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G.R. Gruzalski
University of Nebraska - Lincoln

David J. Sellmyer
University of Nebraska-Lincoln, dsellmyer@unl.edu

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G. R. Gruzalski* and D. J. Sellmyer
Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68588
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Magnetic-susceptibility and high-field magnetization measurements are presented for amorphous $Zr_{40}Cu_{50}M_{10}$ (M denoting Fe, Mn) and $Nb_{50}Ni_{50-x}Fe_x$, with x ranging from zero to about ten. Curie-Weiss fits to the susceptibility data were made to determine effective moments p_{eff} and paramagnetic Weiss temperatures, Θ. The small values of p_{eff} suggest the presence of moment instabilities depending on local environment, and the negative Θ values suggest antiferromagnetic local-moment–conduction-electron interactions. The Fe alloys develop hysteresis at low temperatures indicating the presence of a magnetically ordered state. These alloys can be characterized as *cluster glasses* becuase of the apparent importance of magnetic clusters and the development of an ordered state of spin-glass character. However, the Mn alloys show no evidence of magnetic order down to 1.3 K.

I. INTRODUCTION

There is by now a considerable body of theoretical and experimental literature on the behavior of amorphous transition-metal alloys containing magnetic ions.[1] Many of these alloys exhibit magnetic properties which are quite different from those of crystalline alloys of the same composition. Interpreting magnetic properties of an amorphous material is further complicated if the material is an alloy because of the difficulty in separating effects of chemical disorder (which refers to the number, species, and positions of an atom's near neighbors) from those of structural disorder (which denotes a lack of crystallinity). If unique calculations are to be made, the disorder must be sufficiently characterized; yet, one is usually content with understanding the behavior of an amorphous system *vis-à-vis* a crystalline system by categorizing the former as disordered in some general phenomenological sense. For example, Gubanov's[2] approach uses phenomenological fluctuations in the interimpurity exchange interaction $\mathcal{J}$. This approach can explain the observation that the ordering temperature and spontaneous magnetization of an amorphous alloy are often much lower than those of the corresponding crystalline alloy. An objection to this approach, however, is that it often requires fluctuation in $\mathcal{J}$ of order $\mathcal{J}$, which, at times, may be unlikely. A second approach is to ignore the fluctuations in the exchange and to subject each spin to a local uniaxial anisotropy field with random orientation.[3] Of course, the problem of describing an amorphous magnetic material is far more complicated than choosing one of these two descriptions or some combination of them. As already mentioned, one may wish to distinguish between the effects of chemical and structural disorder. One may also want to investigate the nature of the interimpurity interaction, the effect of disorder on the local moment stability,[4] the role of antiferromagnetic interactions between the localized moments and the conduction electrons, the effect of extremely short electron mean free paths, the effect of magnetic clustering, and so on.

Some of the above-mentioned effects have been studied by systematically investigating the magnetic properties of splat-cooled $Zr_{40}Cu_{60-x}M_x$ (M denoting Fe, Mn, Gd, and Tb) and $Nb_{50}Ni_{50-x}Fe_x$, with x ranging from zero to about ten. These amorphous alloys were chosen for several reasons. First, the magnetism in these alloys is expected to be due to localized moments. Second, rather than having two or more magnetic subnetworks, these alloys contain local moments associated with only *one* type of atom (Fe or Mn); that is, the host alloys (Zr-Cu and Nb-Ni) contain no localized moments. Thus, the analysis should be simpler than that of binary or ternary alloys in which *all* the atoms have moments. Third, these alloys are possible candidates for studying the effect of moment instabilities in that the 4*f* moments are expected to be stable whereas the 3*d* moments may be unstable depending on their environment. Fourth, following the work of Szofran *et al.*[5] on $Zr_{40}Cu_{60-x}Fe_x$, it was desired to see if replacing the solute Fe with Mn, because the likelihood of close-neighbor, antiferromagnetic Mn-Mn interactions, would result in a magnetically dilute glass exhibiting spin-glass-like behavior. It was also desired to see whether the extremely short electron mean free path in these glasses precludes one from understanding the magnetic behavior in terms of a long-range, Ruderman-Kittel-type interaction.

This paper is confined to the above-mentioned al-

loys in which the moments reside on $3d$ elements. Paper II discusses the results for the case of $4f$ moments. This paper is organized as follows. Section II is a description of the experimental procedures employed in studying all the alloys. In Sec. III we give the results and discussion for the $3d$ moments. A summary and conclusions is found in Sec. IV. Preliminary results of this work have appeared elsewhere.[6]

II. EXPERIMENTAL METHODS

Buttons of $Zr_{40}Cu_{60-x}M_x$ (M denoting Fe, Mn, Gd, and Tb, and $0 \leq x \leq 10$) were prepared by arc melting. The following metals were used in preparing the buttons: 99.99%-purity Zr rod and 99.999%-purity Fe rod obtained from the Indium Corporation of America, 99.999% Cu shot obtained from the Gallard-Schlesinger Chemical Manufacturing Corp., 99.99% Mn flakes obtained from Johnson, Matthey and Co., Ltd., and 99.9% Gd rod and 99.99% distilled Tb obtained from Research Chemicals. The arc-melting furnace was operated using a continuous flow of either gettered or prepurified argon gas. Based upon negligible weight changes observed after melting, the compositions were known to well within 1%.

The amorphous samples were produced by melting about 0.1 g of alloy (prepared by the arc-melting technique described above) in a modified arc-melting furnace.[7] The alloys were quenched into foils about 60-μm thick by rapidly propelling a copper plunger onto the melted alloy. The plunger is accelerated at about 40 g and reaches a velocity of almost 10 m/sec. The resulting cooling rate is estimated to be $10^6 - 10^7$ K/sec.

