Spin-glass/ferromagnetic transitions and multicritical points in amorphous transition metal alloys[a)]

M. B. Salamon, K. V. Rao,[b)] and Y. Yeshurun

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

Experimental results on a number of amorphous alloys with compositions $(M_{1-x}M'_x)_{75}P_{16}B_6Al_3$, with M either Fe or Co and M′ either Mn or Ni are summarized for compositions in the vicinity of the boundary between ferromagnetic and spin-glass behavior. The qualitative nature of the phase boundary is very similar to that of the Sherrington-Kirkpatrick model, but with non-classical values for the critical exponents. Critical behavior along the ferromagnetic-paramagnetic, ferromagnetic-spin glass, and spin glass-paramagnetic lines are discussed. Some evidence for a qualitative change within the ferromagnetic phase near the spin-glass transition is also given. These represent the first detailed critical-point studies of such a phase diagram.

PACS numbers: 75.50.Kj, 75.30.Kz, 75.40. – s, 75.20.En

INTRODUCTION

Although the spin-glass state was first discovered in dilute alloys (1), most model calculations envisage a concentrated system with a distribution of exchange interactions (2,3). When the distribution has a non-zero average, the possibility arises that both ordered and spin-glass states may exist over certain ranges of the parameters. A number of systems have given indications for such a situation, most notably Fe-Cr (4) alloys, Au-Fe (5) alloys, and the $Eu_{1-x}Sr_xS$ (6) system. In none of these cases has the region in which both ferromagnetic and spin-glass phases may occur been closely enough examined to determine the nature of the phase transitions nor the properties of the multicritical point at the intersection of the various phase boundaries.

In the present paper, we will describe a series of measurements on several amorphous alloy systems, all of which have both ferromagnetic and spin-glass phases and some of which show reentrant ferromagnetism. These materials offer distinct advantages over other materials suggested for the investigation of this interesting phase diagram since:

i) The materials freeze in the structure of the liquid phase, thus avoiding competing crystalline phases and possible spinodal decomposition (7);

ii) All compositions are attainable within the same phase;

iii) Since the materials are amorphous, only random crystalline anisotropy will appear.

iv) Clustering effects are minimized.

The alloys considered here have the chemical composition $(M_xM'_{1-x})_{75}P_{16}B_6Al_3$ in which M can be Fe or Co and M′ can be Mn or Ni. All samples were kindly prepared by H. S. Chen (8).

The best studied model for the spin-glass/ferromagnetic phase diagram is the Sherrington-Kirkpatrick model (2) in which the distribution of exchange energies is characterized by a mean value $\tilde{J}_o$ and a standard deviation $\tilde{J}$. The phase diagram for this model is sketched in Fig. 1, slightly rescaled from Ref. 2. The three phase boundaries meet at a multicritical point, the properties of which are central to our discussion here. The paramagnetic to ferromagnetic transition occurs along the line labeled pf and is the usual second-order Curie transition. The line pg represents the spin-glass transition whose nature is not yet understood. We will show that, along this line, the susceptibility (which is not directly related to the spin-glass order parameter), scales as it should for a line of phase transitions ending at a multicritical point. We argue that this strongly indicates that the pf transition is a genuine phase transition. Note also that the Sherrington-Kirkpatrick phase diagram suggests the existence of a reentrant ferromagnetic region near the MCP. A central theme of this review is the observation of a line of second order transitions corresponding to the fg line in Fig. 1.

It is possible to put the Sherrington-Kirkpatrick model into the usual Landau-Ginzberg form and to extract mean field exponents (3). We have tabulated these in Table I. The exponents γ and β are the usual exponents for the pf line; $\tilde{\gamma}$ and $\tilde{\beta}$, for the fg line and γ_t and β_t, for the multicritical point. The cross over exponent is ϕ. The reentrant portion of the ferromagnetic phase is thus seen to be symmetric: the magnetization rises as $(T_{pf}-T)^{1/2}$ and then vanishes at lower temperatures as $(T-T_{fg})^{1/2}$. The susceptibility thus diverges along the boundaries of the ferromagnetic phase.

