Phase transformation anomalies at the Curie point during the concentration magnetic transition

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The behavior of the magnetic susceptibility χ_p of a para-process and the specific heat and coercive force is studied near the Curie point T_C for the quasibinary cut alloys $Fe_{65}Ni_{35-x}Cr_x$. The thermodynamic characteristics become singular near T_C when x approaches the critical value $x_c \approx 13$ for which the alloy loses its ferromagnetic properties. The specific heat anomaly at the Curie point degenerates, the temperature corresponding to peak magnetic susceptibility starts to depend anomalously strongly on the magnetic field, and the power law for χ_p breaks down in a larger interval about T_C. The critical index γ' of the susceptibility decreases as $x \to x_c$. The critical behavior of the alloys for $x \lesssim x_c$ is attributed to an increased role played by fluctuations in the magnetization.

1. INTRODUCTION

Much attention has been focused recently on magnetic phase transitions in inhomogeneous systems. It has been found that if some of the positive exchange bonds in a ferromagnet are randomly reversed (replaced by their negatives), the thermodynamic properties are affected much more strongly than would be the case if the system were simply (diamagnetically) diluted.[1–3] In addition, it has been shown that the magnetic phase transition at the Curie point need not be a transition of the second kind if the exchange interaction is of variable sign or fluctuates widely in the alloy; specifically, a phase transition of the first kind or a "blurred" phase transition may occur.[4–6] However, not enough experimental information is available concerning the nature of the phase transitions in inhomogeneous magnets.

The present paper is a continuation of a series (cf., e.g., Refs. 3, 7, 8) that deals with phase transitions in ferromagnetic 3*d*-metals alloyed with antiferromagnetic materials. We studied fcc quasibinary cut alloys of composition for which the ground state changes from ferromagnetic to a "spin glass" state at the critical composition $x_c \approx 13$ (Refs. 3 and 7). This occurs because the direct exchange interactions among the components are not of the same sign ($I_{\rm Ni-Ni} > 0$, $I_{\rm Fe-Ni} > 0$, $I_{\rm Fe-Fe} < 0$), and because the Cr atoms are associated with a "negative spin polarization" (Ref. 9). We studied the susceptibility χ_p and coercive force H_c for $77 \leqslant T \leqslant 700$ K and investigated the specific heat C_m for $77 \leqslant T \leqslant 500$ K in order to compare the behavior of these thermodynamic quantities for alloys of various compositions $x \lesssim x_c$; we included a 99.9% pure polycrystalline Ni sample in all of the measurements to serve as a reference.

2. MEASUREMENT TECHNIQUE

The samples were prepared and the specific heat and coercive force were measured by the techniques described in Refs. 3 and 7. We deduced the susceptibility χ_p by measuring the magnetization as a function of the magnetic field H for field in the intervals $(1.44–1.76)\cdot 10^4$, $(3.8–4.4)\cdot 10^4$, $(7.2–8.8)\cdot 10^4$, and $(20.2–26.2)\cdot 10^4$ A/m; the measurements were accurate to within $\pm(2–3)\%$. The field dependences $\chi_p(H)$ were recorded by the induction method by means of an F190 microfluxmeter and N306 recording potentiometer (we used a special ramp generator to produce a current in the solenoid that increased linearly with time). The measuring coil consisted of two very accurately balanced sections, so that the signal produced by a change in H by 1 kA/m corresponded to a change of less than $1\cdot 10^{-7}$ T in χ_p. We used relatively weak fields in the measurements, because strong magnetic fields suppress the fluctuations.[10] A VRT-2 regulator stabilized the temperature to within ± 0.05 K, and a copper-constantan thermocouple measured the temperature accurate to ± 0.02 K.

