c$ to $x = 0$), we can easily determine whether the spin-glass state is a property of classical Invar.

Another task of the present study was to determine more accurately the magnetic phase diagram of the $Fe_{65}Ni_{35-x}Cr_x$ system. The magnetic diagram of this system was constructed in Refs. 2 and 5 on the basis of neutron-diffraction and magnetic-measurement data. It was assumed that in alloys with $x \sim x_c$ the formation of spin glass begins at $T_f \approx 100$ K. A study of the low-field susceptibility of alloys with close composition ($Fe_{66}Ni_{10}Cr_{18}$, Ref. 6 and $Fe_{64}Ni_{16}Cr_{20}$, Ref. 7), however, yielded substantially lower values of the freezing temperature T_f (20–25 K).

Finally, the question of the differences in the behavior of concentrated spin glasses based on fcc-Fe and of classical spin glasses of the RKKY type has hardly been considered before.

2. PROCEDURE

The magnetic properties of alloys of the $Fe_{65}Ni_{35-x}Cr_x$ system were studied in the temperature range 4.2–600 K. Magnetic fields up to 1 kOe were produced with a copper-wire solenoid. The differential reversible magnetic susceptibility χ was measured with the setup described in Ref. 8. The amplitude of the alternating magnetic field was 0.02–0.05 Oe. A special device was used to demagnetize the samples.

It should be noted that an important factor in the study of the differential magnetic susceptibilities of alloys having long-range magnetic order is the sample shape. The samples usually employed are cylinders with length-to-diameter ratio l/d not more than 5–8 (see, e.g., Refs. 6 and 9), and with a sufficiently large demagnetizing factor. Our investigations of samples with different values of l/d have shown that at $l/d < 10$ the differential-susceptibility curves become greatly distorted. We have therefore measured the susceptibilities of samples with $l/d = 20$ ($l = 100$ mm, $d = 5$ mm).

In the study of the static magnetic properties we used the Weiss-Forrer method. Particular attention was paid to a thorough cancellation of the vertical component of the geomagnetic field (to within not more than ± 0.003 Oe). The temperature was stabilized with a VRT-2 regulator accurate to ± 0.1 K. The errors in the measurements of the differential susceptibility and magnetization were $\pm 5\%$ and $\pm$(3–5)% respectively. The samples were fused by the Central Research Institute for Ferrous Metals in a vacuum furnace, using high-purity ingredients. The chromium content in the alloys was 0, 5, 10, and 15 at. %, the iron content $(65 \pm 0.3)\%$, and the remainder was nickel (the total impurity content did not exceed 0.2–0.3%). The samples were homogenized at 1000 °C for 8 hours and cooled in the furnace.

3. EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependences of the differential magnetic susceptibilities of the $Fe_{65}Ni_{35-x}Cr_x$ system alloys (constant magnetic fields H of various intensities

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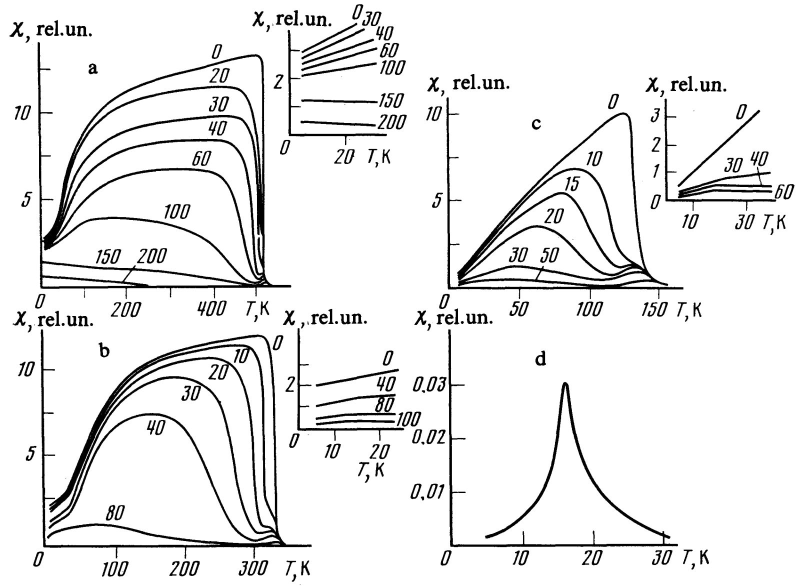

FIG. 1. Temperature dependences of the differential magnetic susceptibility of $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x = 0$ (a), 5 (b), 10 (c) and 15 (d). The numbers on the curves indicate the value of the external constant field in Oe.