In Fig. 2, we show a realization of the Sherrington-Kirkpatrick phase diagram for amorphous Fe-Mn alloys. Although there is strong similarity, we believe that both $\tilde{J}$ and $\tilde{J}_o$ vary with x which makes direct comparison impossible. The MCP occurs at a concentration of x=.36 and at a temperature of 44 K. Clear evidence for the existence of fg transition (squares) will be summarized below (10). Along the pg line (triangles) a finite, cusped susceptibility is found which can be scaled relative to the MCP. Fortuitously, one of our samples has a composition extremely close to the MCP which

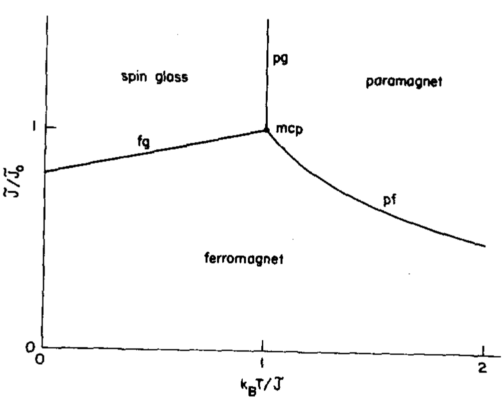

Fig. 1. Phase diagram in the Sherrington-Kirkpatrick model. The critical lines are labeled as referred to in the text.

 0021-8979/81/031687-05$1.10

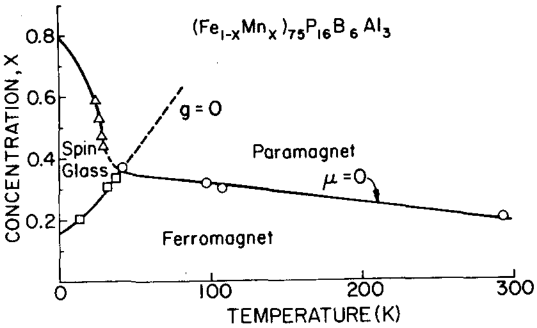

Fig. 2. Magnetic phase diagram for $(Fe_{1-x}Mn_x)_{75}P_{16}B_2Al_3$.

permits us to determine certain multicritical exponents directly.

MAGNETIZATION DATA

A direct method of examining the ferromagnetic phases involves determination of the magnetization. There are experimental difficulties here: the magnetization becomes very hysteretic in the spin-glass regime and very low fields are sufficient to wash out the fg transition. In Fig. 3a, we have plotted magnetization data for Fe-Mn with x=0.32. By way of comparison, the solution of the Sherrington-Kirkpatrick model (9) in a finite field is plotted in Fig. 3b. The qualitative similarity is unmistakable, although the calculated curves seem somewhat more symmetrical. Note that both experimental and theoretical curves have a maximum in magnetization which moves to lower temperature as H is increased. In the Fe-Ni system, quite similar results have been found on the Ni-rich side (a), as seen in Fig. 4 for x=0.8. Analogous results have been reported (10) for Co-Mn alloys and, at this conference, for Co-Ni (11).

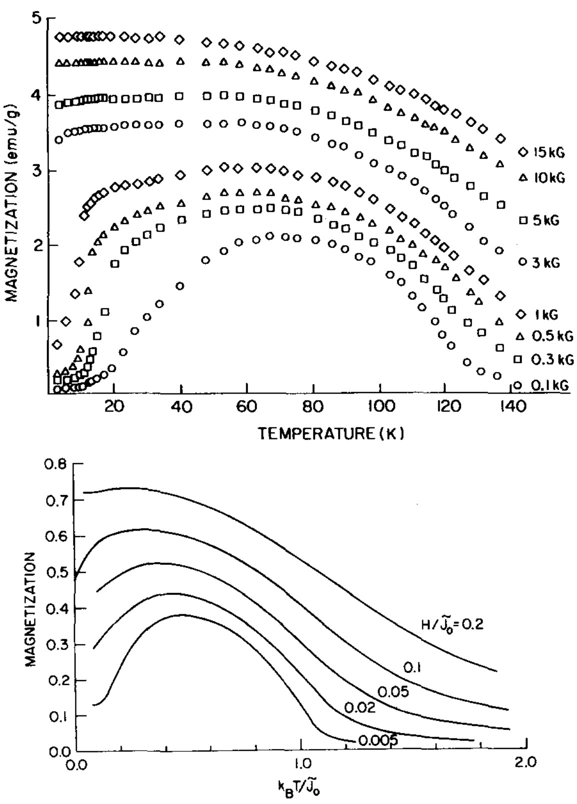

Fig. 3. a) Magnetization curves for Fe-Mn glass for x = 0.32. Magnetization field cooling to each temperature in order to avoid hysteresis.

b) Solution of the Sherrington-Kirkpatrick model for the magnetization in finite fields. We have used $\tilde{J}/\tilde{J}_0 = 0.87$.

