Features of the change in the specific heat in magnetic phase transitions in alloys with a mixed exchange interaction

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A study is made of the specific heat of fcc alloys of the quasibinary tie lines $Fe_{65}Ni_{35-x}Cr_x$ and $Fe_{50}Ni_{50-x}Mn_x$ in the temperature range 5–320 K. It is ascertained that as the alloy composition approaches the critical concentration x_c for the vanishing of the long-range magnetic order, the specific-heat anomaly at the Curie (Néel) point degenerates much faster than the rate of change of the shape of the temperature curves of the magnetization and the susceptibility. Alloys of the system $Fe_{65}Ni_{35-x}Cr_x$ are found to have an anomalous concentration dependence of the coefficient γ of the linear term in the expansion of the low-temperature specific heat in powers of the temperature. It is shown that the high values of γ near x_c in disordered alloys based on fcc Fe are due to the presence of a "cluster spin glass."

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1. INTRODUCTION

The nature of the concentrational magnetic phase transitions in alloys of 3d metals with both positive and negative values of the exchange integral is a question of topical interest. Another matter which has not been adequately studied is the transformation of the phase transition at the Curie (Néel) point as the composition of the alloys approaches the critical concentration x_c for the vanishing of the long-range magnetic order. In particular, it has been shown[1,2] that the specific-heat anomaly at the Curie point decreases considerably with increasing Fe concentration in $Fe_{100-x}Ni_x$ (especially for compositions in the Invar region). However, in the $Fe_{100-x}Ni_x$ system the ferromagnetic–antiferromagnetic (*F–AF*) concentrational phase transition does not reach completion owing to the presence of an fcc–bcc transformation at $x \simeq 30$–33 ($x_c = 25$).[3]

In the present study we attempted to follow how the specific-heat anomaly at the Curie (Néel) point changes with changing composition in disordered fcc alloys of two systems having different types of compositional magnetic phase transitions: $Fe_{50}Ni_{50-x}Mn_x$ [*F–AF* phase transition with $x_c = 18$ (Ref. 4)] and $Fe_{65}Ni_{35-x}Cr_x$ [a conjectured ferromagnetic–spin-glass transition with $x_c = 15$ (Ref. 5)]. We also studied in these alloys the concentration dependence of the coefficient γ of the linear term in the expansion of the low-temperature specific heat in powers of the temperature. There is divided opinion on the nature of the high values of the coefficient γ in the vicinity of the critical concentration x_c; this effect has been attributed to a high density of electronic states at the Fermi level,[6] to the presence of critical fluctuations of the magnetization,[7] and so forth.

We have studied the specific heat of the alloys $Fe_{50}Ni_{50-x}Mn_x$ and $Fe_{65}Ni_{35-x}Cr_x$ in the temperature range 5–320 K on an updated version of the standard model UNTO low-temperature thermophysical apparatus[8] (error $\pm 0.5\%$ for temperatures in the range 20–320 K, and ± 3–6% from 5–20 K). The magnetization was measured by the Weiss–Forrer method to an accuracy of 2–3%.

2. BEHAVIOR OF THE SPECIFIC HEAT NEAR THE CURIE (NÉEL) POINT

Figure 1 shows the temperature dependence of the specific heat at constant pressure (C) for a series of alloys of the tie lines $Fe_{50}Ni_{50-x}Mn_x$ and $Fe_{65}Ni_{35-x}Cr_x$ (the values of the specific heat of the alloys $Fe_{65}Ni_{35}$ and $Fe_{50}Ni_{50}$ were taken from Ref. 2). It can be inferred from Fig. 1 that the alloys with Curie temperatures T_C (or Néel temperatures T_N) lying below 300 K have no substantial anomalies of the specific heat in the vicinity of T_C (or T_N) (the values of T_C and T_N are indicated by arrows in Fig. 1b). Only in the alloy $Fe_{50}Ni_{25}Mn_{25}$ does one see an insignificant feature with a value not in excess of 2% of the total specific heat of the alloy.