X-ray diffraction analyses were performed on all samples by transmission Laue methods using Mo $K\alpha$ radiation. Further analyses were performed on most of the samples with a diffractometer using Cu $K\alpha$ radiation. The Laue pictures exhibited diffuse rings vanishing rapidly with diffraction angle and the diffractograms showed only broad maxima, with the first broad peak for all the samples occurring in the neighborhood of $2\Theta \simeq 39$ deg. Radial distribution analyses required for the detailed characterization of the amorphous structure were not carried out in this work. Any sample showing a deviation from a smooth noncrystalline diffraction pattern was rejected. All measurements were made on as-quenched material.

High-field measurements of the magnetization (M) were made to 80 kOe in a superconducting solenoid. These measurements were made with a vibrating-sample magnetometer (VSM) from 1.3 to about 80 K. Except for the electronics[8] to detect the voltage induced in the pick-up coils, the design in general is similar to other VSM systems.[9]

Two techniques were used to measure the magnetic susceptibilty. The "zero-field" susceptibility was determined from the zero-field VSM data. The "low-field" susceptibility was measured from 1.3 to 300 K with a Faraday apparatus[10] using various fields between 0.23 and 10.4 kOe. Whenever possible, the low-field data were taken at fields in the region where M is linear in the applied field H. When this was not possible, the data were taken at fields as small as possible, yet still large enough to give reasonable signal to noise ratios. For example, the low-field $M(H)$ data for $Zr_{40}Cu_{50}Fe_{10}$ showed considerable curvature over the entire temperature range and the χ data for this sample were taken at 0.7 kOe. For a more complete description of the experimental techniques and apparatus, see Ref. 11.

III. RESULTS AND DISCUSSION

A. $Nb_{50}Ni_{50-x}Fe_x$

The low-field susceptibility $\chi(T)$ of $Nb_{50}Ni_{50-x}Fe_x$ ($x = 0, 5, 10$) was measured at 10.4 kOe. $\chi(T)$ for $x = 0$ exhibits essentially no temperature dependence; however, the data for $x = 5$ and $x = 10$ indicate a local-moment contribution to the susceptibility. Figure 1 shows the field dependence of the magnetization $M(H)$ for the $x = 10$ sample at 4.2 and 296 K and for the $x = 5$ sample at 4.2 K. Apparently, there exists a predominantly ferromagnetic cluster contribution to $M(H)$ in that, even at 296 K, there is a significant nonlinearity. As an initial attempt to understand these data, the $\chi(T)$ data for $x = 5$ and

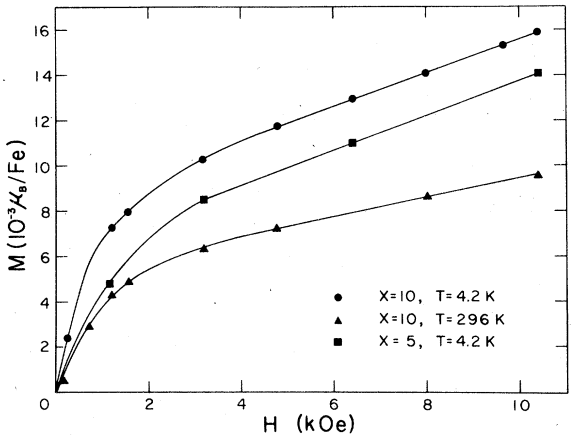

FIG. 1. Field dependence of average moment per Fe atom in $Nb_{50}Ni_{50-x}Fe_x$.

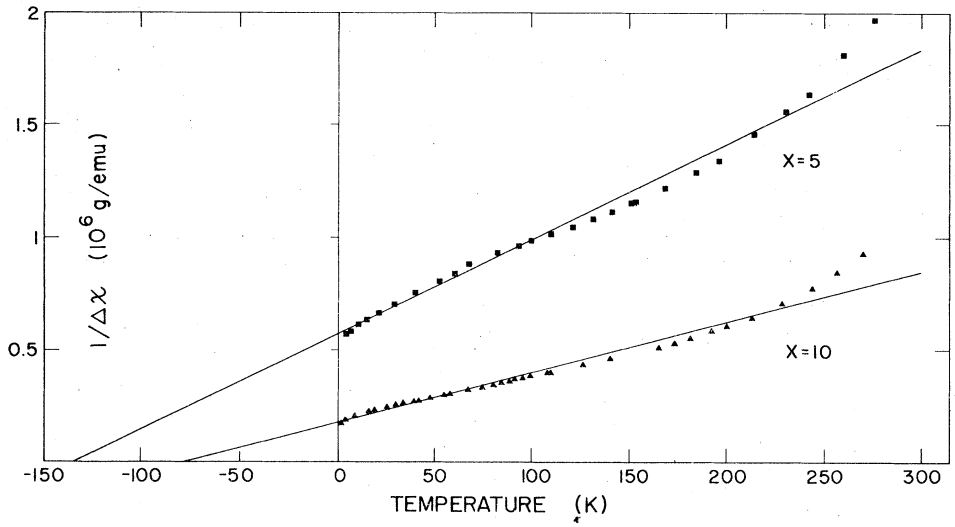

FIG. 2. Plot of $1/\Delta\chi$ vs T for $Nb_{50}Ni_{50-x}Fe_x$. Straight line is Curie-Weiss fit to data over the entire temperature range.

$x=10$ were fitted to the Curie-Weiss expression

$$\chi-\chi_0\equiv\Delta\chi=C(T-\Theta)^{-1}\ . \tag{1}$$

Here χ_0 is a temperature-independent contribution to the susceptibility, C is the Curie constant, and Θ is the paramagnetic Weiss temperature. The resulting fits are displayed in Fig. 2 and the parameters are given in Table I. From Fig. 2 it can be seen that there are systematic deviations from the simple Curie-Weiss law of Eq. (1), which may be due to the cluster contribution mentioned above. However, the effect these predominantly ferromagnetic clusters have on the Curie-Weiss parameters is probably a small one. This will be discussed further in Sec. IV.