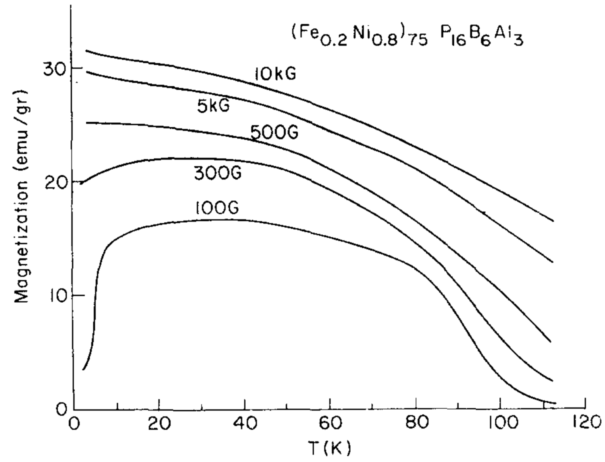

Fig. 4. Magnetization curves for Fe-Ni glass at x = 0.8.

To proceed beyond the qualitative comparison of the phase diagrams, we must address the detailed behavior of these materials near the phase boundaries. The most direct means of doing so makes use of the modern theory of phase transitions to form scale invariant quantities from the measured properties and applied fields (12). In the present case, the magnetization is the measured property and the temperature and internal field, the relevant fields. For the thin sample geometry used here, the difference between applied and internal field is unimportant except at the lowest fields and temperatures, and external field will be used throughout.

Table I. Mean-field values of the critical exponents

β	γ	δ	$\tilde{\beta}$	$\tilde{\gamma}$	$\tilde{\delta}$	$\tilde{\tilde{\beta}}$	γ_t	δ_t	ϕ
½	1	3	½	1	3	½	1	2	1

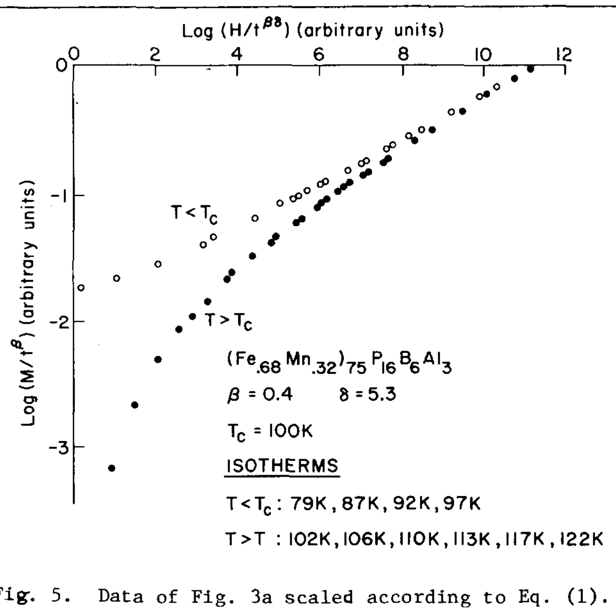

Fig. 5. Data of Fig. 3a scaled according to Eq. (1).

Along the pf line, normal ferromagnetic scaling laws should hold, which means that the magnetization may be written as

$$M = |t|^{\beta}\ m^*(h/t^{\beta\delta}) \qquad (1)$$

where $t = T/T_{pf} - 1$ and β and δ are critical exponents. The reader is reminded that $\gamma = \beta(\delta-1)$, for comparison with Table I. The function $m^*(y)$ has two branches depending on the sign of y. For negative y, $m^*(y\to 0)$ is constant, reflecting the usual behavior of the order parameter. For small positive values, $m^*(y)\sim y$, which yields the divergent susceptibility. For large values of y, $m^*(y)\sim|y|^{1/\delta}$.

In Figs. 5 and 6 we have plotted the data of Figs. 3a and 4 in the scaling form, Eq. (1). The exponents in both cases are $\delta = 5.2 \pm 0.4$ and $\beta = 0.4 \pm 0.04$. The errors represent limits over which the exponents may be varied without giving a qualitatively poorer "collapsing" of the data to a single, smooth function. We note that these exponent values differ significantly from usual Heisenberg values (12), but are quite similar to values reported for other such random alloys (13). This discrepancy remains a puzzle.