3. EXPERIMENTAL RESULTS

Figure 1 shows how the magnetic susceptibility χ_p for the para-process depends on the temperature T for $Fe_{65}Ni_{35-x}Cr_x$ quasibinary cut alloys and for polycrystalline Ni near the Curie point. As x approaches $x_c \approx 13$, for which the alloys lose their ferromagnetic properties, the peak in χ_p at $T = T_C$ becomes broader and lower. For strong external magnetic fields, the peak in $\chi_p(T)$ shifts toward higher T, which indicates that the Curie temperature T_C is sensitive to H. The relative displacement $[T_C(H) - T_C(0)]/T_C(0)$ increases rapidly with the chromium content x in the $Fe_{65}Ni_{35-x}Cr_x$ alloys (the values of $T_C(0)$ in Fig. 2 were found from the Arrott-Noakes curves[11]). For "Invar" ($Fe_{65}Ni_{35}$), $[T_C(H) - T_C(0)]/T_C(0)$ for $H = 2.4\cdot 10^5$ A/m is ≈ 0.05, or five times larger than for nickel. The Curie temperature for $Fe_{65}Ni_{25}Cr_{10}$ is 30% higher for relatively weak applied fields $H = 2.4\cdot 10^5$ A/m (cf. Fig. 2). To our knowledge, such large magnetically induced shifts in T_C have not been noted previously. The difference in the dependence $T_C(H)$ for Ni and $Fe_{65}Ni_{35-x}Cr_x$ is also striking—it is linear for Ni and almost quadratic for $Fe_{65}Ni_{35-x}Cr_x$.

Figure 3 plots the temperature dependences $C(T)$ of the specific heat for alloys $Fe_{65}Ni_{35-x}Cr_x$ with $x = 0$ (Ref. 12), 2, and 6. As more Cr atoms replace the Ni atoms in the

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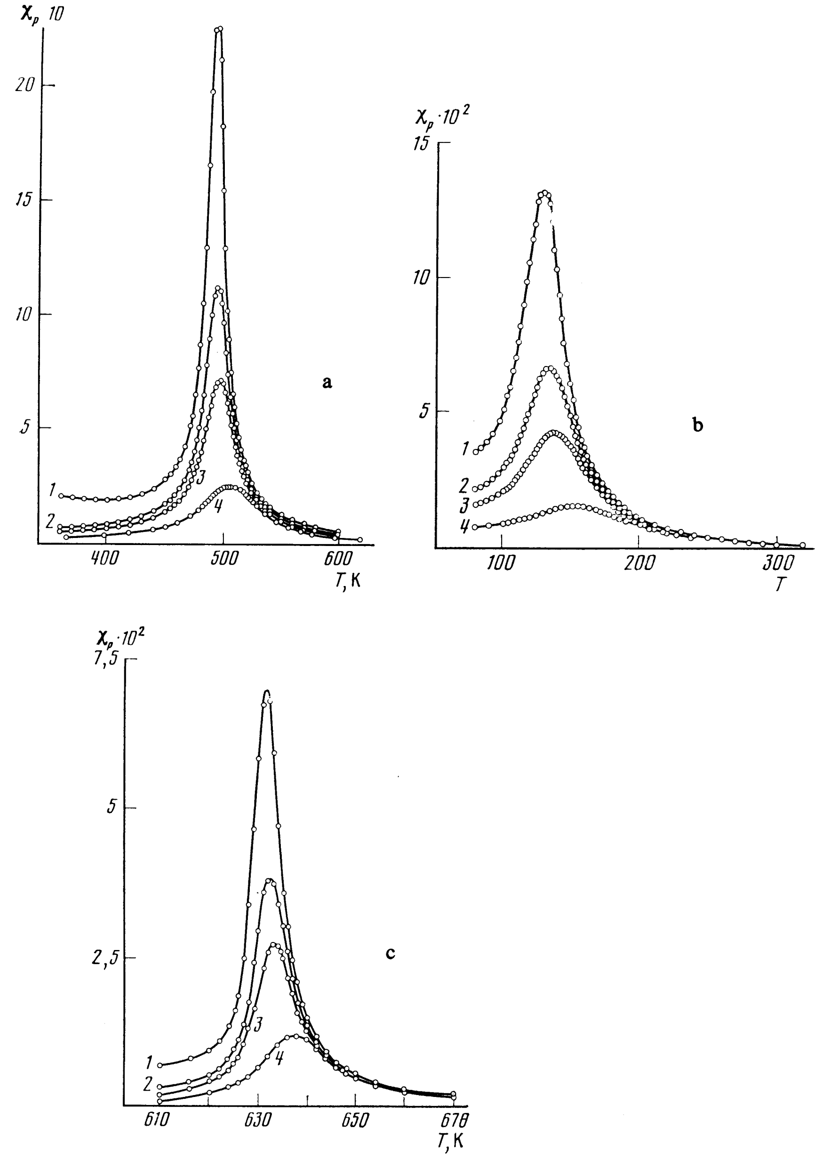

FIG. 1. Temperature dependences of the susceptibility for pure nickel (c) and for $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x = 0$ (a), 10 (b) measured for four magnetic field ranges: 1) $(1.44–1.76)\cdot 10^4$ A/m; 2) $(3.8–4.4)\cdot 10^4$ A/m; 3) $(7.2–8.8)\cdot 10^4$ A/m; 4) $(20.2–26.4)\cdot 10^4$ A/m.