The rather small values of $p_{\rm eff}$ for the Nb-Ni(Fe) alloys are suggestive of moment instabilities on at least some of the magnetic atoms and/or some antiferromagnetic clustering that subsists even at high temperatures. The fact that the experimental values of $p_{\rm eff}$ are essentially the same for the $x=5$ and $x=10$ alloys (Table I) suggests that any mechanism involving clustering is not solely responsible for the small values of $p_{\rm eff}$. It therefore seems reasonable that the more important effect is that of moment instabilities. This conclusion is consistent with the expectation that Fe ions will tend to lose their moments

TABLE I. Curie-Weiss parameters and T_c (see text). $p_{\rm eff}$ was obtained from C using the expression $p_{\rm eff}=(3k_BC/N_i)^{1/2}\mu_B^{-1}$, where N_i is the number of impurity atoms per unit mass of alloy. The parameters for $Zr_{40}Cu_{54}Mn_6$ were obtained from Ref. 13. Values of the angular momentum J were obtained using $p_{\rm eff}=g[J(J+1)]^{1/2}$. Here g, the Landé g factor, was assumed to be 2. $\chi(T)$ for the host alloys shows essentially no temperature dependence and equals about 0.89 μemu/g for $Zr_{40}Cu_{60}$ and about 2.1 μemu/g for $Nb_{50}Ni_{50}$. ND denotes not determined.

Sample	χ_0 (μemu/g)	Θ (K)	$p_{\rm eff}$	J	T_c (K)
$Nb_{50}Ni_{45}Fe_5$	3.2	−134	1.7	0.49	ND
$Nb_{50}Ni_{40}Fe_{10}$	5.7	−79	1.7	0.49	ND
$Zr_{40}Cu_{50}Fe_{10}$	...	...	...	...	~4
Fit *A*	8.4	−38	3.0	1.1	...
Fit *B*	−1.4	−230	6.5	2.8	...
Fit *C*	9.7	−33	2.8	1.0	...
$Zr_{40}Cu_{50}Mn_{10}$	3.7	−1.7	1.5	0.40	<1.3
$Zr_{40}Cu_{54}Mn_6$	1.8	−8.7	1.6	0.44	ND

as their local environment goes from nearly all Ni to nearly all Nb.[12]

The negative Θ values for these samples are suggestive of predominantly antiferromagnetic coupling, either between the impurities or between an impurity and the conduction electrons. (Note that there is nothing inconsistent about large intracluster interactions of one sign coexisting with weaker interimpurity interactions of another sign. The intracluster interactions, being larger than the available thermal energies, do not affect the value of Θ.) Although an unequivocal choice between these two mechanisms cannot be made, the negative Θ values are more than likely due to a conduction-electron–magnetic-impurity interaction of the Kondo-type. This is believed for two reasons. First, if the Fe atoms tended to couple antiferromagnetically, then as the concentration and hence the probability of (antiferromagnetic) coupling increases, one might expect Θ to become more negative. But the opposite is observed. Second, if these large negative Θ values were due to interimpurity couplings, then one might expect $\chi(T)$ to exhibit a maximum somewhere in the temperature range for which measurements were made. Again, this behavior was not observed. [However, it is possible that a maximum in $\chi(T)$ would be observed if the data were taken at a much smaller field.]

In addition to susceptibility measurements, high-field magnetization measurements were made on the $x=10$ alloy. Hysteresis was observed and both the coercive field ($H_c \simeq 150$ Oe) and the remanence remained constant to within experimental error for temperatures below 28.5 K; no hysteresis data were taken above this temperature.

The high-field magnetization measurements showed a continuation of the behavior exhibited in Fig. 1, i.e., the linear portion of the $M(H)$ curves continued to fields up to 80 kOe and temperatures down to 1.3 K. An example of one measurement can be seen in Fig. 3 (Curve *B*). Note that, at 80 kOe and 1.3 K, M equals 0.037 μ_B/Fe, an extremely small value. Fluctuations in the exchange couplings $\mathcal{J}$ are more than likely an important factor contributing to the small values of $M(H)$ as well as the slow approach to saturation. This behavior also is supportive of the ideas mentioned above regarding moment instabilities and antiferromagnetic coupling between the conduction electrons and local moments.

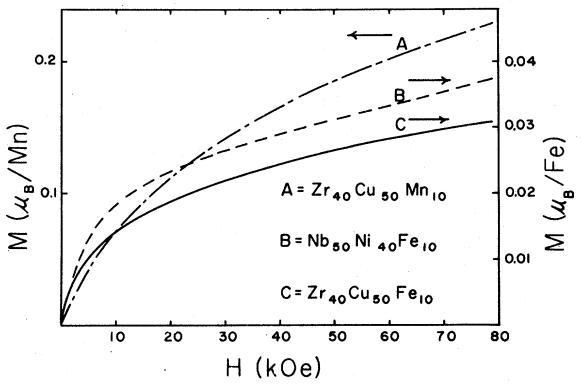

FIG. 3. $M(H)$ of $Zr_{40}Cu_{50}Mn_{10}$, $Nb_{50}Ni_{40}Fe_{10}$, and $Zr_{40}Cu_{50}Fe_{10}$ at 1.3 K.

B. $Zr_{40}Cu_{50}Fe_{10}$

The electronic states and localized magnetic moments and their interactions were studied by Szofran *et al.* in $Zr_{40}Cu_{60-x}Fe_x$ ($0 \leq x \leq 12$) in both the amorphous and crystalline states.[5] Therefore, only new results regarding one alloy in this system ($x=10$) will be discussed here.

As in the Nb-Ni(Fe) alloys, $M(H)$ for $Zr_{40}Cu_{50}Fe_{10}$ exhibited considerable concave-down curvature ($d^2M/dH^2 < 0$) even at room temperature. Again, this behavior suggests the existence of a predominantly ferromagnetic cluster contribution to $M(H)$. Also, as for the Nb-Ni(Fe) alloys, the presence of ferromagnetic clusters will affect the magnetic susceptibility data. Discussion of this subject will be deferred until Sec. IV.