The symmetry of the reentrant ferromagnetic phase in mean field theory (2,3) suggests that an analogous form for the magnetization should hold along the fg phase boundary; namely

$$M = |\tilde{t}|^{\tilde{\beta}}\ \tilde{m}^*(H/\tilde{t}^{\tilde{\beta}\tilde{\delta}}). \qquad (2)$$

where now $\tilde{t} = 1 - T/T_{fg}$, and the tilda denotes the fg values for all quantities. We test this hypothesis for the Fe-Mn data of Fig. 3a in Fig. 7. The scaling form clearly holds with $\tilde{\delta} = 4.5$ and $\tilde{\beta} = 0.4$. Note that $\tilde{\delta}$ is smaller than along the pf line; we do not believe that the values are the same, although it is within the range of experimental uncertainty. Similar results for Co-Ni alloys have been presented at this conference (11) and a complete summary of this important transition published separately (10).

Interesting changes in critical behavior along these two second order lines occur as the MCP is approached. We notice some change in δ as the concentration nears the MCP value, doubtlessly caused by cross over to MCP behavior. We have not yet succeeded in the difficult procedure of scaling all the data in the three-dimensional M-H-T space onto single curves or surfaces, and so cannot report here on cross over to MCP behavior along the pf or fg lines. In the next section, we do discuss cross over effects along the pg line, in the absence of applied fields.

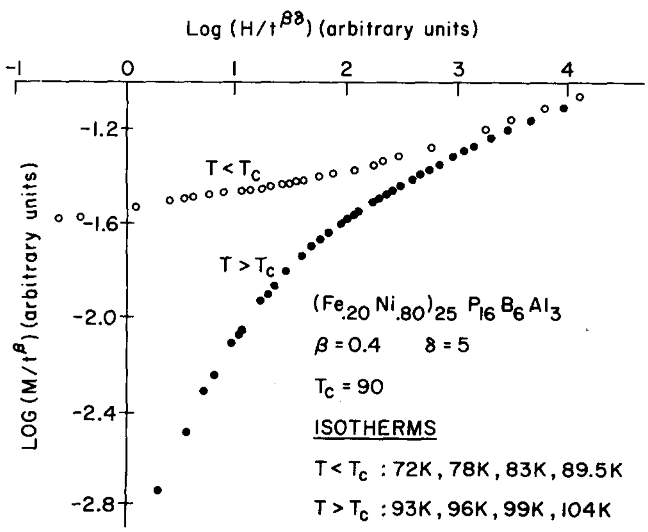

Fig. 6. Data of Fig. 4 scaled according to Eq. (1).

At the multicritical concentration, we enter the spin-glass phase by passing through the MCP. This is not the required path which should avoid both ferromagnetic and spin-glass phases. That path, which we will discuss below, is an extension of the fg line into the paramagnetic phase, sketched as g = 0 in Fig. 2. Nonetheless, we may obtain an approximation of MCP behavior on approaching the MCP along the path x = 0.36 as temperature is reduced. We find a scaling behavior similar to Eqs. (1) and (2), but with a single branch as shown in Fig. 8. The temperature variable is now $t = T/T_{MCP} - 1$. The high field behavior strongly indicates that $\delta_t = 2.2$, quite close to the mean-field value of the exponent (Table I). We do not understand the meaning of $\beta_t = 0.4$ in this case. The susceptibility exponent derived from these data is $\gamma_t = 0.5$, which differs from that obtained more directly below. This may well result from approaching to the MCP nearly parallel to the pf line. Then, true multicritical behavior may be observed only very close to the MCP at low fields.

SUSCEPTIBILITY ALONG THE pg LINE

The single most characteristic feature of the spin-glass transition is the occurence of a cusp in the ac susceptibility (1). In the present system, the amplitude of this cusp must increase as the MCP is approached along the pg line, since the ferromagnetic phase is characterized by infinite susceptibility along its phase boundaries. This being the case, the susceptibility must have a critical exponent characterizing this divergence, and this must be related to the MCP susceptibility exponent by the cross over exponent ϕ.