For the alloys under study it is impossible to correctly separate the magnetic contribution C_m to the specific heat in view of its small value and the significant uncertainly in the lattice and electronic contributions to the specific heat in the temperature range 90–320 K. The fact that there is no anomaly of the specific heat near T_C is extremely unusual, since the saturation magnetization M_s at 4.2 K in $Fe_{50}Ni_{35}Mn_{15}$, for example, exceeds the corresponding value of M_s of pure nickel, while the temperature dependence of the magnetization has the usual form. Starting from the experimental results of Rode *et al.*[9] on the field dependence of the magnetization in the 20–120 kOe range, we calculated the temperature dependence of the high-field susceptibility of $Fe_{65}Ni_{25}Cr_{10}$ in the neighborhood of the Curie point $T_C \simeq 160$ K (Fig. 2). Comparison of the temperature dependence of the specific heat, magnetization, and susceptibility suggests that in the alloys with $T_C \leqslant 300$ K there is no interval of temperatures in a wide vicinity of the Curie point in which the Landau theory of phase transitions applies. The region of applicability of the Landau theory is given by the inequality[10]

$$\left|\frac{T-T_c}{T}\right| \gg \varepsilon_{cr} \infty \frac{1}{(\Delta C_m)^2} \qquad (1)$$

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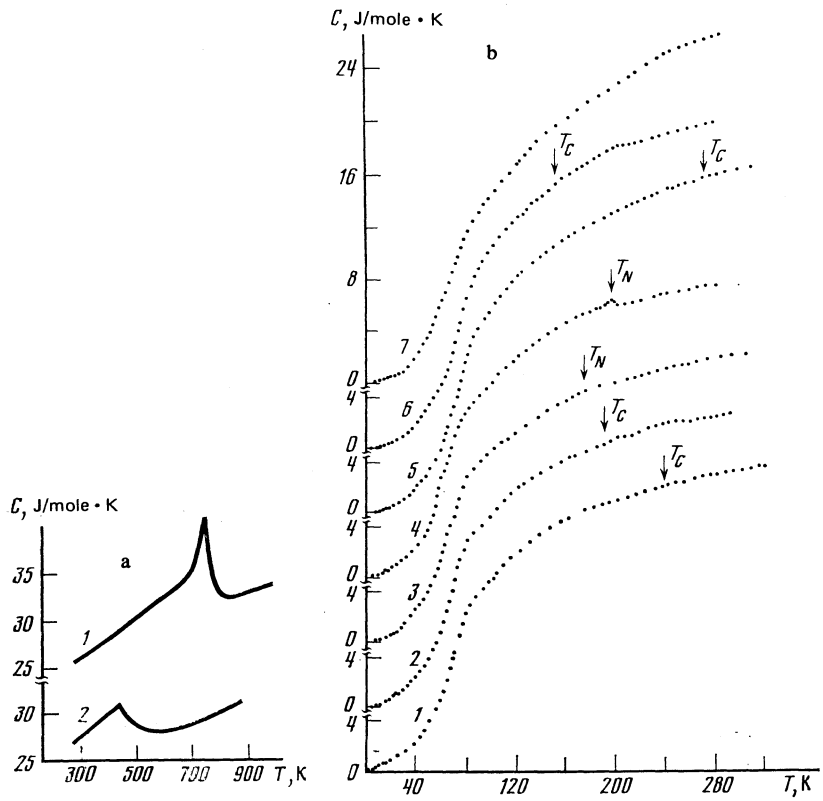

FIG. 1. Temperature dependence of the specific heat of: a) the alloys $Fe_{50}Ni_{50}$ (1) and $Fe_{65}Ni_{35}$ (2) (Ref. 2); b) the alloy systems $Fe_{50}Ni_{50-x}Mn_x$ with $x = 15$ (1), 17.5 (2), 22.5 (3), 25 (4), and $Fe_{65}Ni_{35-x}Cr_x$, with $x = 6$ (5), 10 (6), and 20 (7).

where ΔC_m is the discontinuity of the specific heat at the transition point.

In alloys of the tie lines $Fe_{65}Ni_{35-x}Cr_x$ and $Fe_{50}Ni_{50-x}Mn_x$, the magnitude of ΔC_m decreases rapidly with increasing x, and the region of temperatures around T_C in which the Landau theory is inapplicable expands accordingly. On the other hand, at large absolute values of $(T - T_C)/T$ the order parameter $\eta = M(T)/M(0)$ is not a small quantity and one therefore cannot drop terms of higher orders in the expansion of the thermodynamic potential in powers of η, as is done in the Landau theory.

Our results agree with the conclusions of the theoretical work of Dorogovtsev[11] and Izyumov *et al.*[12] These authors, showed that if the system contains a large amount of nonmagnetic impurity[11] or negative exchange couplings[12] the character of the phase transition at the Curie (Néel) point changes considerably.