Figures 4(a)–4(c) show $\chi(T)$ and three different Curie-Weiss fits for $Zr_{40}Cu_{50}Fe_{10}$. Fitting the data over the entire temperature range (Fit *A*) results in the following parameters: $\chi_0 = 8.4$ μemu/g, $\Theta = -38$ K, and $p_{\text{eff}} = 3.1$. Assuming a Landé g factor of 2, this value of p_{eff} corresponds to a spin angular momentum $S = 1.1$. (Because the orbital angular momentum is essentially quenched for $3d$ solutes, $J \simeq S$, the spin angular momentum.) With the exception of the highest-temperature data, the fits looks like a reasonable one [see Fig. 4(a)]. However, small systematic deviations from a Curie-Weiss law can be seen and, as for the Nb-Ni(Fe) alloys, these deviations may be due to the cluster contribution mentioned above. The value obtained for S, though larger than that for Fe ions in Nb-Ni(Fe), is still smaller than usually exhibited by an Fe solute in a metal solvent. (A reasonable value is $S \simeq \frac{3}{2}$.) This small value of p_{eff} suggests moment instabilities on at least some of the Fe ions. This is reasonable because one expects Fe ions will tend to lose their moments as their local environment goes from all Cu to nearly all Zr.[12] A similar situation existed for Fe in an Nb-Ni solvent.

To obtain a better agreement between experiment and theory at the highest temperatures, the data only above 50 K were fitted to a Curie-Weiss law (Fit *B*). The resulting parameters are given in Table I. Several comments should be made. First, over the temperature range for which the fit was made, the

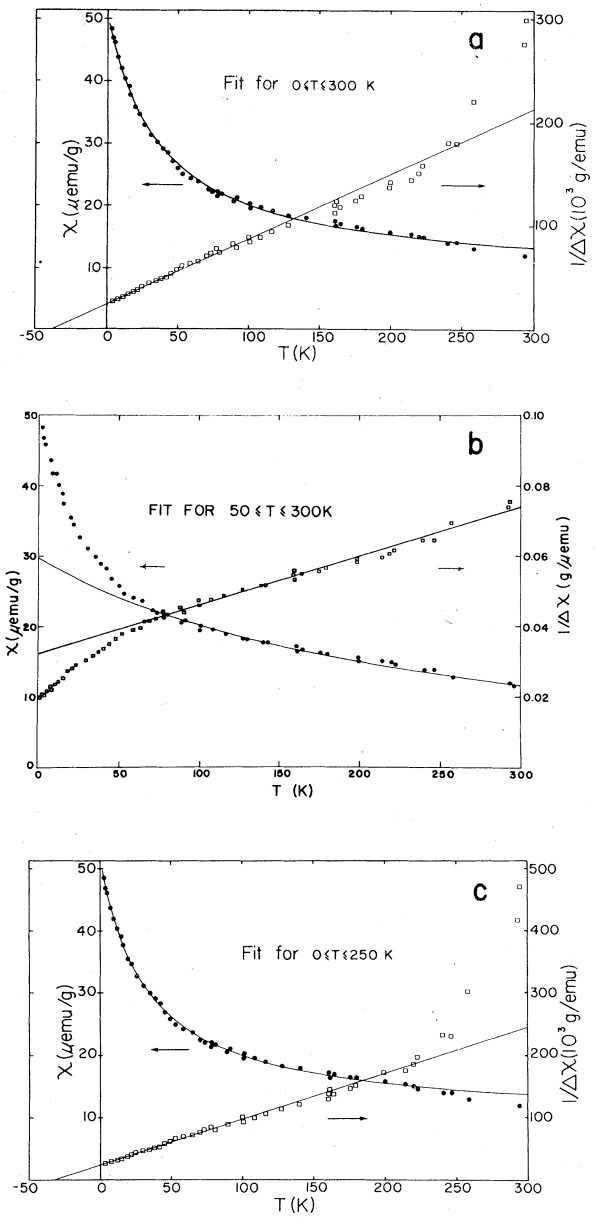

FIG. 4. $\chi(T)$ of $Zr_{40}Cu_{50}Fe_{10}$ (solid circles) at 0.7 kOe. Also plotted are $1/\Delta\chi$ for three values of χ_0 obtained from the best fits over three different temperature ranges. Both straight and curved lines are Curie-Weiss fits. Figures (a), (b), and (c) correspond to the parameters listed for fits *A*, *B*, and *C*, respectively, in Table I.

data fit a Curie-Weiss law reasonably well [Fig. 4(b)]. Again, however, small systematic deviations can be seen. Second, the Fit *B* parameters are substantially different from the Fit *A* parameters. Third, the deviation of the data from the fit below about 60 K suggests the presence of interimpurity ferromagnetic coupling.

The data for temperatures less than 250 K were also fitted to a Curie-Weiss expression (Fit *C*). The resulting parameters are given in Table I and the fit is displayed in Fig. 4(c). If one uses as a measure of goodness of fit the average of the squares of the deviations between fit and data (for the temperature range over which the fit was made), Fit *C* is a better fit than either Fit *A* or Fit *B*.

The behavior of the high-field magnetization for various temperatures is shown in Fig. 5. Again, note the small values of $M(H)$ and the slow approach to saturation. It is interesting to note that even the magnitudes of the magnetization per Fe ion are nearly the same for $Zr_{40}Cu_{50}Fe_{10}$ and $Nb_{50}Ni_{40}Fe_{10}$ (Fig. 3). And again, the possible factors responsible for this behavior include fluctuations in the exchange coupling $\mathcal{J}$, moment instabilities, and conduction-electron–local-moment interactions of the Kondo-type. However, it is difficult to estimate the relative importance of these factors.