were additionally applied in the course of the measurements). The temperature dependence of the susceptibility $\chi(T)$ of the alloy with $x = 15$ has a form typical of spin glasses (Fig. 1d). The $\chi(T)$ curves of the alloys with $x = 5$ and 10, measured in the presence of a field H of sufficient intensity, show two maxima, one at low temperatures and the other in the vicinity of the Curie point. The low-temperature maximum of the susceptibility is customarily attributed to the onset of the spin-glass state.[6,9] The low-temperature maximum of χ is quite weakly pronounced for the $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x = 5$ or 10, and is absent for Invar ($x = 0$). The low-temperature sections of the susceptibility curves are shown in greater detail in the insets of Fig. 1. It can be seen that at $H \gtrsim 40$ Oe and below 20 K the $\chi(T,H)$ dependence of Invar differ fundamentally from that of alloys containing 5 and 10 at. % chromium. By determining the freezing temperature T_f of the spin glass from the position of the low-temperature maximum of the differential susceptibility (of the alloy with $x = 15$ at $H = 0$ and of the alloys with $x = 10$ and 5 at $H \geqslant 40$ Oe) we obtain for T_f the respective values 16, 17, and 12 K.

The temperature dependences of the low-field magnetization of invar and of the $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x \geqslant 5$ also differ. The alloys containing 5–15 at. % chromium, cooled in the absence of a magnetic field and then heated from 4.2 K, have magnetization curves with maxima. If the preliminary cooling of the sample was in the presence of a magnetic field H_0, the maximum of the magnetization was much weaker ("thermomagnetic accommodation," Ref. 10). The low-field magnetization has a maximum at the same temperature as the low-temperature maximum on the $\chi(T,H)$ curve (see Figs. 1b,c) and corresponds to the spin-glass freezing point T_f. The low-field magnetization of Invar ($x = 0$) decreases monotonically when heated from 4.2 K, and there is no thermomagnetic accommodation.

The described features of the magnetization behavior are typical of spin glasses and are customarily attributed to the metastability of the magnetic state below T_f.[11–12] The disequilibrium of the magnetic state usually manifests itself most strongly in aftereffects. Indeed, we have observed in the $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x = 5$ to 15 a substantial magnetic viscosity (no magnetic aftereffect was observed, however in the alloy with $x = 0$). We measured the time dependence of the isothermal remanent magnetization M_r. In a period from 20 to 1000 sec from the removal of the magnetic field the time dependence of M_r is satisfactorily described by the logarithmic relation

$$M_r(t) = M_r(0) - S \ln t, \tag{1}$$

where $S = \ln(1/\tau)$ and τ is the average relaxation time.[13–15] From the slopes of the straight lines $M_r = f(\ln t)$ we determined the coefficient S (Fig. 2). For $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x = 10$ and 15, S has a maximum at $T/T_f \approx 0.5$–0.6 (a similar behavior of S was observed in the "classical" AuFe spin glasses[11]). As for the alloy with $x = 5$ (Fig. 2a), its maximum of S probably corresponds to a temperature lower than 4.2 K.

In the theory of magnetic aftereffect[13–15] the temperature dependence of the coefficient S is determined by the form of the distribution function of the energy barriers that hinder the change of orientation of the cluster magnetic moments. The form of the distribution function of the energy barriers (of the temperatures T_f^i at which the magnetic mo-

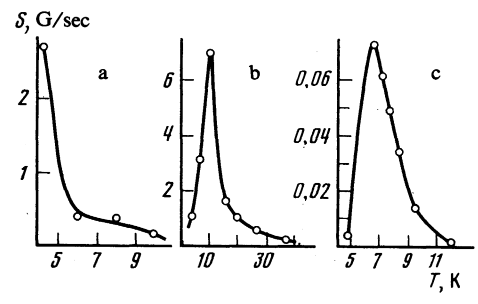

FIG. 2. Temperature dependences of the coefficient S from expression (1) for alloys with $x = 5$ (a), 10 (b), and 15 (c).

ments are blocked) can be determined by investigating the spectrum of the partial remanent magnetizations. We investigated these spectra by a procedure described in Refs. 11 and 16. In alloys with sufficient chromium content (10–15 at. %) we again observed an analogy with the properties of typical AuFe spin glasses.[11] In particular, the spectrum of the partial remanent magnetizations of the alloys $Fe_{65}Ni_{25}Cr_{10}$ and $Fe_{65}Ni_{20}Cr_{15}$ is of the same form as the temperature dependence of the coefficient S. No unambiguous form of the partial residual magnetizations was obtained for the alloy with $x = 0$. Ferromagnetic clusters of finite size therefore do not exist in invar.[16]

In $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x \sim x_c$, below the freezing temperature T_f, strong increases take place in the coercive force H_c, in the shift ΔH of the hysteresis loop (after preliminary cooling in a magnetic field H_0) (Fig. 3), and also in the thermoremanent magnetization.