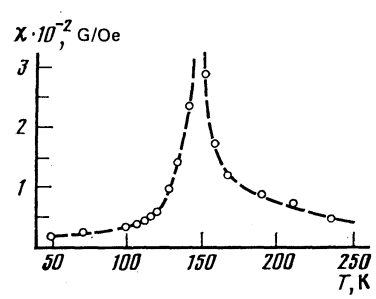

FIG. 2. Temperature dependence of the high-field susceptibility of the alloy $Fe_{65}Ni_{25}Cr_{10}$ as calculated from the data of Ref. 9.

Our data yield evidence that as the percolation threshold is approached in disordered alloys having both positive and negative exchange interactions, the specific-heat anomaly near T_C is smeared out at a much faster rate than the rate at which changes occur in the shape of the temperature dependence of the magnetic properties.

It should be noted that the ordered alloys $Pt_3Mn_xFe_{1-x}$ (Ref. 13) and $(Pd_xPt_{1-x})_3Fe$ (Ref. 14) at concentrations close to the critical display substantial anomalies in the specific heat at the Curie (Néel) point. On this basis it can be supposed that the character of the phase transition at $T_C(T_N)$ is different in ordered and disordered alloys with both positive and negative exchange integrals.

3. LOW-TEMPERATURE SPECIFIC HEAT

It can be inferred from Fig. 1 that the temperature dependence of the specific heat of all the alloys studied displays no noticeable features in the region 25–50 K, where anomalies appear on the temperatures curves of the susceptibility[15] and magnetoresistance[16] (these anomalies are commonly attributed to the onset of a spin-glass state). A least-squares computer analysis showed that the values of the specific heat at temperatures in the 5–20 K range are best described by the expression

$$C = \gamma T + \beta T^3, \quad \beta \propto \Theta^{-3}, \tag{2}$$

where Θ is the Debye temperature.

The concentration dependence of the coefficient γ and Debye temperature Θ for alloys of the system $Fe_{50}Ni_{50-x}Mn_x$ and $Fe_{65}Ni_{35-x}Cr_x$ are given in Figs. 3 and 4 (the ar-

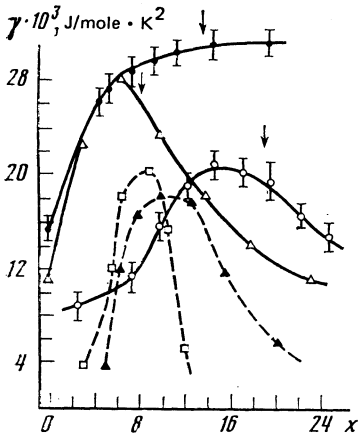

FIG. 3. Concentration dependence of the coefficient γ obtained from the data on the low-temperature specific heat for alloys of the systems $Fe_{65}Ni_{35-x}Cr_x$ (●), $Fe_{50}Ni_{50-x}Mn_x$ (○), $Fe_{65}Ni_{35-x}Mn_x$ (△) (Ref. 6) and the results of our calculation of the contribution γ_{cl} for alloys of the systems $Fe_{65}Ni_{35-x}Cr_x$ (▲) and $Fe_{65}Ni_{35-x}Mn_x$ (□).

rows in the figures indicate the values of the critical concentrations x_c). Figure 3 also shows the values of the coefficient γ for alloys of the system $Fe_{65}Ni_{35-x}Mn_x$ (Ref. 6). In the quasibinary tie line $Fe_{50}Ni_{50-x}Mn_x$ the coefficient γ is maximum near x_c, which is typical for systems of disordered alloys in which various sorts of compositional magnetic phase transitions (*F–P, F–AF, AF–P*) occur.[6,7] A feature of the function $\gamma(x)$ in the quasibinary tie line $Fe_{50}Ni_{50-x}Mn_x$ is the shift of the maximum of γ into the ferromagnetic region of compositions. The concentration dependence of γ in $Fe_{65}Ni_{35-x}Cr_x$ is unusual: The coefficient γ reaches its highest values near x_c but does not fall off in the nonferromagnetic region of composition (Fig. 3). The Debye temperature Θ in the alloy systems $Fe_{50}Ni_{50-x}Mn_x$ and $Fe_{65}Ni_{35-x}Cr_x$ increases monotonically with x (Fig. 4). The significant growth of Θ with increasing x in the tie line $Fe_{65}Ni_{35-x}Cr_x$ is apparently due to the peculiar elastic properties of the "Invar" alloy $Fe_{65}Ni_{35}$.