High-field hysteresis loops were taken on $Zr_{40}Cu_{50}Fe_{10}$ and the temperature dependence of H_c was determined from these data. $H_c(T)$ dropped from about 110 Oe at 1.3 K to essentially zero at about 4 K. The "ordering temperature" T_c was defined as that temperature for which H_c vanishes. It is interesting to compare the temperature $T_c \simeq 4$ K with the ordering temperature suggested by the M^2 vs H/M curves shown in Fig. 6. These plots were constructed by using $M(H)$ data obtained by increasing H. Since the sample was not heated to above the ordering temperature each time, these $M(H)$ curves are not virgin curves in the usual sense. Note too that H is the applied field and that demagnetizing effects have not been taken into account; thus, if $Zr_{40}Cu_{50}Fe_{10}$ is a random ferromagnet, then Fig. 6 suggests an ordering temperature above 1.3 K and below 4.5 K, a range of temperatures within which falls $T_c \simeq 4$ K. (The "extrapolation" behavior of Fig. 6 makes no unequivocal statement regarding what type of ordered phase develops, e.g., it is not clear what sort of extrapolation behavior would be exhibited by a spin glass.) The inset of Fig. 6 displays $\chi(T)$ obtained from the H/M intercepts. The magnitude of this zero-field susceptibility data is in general agreement with the low-field data shown in Fig. 4; however, the maximum in the zero-field data is not exhibited by the low-field data, presumably because the 0.7 kOe field was high enough to interfere with the "freezing" of the spins. (This dependence on field strength also was seen in the 4*f* moments dissolved in Zr-Cu, as discussed in Paper II.) The maximum in this zero-field data supports the idea of a random magnetic state developing near 4 K. The precise character of this ordered magnetic state is dif-

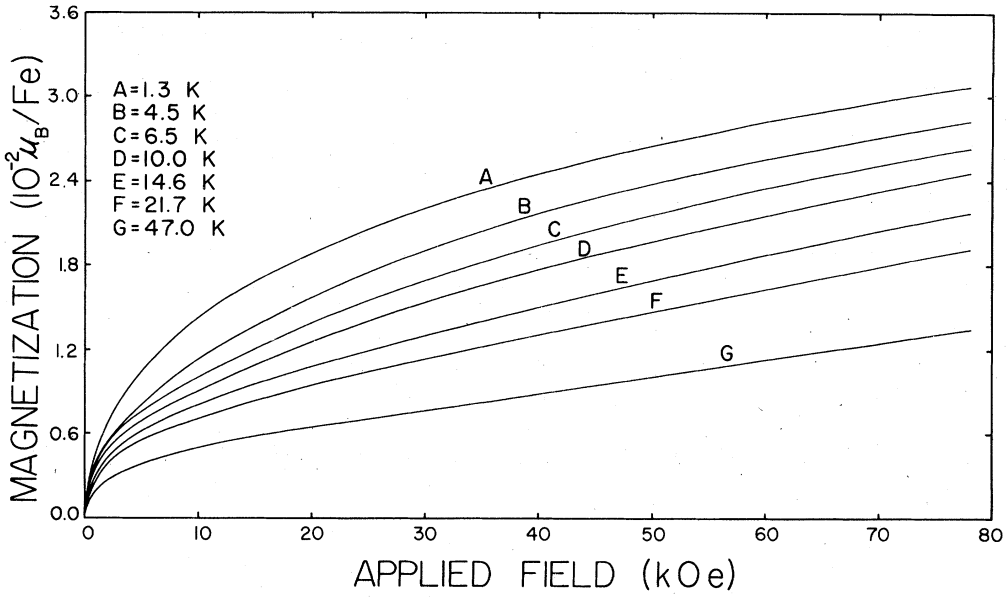

FIG. 5. $M(H)$ of $Zr_{40}Cu_{50}Fe_{10}$ at various temperatures.

ficult both to determine and to describe because of the presence of the complicating factors mentioned above (moment instabilities, Kondo-like interactions, and fluctuations in $\mathcal{J}$). However, based on the very small high-field magnetization, the small values of remanence, and the expected presence of exchange fluctuations, it seems reasonable to describe these Fe alloys as *cluster glasses,* that is, magnetically dilute alloys in which moments are found only on certain of the Fe atoms or groups of Fe atoms in close proximity, and in which the Fe cluster moments freeze below a certain temperature. The state of magnetic order of a cluster glass, as defined here, has many of the characteristics of ordinary spin glasses.

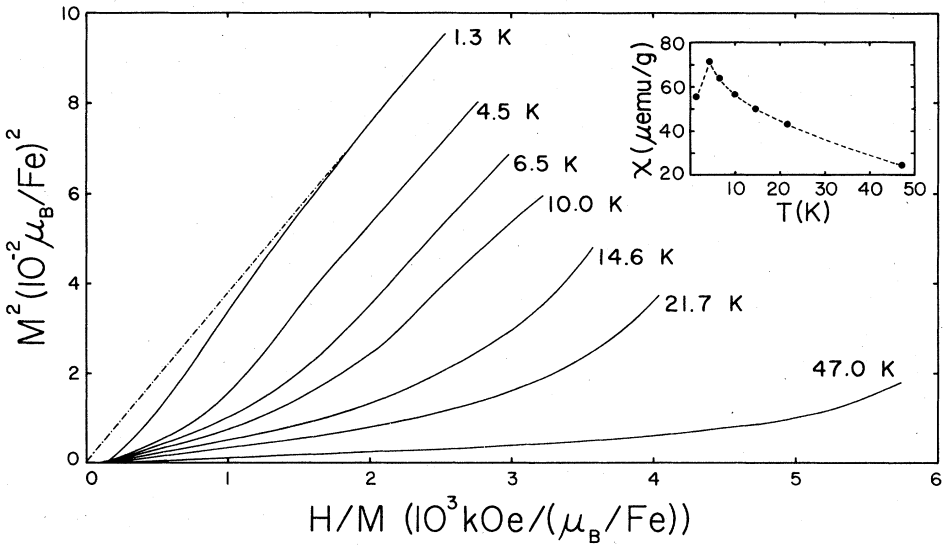

FIG. 6. Curves of M^2 vs H/M for $Zr_{40}Cu_{50}Fe_{10}$. These were obtained from "virgin" curve $M(H)$ data, where H is the applied field. The inset displays $\chi(T)$ obtained from H/M intercepts. For this alloy, 1 gOe/μemu $\equiv 1(\mu\text{emu/g})^{-1}$ $\simeq 7549$ kOe/(μ_B/Fe) .