The hysteresis loop of $Fe_{65}Ni_{20}Cr_{15}$ cooled from high temperatures to 4.2 K in the absence of a magnetic field has an unusual shape. The magnetization curve $M(H)$ is that typical of ferromagnets, but when H is subsequently decreased to zero the resultant remanent magnetization is directed opposite to the applied field. On the contrary, magnetization in a "negative" magnetic field leads to formation of "positive" remanent magnetization (Fig. 4a). After repeated magnetization reversals at 4.2 K the hysteresis curve remains "inverted." On heating above 8–10 K, however, the hysteresis curve of $Fe_{65}Ni_{20}Cr_{15}$ acquires the normal shape (Fig. 4b). No "inversion" of the hysteresis loop was observed for $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x = 0$ to 10.

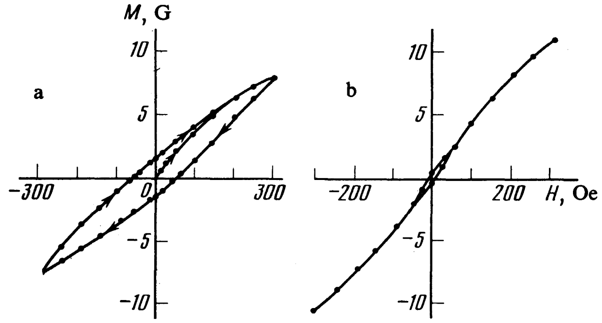

FIG. 4. Hysteresis loops of $Fe_{65}Ni_{20}Cr_{15}$ alloys at 4.2 (a) and 15 K (b).

4. DISCUSSION

From the results of the investigations of the differential magnetic susceptibility, of the low-field magnetization, and of the magnetic after effect, the magnetic phase diagram of the quasibinary $Fe_{65}Ni_{35-x}Cr_x$ tie-line can be represented in the form shown in Fig. 5. The spin-glass freezing temperatures T_f do not exceed 20 K in this system, in satisfactory agreement with the data of Refs. 6 and 7. The minimum on the temperature dependence of the intensity of small-angle neutron scattering[2,5] corresponds to substantially higher temperatures and therefore cannot be used to estimate T_f.

The absence of a low temperature maximum from the differential-susceptibility curves (measured in the presence of a magnetic field, Fig. 1), of the magnetic aftereffect, and of thermomagnetic accommodation in the case of the Invar $Fe_{65}Ni_{35}$ suggests that no spin-glass state is realized in this alloy. The anomalies of the high-field susceptibility and of the magnetoresistance of Invar in the interval 30–35 K (Refs. 3 and 4) are apparently due to the presence of individual spins that are oriented, even at magnetic saturation of the alloy, antiparallel to the predominant direction of the magnetization. The number of such "inverted" spins is small, and they make naturally no noticeable contribution to the low-field susceptibility (which is determined mainly by the displacement of the domain walls). In high magnetic fields, however, the sample is in a nearly single-domain state, and the contribution to the susceptibility from the inverted spins is substantial. The hypothesis that invar alloys contain individual spins oriented counter to the predominant magnetization direction was first advanced by Kondorskiĭ.[17] This state was named latent antiferromagnetism and was attributed to the fact that the exchange integral $J_{\text{Fe-Fe}}$ is negative. The results of our investigations of low-field magnetic susceptibility, and also their comparison with data[3] on the high-field susceptibility of the Invar $Fe_{65}Ni_{35}$, support Kondorskiĭ's

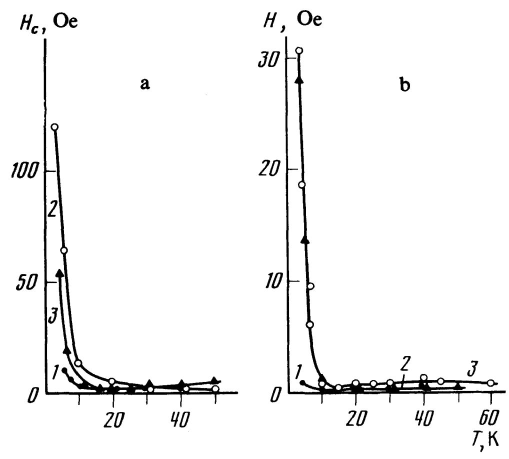

FIG. 3. Temperature dependences of the coercive force H_c (a) and of the shift ΔH of the hysteresis curve (b) of $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x = 5$ (1), 10 (2) and 15 (3). The shift of the hysteresis loop was measured after cooling in a magnetic field $H_0 = 50$ (curves 1 and 2) and 20 Oe (curve 3).