The high values of the coefficient γ in the alloys $Fe_{65}Ni_{35-x}Cr_x$ and $Fe_{50}Ni_{50-x}Mn_x$ could be due to either a high density of states at the Fermi level[6,7] or to the occurrence of a peculiar, "cluster spin-glass" low-temperature magnetic state.[3,5,17] It is known that below the freezing temperature T_f the experimental values of the specific heat of spin glasses depend linearly on the temperature. This circumstance is assumed to stem from the presence of many-particle excitations in the spin glass.[18] It has been shown[7,19] that allowance for the contribution γ_e, which is proportional to the density of states at the Fermi level, does not explain the values of the coefficient γ observed near x_c in binary alloys of the Ni–Pt type. Moreover, the contribution γ_e cannot explain the anomalously high values of γ in the vicinity of x_c in alloys of the systems $Fe_{65}Ni_{35-x}Cr_x$ and $Fe_{50}Ni_{50-x}Mn_x$ (which are 1.5–2 times larger than the analogous values of γ at $x \simeq x_c$ in alloys of the binary systems Pd–Ni, Pd–Fe, Ni–Cr, etc.[7]). It is also hard to picture the form of the density-of-states curve which would bring about such high values of γ over the wide range of concentrations $x = 10$–20 in the system $Fe_{65}Ni_{35-x}Cr_x$ (Fig. 3).

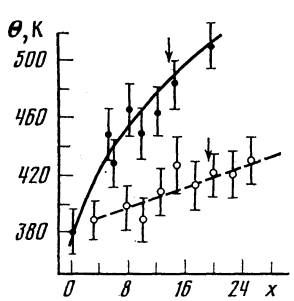

FIG. 4. Concentration dependence of the Debye temperature in the alloy systems $Fe_{65}Ni_{35-x}Cr_x$ (●) and $Fe_{50}Ni_{50-x}Mn_x$ (○).

Owing to the lack of proper theoretical estimates of the specific heat of a cluster spin glass, in calculating the magnetic contribution to γ we arbitrarily separated it into the contribution of the magnetic clusters γ_{cl} and the contribution of a uniform spin glass γ_{sq}:

$$\gamma_m = \gamma_{cl} + \gamma_{sg} = \gamma_{cl}^{\Phi} y_{cl}^{\Phi} + \gamma_{cl}^{A\Phi} y_{cl}^{A\Phi} + \gamma_{sg}^{0} y_{sg}, \qquad (3)$$

where y_{cl}^{F} and y_{cl}^{AF} are the volume fraction of finite ferromagnetic and antiferromagnetic clusters, respectively, y_{sq} is the volume fraction of the spin glass (the regions of disoriented spins between clusters, for which the ferromagnetic and antiferromagnetic contributions to the free energy are approximately equal), γ_{cl}^{F}, γ_{cl}^{AF}, and γ_{sq}^{0} are the contributions to the coefficient γ per magnetoactive atom in the ferromagnetic and antiferromagnetic clusters and in the regions of the uniform spin glass, respectively.

We have made estimates for alloys of the systems $Fe_{65}Ni_{35-x}Cr_x$ and $Fe_{65}Ni_{35-x}Mn_x$, which have been studied in sufficient detail by magnetic and neutron-diffraction methods. It should be noted that our estimates are very approximate because of the insufficient development of the theory of concentrated alloys with both positive and negative exchange integrals.

The properties of a system with a strong exchange interaction between ferromagnetic (or antiferromagnetic) clusters have been analyzed in detail in the model of Levin and Soukoulis[20] (however, the zones between clusters were not considered in this model). It was found that at temperatures below the magnetic-ordering temperature of the spins in a cluster, the specific heat of such a system in first approximation is linear in the temperature. For clusters of $N = 3$–6 spins the results of Ref. 20 for the case of $Fe_{65}Ni_{35-x}Cr_x$ and $Fe_{65}Ni_{35-x}Mn_x$ with $x \simeq x_c$ yield the values $\gamma_{cl}^{F} \simeq 0.8 \cdot 10^{-2} k_B$ and $\gamma_{cl}^{AF} \simeq 1 \cdot 10^{-2} k_B$.

Most of the theories of the spin-glass state, starting with the fundamental work of Edwards and Anderson,[21] predict a linear temperature dependence of the specific heat at temperatures substantially below T_f. However, it was later shown that models based on the theory of Edwards and Anderson do not give entirely correct results at low temperatures (in particular,[18] they give a negative value of the entropy at 0 K). Therefore, for an estimate of the

uniform-spin-glass contribution γ_{sq}^0 we used the experimental values of the specific heat of CuMn spin glasses with a small content of magnetoactive atoms,[22] for which cluster effects are relatively small. According to the data of Ref. 22, the uniform-spin-glass contribution per magnetoactive Mn atom in dilute CuMn alloys is $\gamma_{sq}^0 \simeq 0.3/A$ J/mole·K^2 (A is Avogadro's number).