C. $Zr_{40}Cu_{50}Mn_{10}$

The low-field (say, less than 3 kOe) $M(H)$ data for $Zr_{40}Cu_{50}Mn_{10}$ shows more concave-down curvature at room temperaure than at lower temperatures. Again, this behavior is suggestive of some predominantly ferromagnetic clustering, though in this case, a relatively small amount. The deviation from linearity was not large and its effect on the susceptibility is expected to be small.

The susceptibility data for this alloy were obtained at 3.2 kOe. The data could be fitted well to a Curie-Weiss expression with no obvious systematic deviations from the fit. Table I gives the parameters obtained for the best Curie-Weiss fit, as well as those obtained by Mizoguchi and Kudo[13] for a 6-at.%-Mn alloy. A comparison for the Curie-Weiss parameters of the Zr-Cu(Mn) alloys with those of the Nb-Ni(Fe) alloys shows several similarities. The values of χ_0 are roughly proportional to the solute concentration, the values of Θ are negative and become more negative as the solute concentration decreases, and the values of p_{eff} are essentially concentration independent and are much smaller than expected. Thus, as before, one expects that moment instabilities and antiferromagnetic interactions between the local moments and the conduction electrons are significant in determining the magnetic behavior of this alloy.

In addition to these similarities, several notable differences exist between the 10-at.%-Mn alloy and the 10-at.%-Fe alloys. The first difference is exhibited at high temperatures. As was stated above, the low-field $M(H)$ data displays concave-down curvature at room temperature. However, as the field is increased, the curvature changes to concave up. At room temperature, this change in concavity occurs in a field of about 8 kOe. From Fig. 7 it can be seen that concave-up curvature is still in evidence at 78 K but not at 46 K. [If $H = aM + bM^3 + \cdots$, then d^2H/dM^2 and $dM^2/d(H/M)$ will have the same sign as b.] A possible explanation for this behavior is the following: Suppose that some antiferromagnetic clustering subsists to room temperature and that the clusters experience local anisotropy. (Note that the coexistence of both ferromagnetic and antiferromagnetic clustering does not present a problem.) A magnetic field could then induce spin-flop-like transitions in the clusters. The net effect of these spin flops would not be a sudden increase in the magnetization as observed in antiferromagnetic crystals below the Néel

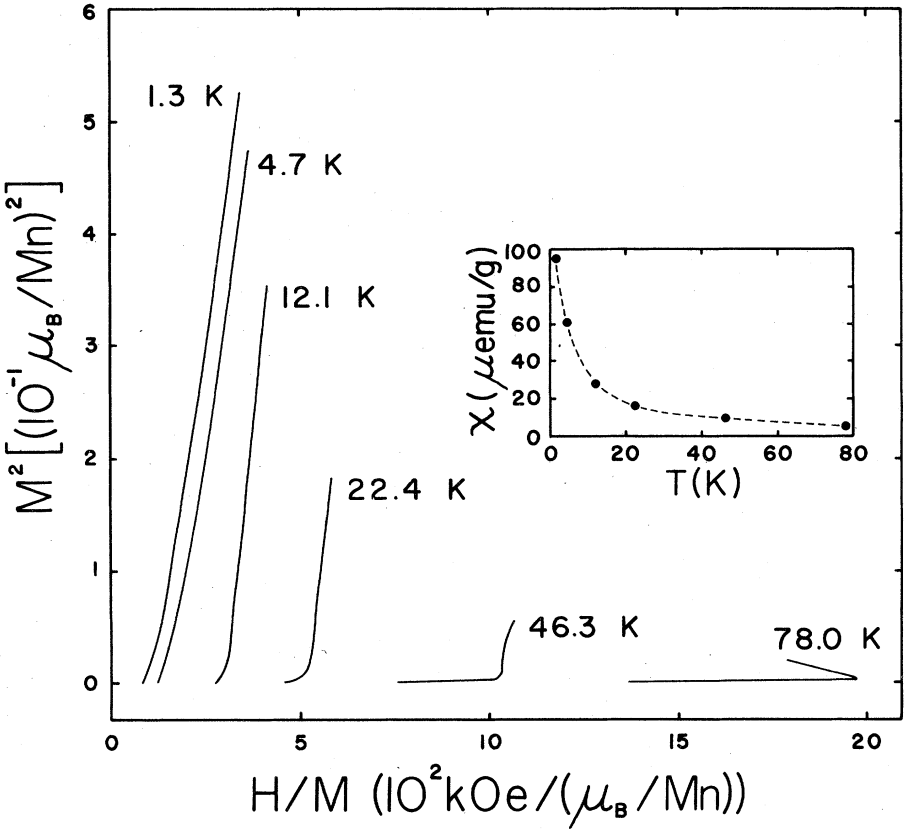

FIG. 7. For $Zr_{40}Cu_{50}Mn_{10}$, curves of M^2 vs H/M and $\chi(T)$ as in Fig. 6. For this alloy, 1 gOe/μemu $\simeq$ 7543 kOe/(μ_B/Mn) .

temperature, but a gradual increase, perhaps similar to that indicated by Fig. 7. That this behavior is not seen at lower temperatures may imply that large thermal fluctuations are needed to induce the transition and/or the effects of some other phenomenon are overshadowing those of the spin-flop-like transitions.