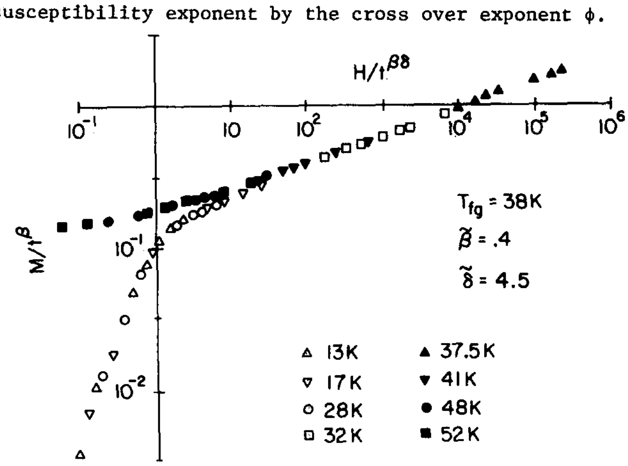

Fig. 7. Data of Fig. 3a scaled according to Eq. (2).

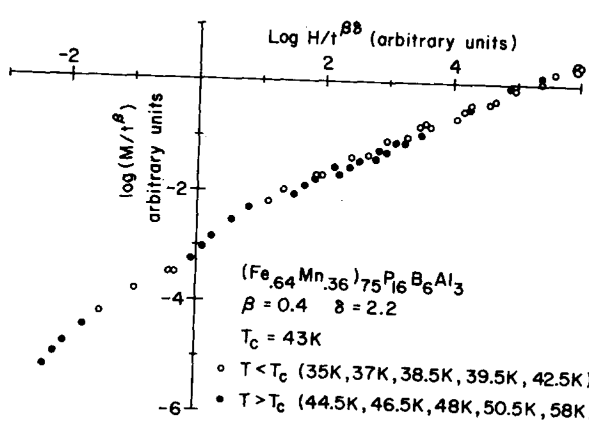

Fig. 8. Scaled magnetization for Fe-Mn glass at x = 0.36. This path carries the system into the spin-glass phase very close to the MCP.

To see this, we write (14) the behavior of the susceptibility when the fundamental length scale of the system is changed by a factor λ as

$$\chi(T,x) = \lambda^{\gamma}\chi(\lambda\mu(T,X),\ \lambda^{\phi}\, g(T,x)). \qquad (3)$$

The fields μ and g are determined by the geometry of the multicritical point. We take $g = 0$ to be the extension of the fg line, and $\mu = 0$ to be the extension of the pf line. With this choice, the MCP is at the point $\mu = g = 0$. Since the length scale is at our disposal, we may choose to keep $\lambda\, g = 1$ which gives the scaling form

$$\chi(T,x) = g^{-\gamma_t/\phi}\, \chi^{*}(\mu/g^{1/\phi}). \qquad (4)$$

In this formulation, the $\chi^{*}(y)$ is a smooth function with a cusp at y = const, which then characterizes the pg line. The tendency of the peak to diverge in amplitude is contained in the leading factor whose exponent is the MCP exponent divided by the cross over exponent.

In a previous publication (14), we demonstrated the applicability of Eq. (4) to the Fe-Mn system. However, we did not know the position of the fg line at that time, so that must be regarded as an approximation. Knowing the position of the pf and fg lines, we may now write

$$g = (x/x_{MCP} - 1) + b(T/T_{MCP} - 1), \qquad (5)$$

and

$$\mu = (T/T_{MCP} - 1) + c(x/x_{MCP} - 1), \qquad (6)$$

and find that $b = -0.7$ and $c = 7.5$ for Fe-Mn alloys. The susceptibility, rescaled with these scaling fields and with concentration determined by scanning microprobe analysis, is shown in Fig. 9. The hypothesis that the susceptibility should scale along the pg line is clearly borne out, and this gives strong evidence that this line is indeed a line of phase transitions. It should be noted that χ is not the susceptibility of the Edwards-Anderson order parameter, so that this result tells us nothing about the nature of order in the spin-glass phase. It is significant, nonetheless, that this region is bounded by a critical line along which normal scaling ideas seem to work.

The exponents in Fig. 9 are $\phi = 0.77$ and $\gamma_t = 1.1$. The cross over exponent is identical to that reported previously, although γ_t is slightly smaller. We cannot rule out the possibility that $\gamma_t = 1.0$, but ϕ is definitely less than unity.