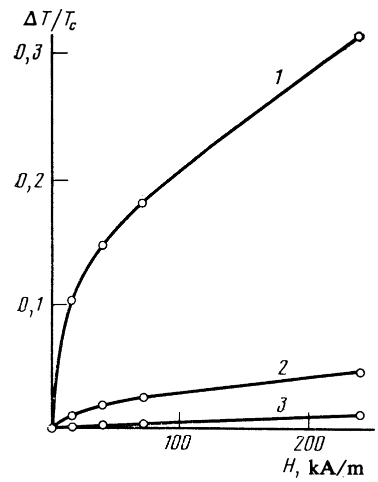

FIG. 2. Relative shift in the susceptibility peak with varying external magnetic field for $Fe_{65}Ni_{65}$ (2), $Fe_{65}Ni_{25}Cr_{10}$ (1) and Ni (3).

$Fe_{65}Ni_{35}$ alloy, the anomaly $\Delta C_m(T_C)$ at the Curie point rapidly disappears (degenerates). Thus, although $\Delta C_m(T_C)$ is $\approx 15\%$ of the total specific heat C for Invar,[12] it is less than 1% of C for $Fe_{65}Ni_{33}Cr_2$ and less than the 0.4% experimental error for alloys $Fe_{65}Ni_{35-x}Cr_x$ with $x \geqslant 6$.

The coercive force H_c also behaves anomalously near

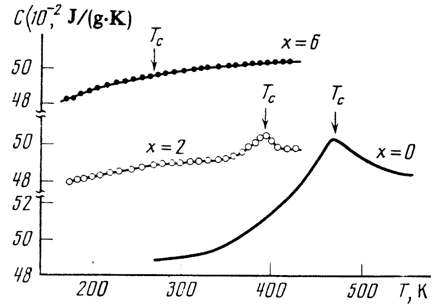

FIG. 3. Temperature dependences of the specific heats for $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x = 0$ (Ref. 12), 2, and 6 (our data).