The volume fraction of ferromagnetic clusters y_{cl}^F was calculated in the framework of percolation theory with the aid of the expressions found in Ref. 23. In calculating the volume fraction of antiferromagnetic clusters y_{cl}^{AF} we used the results of neutron-diffraction studies[3] of the fcc alloys $Fe_{65}Ni_{35-x}Cr_x$ and $Fe_{65}Ni_{35-x}Mn_x$. The authors of Ref. 3 estimated the dimensions of the antiferromagnetic regions in these alloys at a temperature of 4.2 K. They also showed that the nucleating centers for the antiferromagnetic clusters in $Fe_{65}Ni_{35-x}Mn_x$ alloys are Fe atoms whose nearest neighbors include only Fe and Mn atoms, while in alloys of the $Fe_{65}Ni_{35-x}Cr_x$ system the nucleating centers are Fe atoms having only Fe atoms or else 11 Fe atoms and one Cr atom in their first coordination sphere. The remaining concentration fluctuations for which the central Fe atom has no Ni atoms as nearest neighbors, according to the data of Ref. 3, are nucleating centers of a paramagnetic region or a spin-glass region. In evaluating y_{cl}^{AF} we assumed that the composition fluctuations are described by the binomial distribution and used expressions analogous to those used in Ref. 3.

The dashed curves in Fig. 3 show the calculated results for the cluster contribution γ_{cl} in alloys of the sytems $Fe_{65}Ni_{35-x}Cr_x$ and $Fe_{65}Ni_{35-x}Mn_x$. It follows from Fig. 3 that by taking into account only the contribution γ_{cl} in expression (3), one can qualitatively explain the $\gamma(x)$ curve in the tie line $Fe_{65}Ni_{35-x}Mn_x$ that was obtained by Kawarazaki *et al.*[6] from an analysis of the specific-heat results.

In the quasibinary tie line $Fe_{65}Ni_{35-x}Cr_x$ the curves of $\gamma(x)$ and $\gamma_{cl}^{(x)}$ do not agree even qualitatively. However, if the contribution γ_{sq} in Eq. (3) is taken into account, one can, in principle, obtain agreement with experiment. In particular, if it is assumed that γ_{sq}^0 has about the same value per magnetoactive atom in the uniform-spin-glass regions in $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x \geqslant x_c$ as it has in dilute CuMn glasses,[22] then in order to obtain agreement between the experimental values of γ and the calculated values in Fig. 3 it must be assumed that the relative volume of the uniform spin glass in the temperature range 5–20 K is 10–20%. This is entirely possible, since the results of our calculations imply that the sum $y_{cl}^F + y_{cl}^{AF}$ for $Fe_{65}Ni_{35-x}Cr_x$ alloys with $x \geqslant x_c$ at 4.2 K does not exceed 30%. The remaining volume of the alloy should be occupied by paramagnetic and spin-glass regions.

In summary, allowance for the magnetic contribution due to the occurrence of a cluster-spin-glass state permits one to explain the anomalous shape of the concentration dependence of the coefficient γ in the system $Fe_{65}Ni_{35-x}Cr_x$. This gives one grounds to suppose that the high values of the linear term in the temperatrue expansion of the low-temperature specific heat in disordered alloys based on fcc Fe at concentrations close to the critical is due to the presence of a spin-glass state. It must be pointed out that for the ferromagnetic–antiferromagnetic compositional phase transition in the system of ordered alloys $(Pd_xPt_{1-x})_3Fe$ one does not see[24] a maximum of the coefficient γ in the vicinity of x_c. This is probably due to the fact that compositional magnetic phase transitions in ordered alloys are not accompanied by the appearence of an intermediate spin-glass state.

In conclusion we note that the correct separation of the magnetic contribution to the specific heat in the vicinity of the freezing temperature T_f of the spin glass (25–50 K) is complicated by the absence of appreciable anomalies on the specific-heat curves in this temperature interval (Fig. 1b), and also by the significant lattice contribution to the specific heat. At temperatures above 20 K the lattice contribution to the specific heat becomes dominant, and owing to the appreciable temperature dependence of the Debye temperature,[25] it is difficult to make an exact allowance for this contribution.

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