A second difference between the 10-at.%-Mn alloy and the 10-at.%-Fe alloy is that, even though the values obtained for p_{eff} are roughly the same magnitude, the magnetization per Mn ion in $Zr_{40}Cu_{50}Mn_{10}$ is much larger than the magnetization per Fe atom in either $Zr_{40}Cu_{50}Fe_{10}$ or $Nb_{50}Ni_{40}Fe_{10}$ (Fig. 3). Many possible factors could contribute to this behavior. For example, Kondo-like interactions or antiferromagnetic interimpurity interactions may be more pronounced in the Fe alloys than in the Mn alloys. Another factor could be that there is some local random anisotropy which is greater in the Fe alloys than in the Mn alloys (which is not inconsistent with what was said in the above paragraph). Because the effect of random anisotropy becomes more pronounced as the magnetization is increased, a properly scaled $M(H)$ curve (say, Curve C in Fig. 3) which lies above another curve (say, Curve A) at low fields, but below it at high fields, is consistent with the idea that anisotropy is more important in the system belonging to Curve C (Fe) than in the system belonging to Curve A (Mn).

The third difference between the 10-at.%-Mn alloy and the 10-at.%-Fe alloy is that no hysteresis developed for the Mn alloy down to 1.3 K. This lack of hysteresis is consistent with the idea that the local random anisotropy strength is smaller in this alloy than in the Fe alloys.[1,3,14]

Finally, it is noted that no maximum is exhibited in the zero-field susceptibility for $Zr_{40}Cu_{50}Mn_{10}$ down to 1.3 K. This can be seen in the inset of Fig. 7. Of course, it can always be said that the strength of the interactions in the Mn alloy is so weak that magnetic order would develop only at very low temperatures. However, down to 1.3 K there is no evidence for magnetic order.

IV. CONCLUSIONS

The simplest ferromagnetic system imaginable consists of only one type of magnetic atom. The most naive approach to understanding such a system is to assume that all the magnetic atoms are equivalent and that each one interacts with the remainder of the system by an effective magnetic field given by

$$\vec{H}_e = \lambda \vec{M} , \tag{2}$$

where λ is usually called the Weiss molecular-field constant. If no anisotropy is present, $\vec{M}$ points in the direction of the applied field and its magnitude is given by

$$M = g\mu_B J B_J(x) , \tag{3}$$

where

$$x = g\mu_B J(H + \lambda M)/k_B T \tag{4}$$

is the ratio of magnetic and thermal energies and $B_J(x)$ is the Brillouin function. For $x \ll 1$, Eq. (3) becomes the Curie-Weiss law

$$\chi = M/H = \mu_{\text{eff}}^2/3k_B(T - \Theta_W) , \tag{5}$$

where

$$\mu_{\text{eff}}^2 = g^2\mu_B^2 J(J+1) \tag{6}$$

and

$$\Theta_W = \mu_{\text{eff}}^2/3k_B . \tag{7}$$

The condition $x \ll 1$ usually is satisfied in the paramagnetic regime for H small and T large. It is interesting that the susceptibility of many systems more complex than the one described above also satisfies a Curie-Weiss law for H small and T large. For example, Patterson *et al.*[14] show that (in the local-mean-field approximation) a Curie-Weiss expression is the appropriate one for the susceptibility of the relatively complex system in which each spin is subjected to a local uniaxial anisotropy field with random orientation. Even systems for which there are fluctuations in the local molecular field do not pose a problem. What must be remembered is that when pertaining to more complex systems, the Curie-Weiss parameters represent some sort of average values.

The magnetic behavior of the metallic glasses discussed in this paper is very complicated. In all of the alloys, some magnetic clustering was in evidence even at room temperatures. It is not clear whether the magnetic clusters are intrinsic (due to purely random concentration fluctuations) or extrinsic (due to different chemical affinities between atoms giving rise to atomic associations different from those expected from purely random concentration fluctuations). However, in systems for which clustering is in evidence, one should not expect *a priori* a linear response to magnetic fields that are small but not approaching zero. That is, the Curie-Weiss parameters one obtains from fitting the susceptibility data of such a system to Eq. (1) may depend upon the strength of the field used while taking the data. This, unfortunately, places the values of these parameters in a vulnerable position, and any speculations arising from detailed analyses based upon the magnitude of these parameters should be regarded with a degree of skepticism.

Clustering can affect the intepretation of Curie-Weiss parameters in various ways. If the intracluster interactions are larger than the thermal energies at

the highest temperature for which data is taken, then their presence may affect the values of p_{eff} and χ_0 but will not affect the value of Θ. If these interactions are less than the thermal energies at the highest temperatures but greater than those at the lowest temperatures, then complicated behavior should be expected. It is only when the thermal energies are much larger than the magnetic energies that the values of the parameters are good measures of the local-moment properties. If this condition is not satisfied, then interpretation of the parameters, especially p_{eff}, poses a problem. However, in certain situations one can estimate the effect clustering has on these parameters.

For example, suppose that the local-moment magnetism arises from a superposition of the response due to isolated and ferromagnetically clustered ions. Assume further that the clusters are saturated in the applied field. The presence of these clusters will certainly increase the value of the low-field susceptibility over that expected if clustering were not present. However, because these clusters are saturated, the temperature-dependent magnetism is due to the "essentially isolated" moments. Hence, a knowledge of the concentration of solute atoms involved in the clustering is all that is needed to obtain the value of the average effective moment of an essentially isolated ion.

The linear behavior of the high-field magnetization data for the Nb-Ni(Fe) alloys and the fact that extrapolation of these high-field data to $H=0$ gives similar values of $M(H=0)$ at both 4 and 296 K suggest that this system may be qualitatively similar to the one described in the above paragraph. Also, the extrapolated $M(H=0)$ values suggest that as little as 0.2% of the Fe atoms are in ferromagnetic clusters.[6] So, in this case, the values of p_{eff} obtained in the usual way may be good measures of the average effective moment per isolated Fe ion. This, of course, assumes that the effect of antiferromagnetic coupling is negligible, which is reasonable. In fact, that p_{eff} is independent of concentration is a good indication that large intracluster interactions (ferromagnetic or antiferromagnetic) involve only a small amount of the solute atoms. Recall that concentration independent values of p_{eff} were observed in both the Nb-Ni(Fe) and Zr-Cu(Mn) systems.