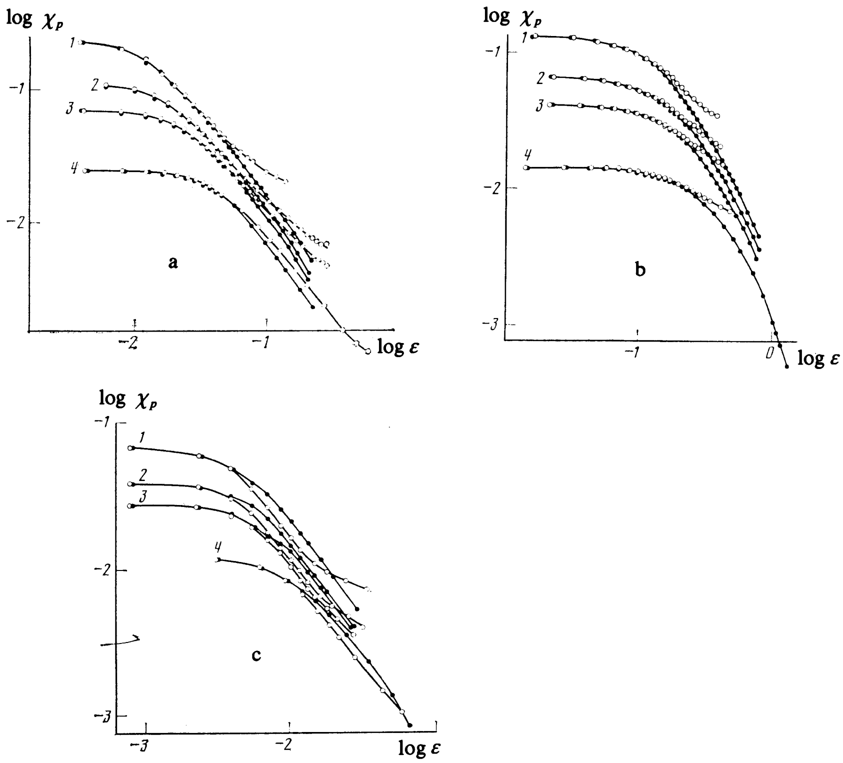

FIG. 4. The logarithm $\log(\chi_p)$ as a function of $\log(\varepsilon)$ for $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x = 0$ (a) and 10 (b), and for polycrystalline nickel (c). The dark and open circles correspond to $T > T_C$ and $T < T_C$, respectively. As in Fig. 1, the curves are labeled by the magnetic field ranges for which χ_p was measured.

T_C. For the alloys H_c rises rapidly as T approaches T_C, whereas no such increase is found for nickel. We note that a rapid increase in H_c as $T \to T_C$ was first noted by Zaĭmovskiĭ[13] for $Fe_{50}Ni_{50}$, although no explanation was given.

4. DISCUSSION

In the modern theory of phase transitions, the power laws[10]

$$\chi = \begin{cases} \text{const} \cdot \varepsilon^{-\gamma'}, & \varepsilon > 0 \\ \text{const} \cdot \varepsilon^{-\gamma}, & \varepsilon < 0 \end{cases}, \tag{1}$$

$$C_m = \begin{cases} \text{const} \cdot \varepsilon^{-\alpha'}, & \varepsilon > 0 \\ \text{const} \cdot \varepsilon^{-\alpha}, & \varepsilon < 0 \end{cases}, \tag{2}$$

are assumed to describe the changes in the thermodynamic characteristics near the Curie point. Here $\varepsilon = (T_C - T)/T_C$, C_m is the magnetic contribution to the specific heat, and $\alpha, \alpha', \gamma, \gamma'$ are the critical indices.

We used expressions (1), (2) to analyze our experimental results. Because C_m was extremely small for $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x \geqslant 2$ (cf. Fig. 3), we were unable to test Eq. (2) on our specific heat data. We checked Eq. (1) by plotting $\log(\chi_p)$ as a function of $\log(\varepsilon)$ (Fig. 4). Clearly, the power law (1) breaks down in a neighborhood of T_C whose width Δ increases with H and x (the corresponding region on the H-T diagram is hatched in Fig. 5). We see that although the dependence $\log(\chi_p) = f(\log \varepsilon)$ is almost linear for Ni for $\varepsilon > 0.006$–0.01, it is linear for $Fe_{65}Ni_{25}Cr_{10}$, e.g., only if $\varepsilon > 0.1$.

We can divide the region of linear $\log(\chi_p) = f(\log \varepsilon)$ in the H-T diagram into two regions II and III (cf. Fig. 5). The

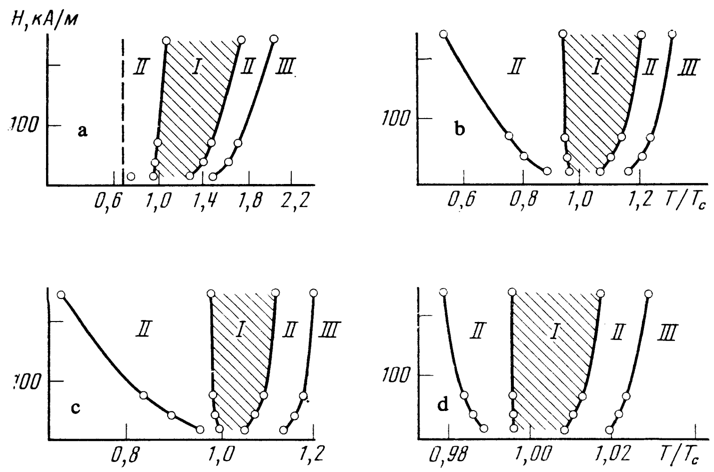

FIG. 5. H-T diagrams for $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x = 0$ (c), 5 (b), 10 (c) and for pure Ni (d). The power law for $\chi_p(T)$ breaks down in region I; II is the fluctuation region, and the mean-field approximation is valid in region III.

critical index γ is somewhat higher in region II and is approximately equal to 1.3–1.4(1.33 $\pm$ 0.02 for $Fe_{65}Ni_{35-x}Cr_x$ with $x = 0.5$ and for nickel, and 1.40 $\pm$ 0.02 for $Fe_{65}Ni_{25}Cr_{10}$). In region II, γ' is equal to 1.30 $\pm$ 0.02 for Ni and to 1.10 $\pm$ 0.02 for $Fe_{65}Ni_{35-x}Cr_x$ with $x = 0.5$; γ' is independent of H. For $Fe_{65}Ni_{25}Cr_{10}$, the index γ' decreases from 0.87 $\pm$ 0.02 to 0.55 $\pm$ 0.02 as H increases from 10^3 to $2.4\cdot10^5$ A/m.