In the presence of an applied field, the ac susceptibility at constant composition on the ferromagnetic side of the MCP can be scaled in terms of both field and temperature, and has the form

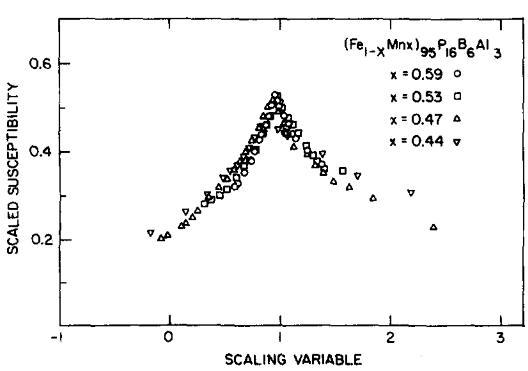

Fig. 9. Susceptibility along the spin glass line scaled according to Eq. (4). The axes are defined by Eq. (5) and Eq. (6).

$$\chi_{pf} = t^{-\gamma}\chi^{*}(H/t^{\beta\delta},\ g/t^{\phi}) \qquad (7)$$

along the pf line, and

$$\chi_{fg} = \tilde{t}^{-\tilde{\gamma}}\,\tilde{\chi}^{*}(H/\tilde{t}^{\tilde{\beta}\tilde{\delta}},\ g/\tilde{t}^{\tilde{\phi}}) \qquad (8)$$

along the fg phase boundary. Now, any feature which occurs in a field H_1 at temperature t_1 will occur at $t_2 = t_1(H_2/H_1)^{1/\beta\delta}$ in a field H_2 by virtue of the scaling of Eq. (7). Similarly, features associate with the fg transition will move down in temperature by the same amount. Hence, a useful way to detect the presence of two transitions very close to the MCP is to examine the ac susceptibility in small dc fields. This can be seen quite nicely in the Fe-Ni system for x = 0.83. Fig. 10 shows the singly peaked ac susceptibility of this alloy at zero field to be split by the application of a small field into two weak peaks which move apart. The scaling of (7) and (8) is approximately obeyed. This seems to imply that the MCP is a unique point on the T-x-H phase diagram rather than a point on a line of multicritical transitions.

DISCUSSION

The magnetic phase diagram of a number of amorphous alloys has been demonstrated to contain three phases: paramagnetic, ferromagnetic, and spin-glass. Whether the spin-glass phase is entered directly from the paramagnetic phase or through the reentrant ferromagnetic region, it is characterized by vanishing spontaneous magnetization, hysteresis, isothermal and thermal-remanent magnetization--in short, the same properties which characterize the spin-glass phases of dilute systems. Quite surprisingly, many of these features appear in the ferromagnetic range, below the temperature of the maximum in the magnetization.

There are two possibilities to consider: either the change in behavior is representative of a cross over from truly ferromagnetic to mainly random behavior, or there is still another phase. Indeed, from ac susceptibility data, it has been suggested (15) that the ferromagnetic to spin-glass transition occurs at the temperature at which the ac susceptibility begins to

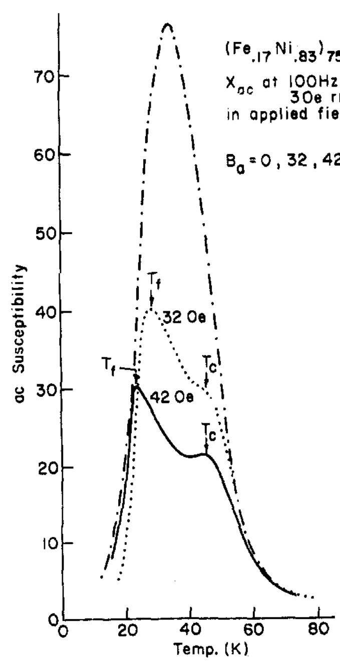

Fig. 10. Ac susceptibility of FeNi glass at x = 0.83 as a function of applied dc field.

decrease from its maximum value, the inverse of the demagnetization factor. For the alloys studied here, a similar drop in ac susceptibility occurs near the maximum in the spontaneous magnetization, at which temperature hysteresis and remanance effects become noticeable. In fact, the opening of the hysteresis loop at these temperatures has been suggested (16) as the cause of the drop in ac susceptibility. These features are indicative of a qualitative change in behavior, but not a phase transition in the usual sense.