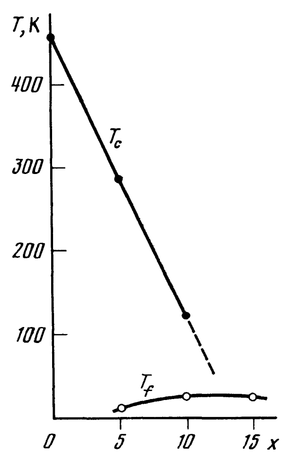

FIG. 5. Magnetic phase diagram of the system $Fe_{65}Ni_{35-x}Cr_x$.

latent-antiferromagnetism hypothesis.

The spin-glass state is apparently a characteristic of $Fe_{65}Ni_{35-x}Cr_x$ alloys with chromium content 5 and more at. %. This is indicated by the presence of a low-temperature maximum on the plots of the differential susceptibility $\chi(T,H)$ (Fig. 1) and of the low-field magnetization of alloys with $x \geqslant 5$, and by the strong dependence of their magnetization on the time (Fig. 2). This assumption agrees with results of calculations within the framework of the "cluster" model of a concentrational magnetic transition.[18] It is probable that no long-range order occurs in the $Fe_{65}Ni_{35-x}Cr_x$ system. This follows both from the results of neutron-diffraction measurements[2,5] and from the form of the concentration dependence of the coefficient of the contribution, linear in temperature, to the low-temperature heat capacity γ (Ref. 18). The point is that Cr atoms produce in an fcc lattice a "negative spin polarization" and hinder the onset of either ferromagnetic or antiferromagnetic long-range order.[10]

In the vicinity of the critical concentration $x_c = 14$ the state of the alloys is obviously characterized by the presence of not only ferro- but also antiferromagnetic correlations.[5,19] This explains some difference between the low-temperature magnetic properties of alloys with $x = 5$ and $x = 10$ or 15. The increase of coercive force (Fig. 3) and of the remanent magnetization of an alloy with 5 at. % chromium is observed starting with T_f. A similar behavior of the remanent magnetization is a feature of "classical" spin glasses of the AuFe type.[11] For the alloys with $x = 10$ and 15, the temperature dependences of the shift of the hysteresis loop and of the residual magnetization show an inflection near $0.5T_f$ (Fig. 3). This difference is apparently due to the fact that in alloys with 10 or 15 at. % chromium an important role is played by antiferromagnetic (AFM) correlations, which are formed at lower temperatures than the ferromagnetic (FM) ones. AFM clusters are characterized by higher values of the crystallographic anisotropy constant than FM ones ($K_a^{AFM} \gg K_a^{FM}$). As a result, when the AFM of the clusters sets in the coercive force and the shift of the hysteresis loop should increase, as is indeed observed in experiment (Fig. 3).

The reversal of the hysteresis loop (Fig. 4) is probably also due to formation of AFM clusters. For this effect to occur, however, it is necessary that the number of AFM clusters and the value of the anisotropy constant K_a^{AFM} be large enough (as in the case for the $Fe_{65}Ni_{20}Cr_{15}$ alloy). It is important to note that we succeeded in observing for the first time the reversal of the remanent magnetization M_r in isothermal magnetization reversal, and not only after "exposing" the magnetic field in a definite temperature interval (as, e.g., in Refs. 20 and 21). In the case of isothermal reversal of M_r, however, it is apparently possible to use the theory developed by Néel for self-reversal of remanent magnetization (what is most readily realized is the exchange self-reversal mechanism 14).

5. CONCLUSION

Our investigations led to a more accurate magnetic phase diagram of the $Fe_{65}Ni_{35-x}Cr_x$ system. The spin-glass state sets in at $x \geqslant 5$, but the freezing temperatures T_f are considerably lower than previously proposed.[2,5] Invar ($x = 0$) does not have properties indicative of spin glass, but is characterized by a state of latent antiferromagnetism (which manifests itself only in measurements in high magnetic fields).

The spin-glass state in FeNiCr alloys has much in common with the analogous state in dilute alloys. At the same time, at temperatures below $0.5T_f$, effects appear hitherto not observed for "classical" spin glasses (reversal of the hysteresis loop, inflection on the temperature dependences of the coercive force, shifts of the hysteresis loop and of the remanent magnetization, and others). The reason for these effects is apparently that the spin-glass state in concentrated alloys is characterized by the presence of not only ferromagnetic but also antiferromagnetic correlations.

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