In region III on the H-T diagram, γ is close to unity for all of the $Fe_{65}Ni_{35-x}Cr_x$ studied and is independent of H. The values of the critical index for the susceptibility χ_p indicate that fluctuations dominate the behavior in region II, while the mean field approximation is valid for region III.

The breakdown of (1) for $T \approx T_C$ (region I on the H-T diagram) is generally attributed to mechanisms which keep the correlation radius of the fluctuations finite.[1] According to Fig. 4, this effect is more pronounced for alloys with $x \sim x_c$ than for nickel, presumably because there are more magnetic inhomogeneities.

The fluctuations in highly inhomogeneous magnetic alloys such as $Fe_{65}Ni_{25}Cr_{10}$ are clearly decisive and in fact determine the behavior of the thermodynamic quantities even quite far away from the Curie point ($\varepsilon = 0.1$–0.3, cf. Fig. 4b). These effects are enhanced by the static fluctuations in the order parameter (associated with spatial magnetization gradients) which exist even at low temperatures in alloys with a variable-sign exchange interaction for compositions $x \approx x_c$. That such static fuctuations are present is indicated, among other things, by an observed increase in small-angle neutron scattering at low temperatures.[14] On the other hand, these fluctuations may cause the approximation (1) for $\chi_p(T)$ to become inaccurate for T very close to T_C. Because the simple power law (1) ignores the combined effects of spatial and thermal fluctuations in the order parameter, it may break down if the static (spatial) fluctuations start to amplify the dynamic (thermal) fluctuations appreciably.

The spatial fluctuations might involve the "breakup" of topologically infinite ferromagnetic clusters into finite clusters as T approaches T_C.[15,16] This is suggested by the rapid increase in H_c for the $Fe_{65}Ni_{35-x}Cr_x$ alloys for T very close to T_C. The diameter of most finite clusters becomes less than the monodomain diameter for $T \lesssim T_C$ (Ref. 17), which suggests that cluster breakup should occur; moreover, the coercive force for single-domain particles is known to be very high. At any rate, it is difficult to imagine any other explanation for the large (almost hundredfold) increase in H_c as $T \to T_C$.

If we are correct in attributing the anomalous behavior of the magnetic transition in inhomogeneous ferromagnets at the Curie point T_C to spatial (static) fluctuations in the order parameter, then the transition should have some of the characteristic features associated with phase transitions of the first kind ("blurred" phase transition).[4–6]

CONCLUSIONS

Our studies show that the behavior of the susceptibility and specific heat changes near the Curie temperature T_C for $Fe_{65}Ni_{35-x}Cr_x$ alloys with composition x close to the critical value x_c for loss of ferromagnetic properties. The anomalous behavior in the specific heat at $T = T_C$ degenerates even for x quite far from x_c. As $x \to x_c$, the peak in the susceptibility becomes much broader and the position of the peak (the Curie temperature) becomes anomalously sensitive to the magnetic field H. Increases in H and in the chromium content x are accompanied by an increase in the width Δ of the interval about T_C for which χ_p violates the power law (1). On the other hand, fluctuation behavior is present for anomalously large $\varepsilon \approx 0.1$–0.3 for the alloy $Fe_{65}Ni_{25}Cr_{10}$, probably because the static (spatial) fluctuations amplify the dynamic (thermal) fluctuations. The observed increase in small-angle neutron scattering for low temperatures[14] and in the coercive force H_c (as $T \to T_C$) indicates that static fluctuations in the magnetization are present in $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x \sim x_c$. The critical index γ' of the susceptibility decreases as x approaches x_c. A change in the critical indices during the homogeneous→inhomogeneous transition in magnetic materials has been predicted on theoretical grounds (cf., e.g., Ref. 5).

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