For $Zr_{40}Cu_{50}Fe_{10}$, the data were taken at a relatively low field (0.7 kOe) and the clusters did not appear to saturate; thus it is possible that in this system the effect on the parameters due to the presence of the clusters was significant. That Fit *B* significantly differs from Fits *A* and *C* may also be an effect of this rather complex clustering. Suppose, for example, that the thermal energies at about 250 K are greater than or approximately equal to the average strength of the ferromagnetic intracluster interactions. Under these circumstances the effective moment p_{eff} and the magnitude of the Kondo parameter Θ obtained from fitting the higher-temperature data may be larger than those parameters obtained from fitting the lower-temperature data (because of the increased number of "isolated" Fe atoms). Also, χ_0 obtained from the higher-temperature data may be smaller (because the temperature-independent cluster contribution to the susceptibility is smaller).

Even though these relatively dilute metallic glasses each contain moments associated with only one type of $3d$ magnetic atom, their magnetic behavior is very complicated. Moment instabilities, conduction-electron–local-moment interactions of the Kondo-type, fluctuations in exchange couplings, local random anisotropy, magnetic clustering, and very short electron mean free paths are probably present to some degree in all of them.

Despite these complexities, the following conclusions can reasonably be drawn from this work. (i) A low-temperature random magnetic state develops in the Fe alloys. It is suggested that the Fe alloys be called cluster glasses because of their similarities to spin glasses. (ii) The Mn alloy exhibits no evidence of order down to 1.3 K. (iii) Ferromagnetic clustering is present in all the alloys but is most prominent in the alloys containing Fe. Both ferromagnetic and antiferromagnetic clustering may be present in the Mn alloys. (iv) The small values of p_{eff} and the negative values of Θ exhibited by the Nb-Ni(Fe) and Zr-Cu(Mn) alloys are primarily attributable to moment instabilities and Kondo-like interactions, respectively. (v) Magnetic clustering is responsible for the dispersion of Curie-Weiss parameters obtained from the $Zr_{40}Cu_{50}Fe_{10}$ susceptibility data.

In Paper II,[15] the magnetic properties of metallic glasses with rare-earth solutes are presented. Because these materials are also amorphous, one still expects short electron mean free paths and molecular-field fluctuations to add to the complexity. However, when rare-earth atoms are dissolved in metals, they normally carry the same ionic Hund's rule magnetic moments as in insulators. Thus, moment instabilities should not contribute to the complexity. Also, effects of conduction-electron–local-moment interactions and strong magnetic clustering are expected to be negligible. Furthermore, by choosing solutes which have states of different angular momentum, the effect of local random anisotropy can be controlled to some extent. Thus, interpreting the behavior of such alloys should be less difficult.

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*Present address: Div. of Appl. Sci., Harvard Univ., Cambridge, Mass. 02138

[1]See the following recent reviews and treatises: J. M. D. Coey, J. Appl. Phys. 49, 1646 (1978); R. Alben, J. J. Becker, and M. C. Chi, J. Appl. Phys. 49, 1653 (1978); R. W. Cochrane, R. Harris, and M. J. Zuckermann (unpublished); and *Amorphous Magnetism II,* edited by R. A. Levy and R. Hasegawa (Plenum, New York, 1977).

[2]A. I. Gubanov, Fiz. Tver. Tela (Leningrad) 2, 502 (1960).

[3]R. Harris, M. Plischke, and M. J. Zuckermann, Phys. Rev. Lett. 31, 160 (1973); see also Ref. 1.

[4]When transition-metal atoms are dissolved in metallic host, they often do not exhibit the magnetic moment predicted by Hund's rule. For example, Fe does not have a magnetic moment when dissolved in Al, but when dissolved in Pd, each Fe impurity contributed $13\mu_B$ to the magnetization. Moment stability refers to the fact that the magnitude of the moment for a given type of atom may depend upon its local environment.

[5]F. R. Szofran, G. R. Gruzalski, J. W. Weymouth, D. J. Sellmyer, and B. C. Giessen, Phys. Rev. B 14, 2160 (1976).

[6]G. R. Gruzalski, J. W. Weymouth, D. J. Sellmyer, and B. C. Giessen, in *Amorphous Magnetism II,* edited by R. A. Levy and R. Hasegawa (Plenum, New York, 1977), p. 235; G. R. Gruzalski, J. D. Patterson, and D. J. Sellmyer, J. Appl. Phys. 49, 1696 (1978).

[7]A similar apparatus is described by M. Ohring and A. Haldipur, Rev. Sci. Instrum. 42, 530 (1971).

[8]For details of the electronic detection system, see J. A. Gerber and D. J. Sellmyer (unpublished).

[9]See, e.g., M. Springford, J. R. Stockton, and W. R. Wampler, J. Phys. E 4, 1036 (1971).

[10]B. Dellby and H. E. Ekström, J. Phys. E 5, 342 (1971).

[11]G. R. Gruzalski, Ph.D. thesis (University of Nebraska, 1977) (unpublished).

[12]See, e.g., R. Orbach, *Magnetism and Magnetic Materials-1974,* edited by C. D. Graham, Jr., G. H. Lander, and J. J. Rhyne, AIP Conf. Proc. No. 24 (AIP, New York, 1975), p. 3, and references therein.

[13]T. Mizoguchi and T. Kudo, *Magnetism and Magnetic Materials-1975,* edited by J. J. Becker, G. H. Lander, and J. J. Rhyne, AIP Conf. Proc. No. 29 (AIP, New York, 1976), p. 167.

[14]J. D. Patterson, G. R. Gruzalski, and D. J. Sellmyer, Phys. Rev. B 18, 1377 (1978).

[15]G. R. Gruzalski and D. J. Sellmyer, Phys. Rev. B 20, 194 (1979) (following paper).