Recently, Bray and Moore (17) have suggested that an intermediate phase, which remains ferromagnetic, will be found between the ferromagnetic and spin-glass phases in the reentrant regime. In this new phase, the symmetry of replicas in the Sherrington-Kirkpatrick model is broken, and this signals the approach of the spin-glass phase. The physical meaning of this suggestion is not clear, nor are the properties of this new phase. We simply suggest that the changes which occur in the ferromagnetic regime, though not a phase transition may be connected to the new phase. Further work is required to realize this.

In Table II we have listed our estimates of the various critical exponents based on a number of materials. The uncertainties mirror the range of observed values. Comparison with Table I seems to show that the MCP has nearly mean-field behavior. Along the pf and fg lines, nonclassical behavior is found. The fg line, despite its unusual nature, seems close to a Heisenberg ferromagnetic transition, based on its critical exponents. The pf line is distinctly different. This is surprising, since the conventional wisdom is that for isotropic systems there should be no change in critical behavior when randomness is introduced. Indeed, amorphous metals do have sharp, Heisenberg-like transitions when there is only a single transition metal component (18). Alloys, such as treated here, tend to have a different set of critical exponents when sufficiently impure. This area is one in need of further exploration.

We conclude that, despite their unphysical aspects, mean field theories of the Sherrington-Kirkpatrick type give a good qualitative description of mixed magnetic systems. The data presented here, while supporting the qualitative picture, point to the need for much more experimental and theoretical effort before the nature of random-system magnetism is fully understood.

Table II. Experimental critical exponents

β	δ	$\tilde{\beta}$	$\tilde{\delta}$	β_t	γ_t	δ_t	ϕ
0.4	5.2	0.4	4.5	.4	1.1	2.2	0.77
±.04	±.4	±0.04	±0.4	±.05	± .1	±0.4	± .05

REFERENCES

a) Supported in part by the NSF-MRL grant No. DMR-77-23999 and by the NSF-DMR-78-07763.

b) Present address: Dept of Solid State Physics, Royal Institute of Technology, Stockholm.

1) V. Cannella and J. A. Mydosh, AIP Conf. Proc. 10, 785 (1973).
2) D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett. 35, 1792 (1975); S. Kirkpatrick and D. Sherrington, Phys. Rev. B17, 4384 (1978).
3) J- H. Chen and T. C. Lubensky, Phys. Rev. B16, 2106 (1977).
4) C. R. Fincher, Jr., S. M. Shapiro, A. H. Palumbo and R. D. Parks, Phys. Rev. Lett. 45, 474 (1980).
5) B. R. Coles, B.V.B. Sarkissian and R. H. Taylor, Phil. Mag. B37, 489 (1978).
6) H. Maletta and P. Convert, Phys. Rev. Lett. 42, 108 (1979).
7) D. Hüser, G. Daub, M. Gronau, S. Methfessel and D. Wagner, in W. Zinn, et al. eds. International Conference on Magnetism (North Holland, Amsterdam, 1980) p. 207.
8) H. S. Chen, Rev. Prog. Phys. 43, 353 (1980).
9) Y. Yeshurun, K. V. Rao, and M. B. Salamon, (Preprint, 1980).
10) Y. Yeshurun, M. B. Salamon, and K. V. Rao, (Submitted for publication).
11) Y. Yeshurun, K. V. Rao, M. B. Salamon, and H. S. Chen (this conference).
12) H. E. Stanley, Introduction to Phase Transitions and Critical Phenomena (Oxford, New York, 1971) p. 185.
13) E. Figueroa, L. Lundgren, O. Beckman and S. M. Bhagat, Solid State Commun. 20, 961 (1976).
14) M. B. Salamon, K. V. Rao and H. S. Chen, Phys. Rev. Lett. 44, 596 (1980).
15) B. H. Verbeck, G. J. Nieuwenhuys, H. Stocker and J. A. Mydosh, Phys. Rev. Lett. 40, 586 (1978).
16) D. W. Carnegie and H. Claus, Phys. Rev. B20, 1280 (1979).
17) A. J. Bray and M. A. Moore, J. Phys. C13, 419 (1980).
18) L. J. Schowalter, M. B. Salamon, C. C. Tsuei and R. B. Craven, Solid State Commun. 24, 525 (1977).