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Electronic and magnetic properties of amorphous and crystalline $\text{Zr}_{40}\text{Cu}_{60-x}\text{Fe}_x$ alloys*

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Electronic states and localized magnetic moments and their interactions were studied in amorphous and crystalline $\text{Zr}_{40}\text{Cu}_{60-x}\text{Fe}_x$ alloys for $0 \leq x \leq 12$. Electrical resistivity, magnetic susceptibility, and high-field magnetization measurements were performed. In the dilute crystalline alloys Curie-Weiss behavior is seen in the susceptibility and is associated with localized moments ($\mu_{\text{eff}} \approx 3\mu_B$) on the iron atoms. At higher iron concentrations ferromagnetism is observed. Curie-Weiss behavior also is seen in the susceptibility of the dilute ($0 < x \leq 6$) amorphous alloys; however, for these alloys the dependence on Fe concentration appears complex and the effective moments on the iron atoms are very small ($\mu_{\text{eff}} \approx 0.7\mu_B$). There is some evidence that the local environment of the Fe atoms is important and may depend sensitively on the quench rate used in making the samples or, perhaps, on room-temperature ageing effects in the samples. The dilute amorphous alloys exhibit a negative $d\rho/dT$ from 1.4 to 300 K. This is not to be associated with Kondo spin-flip scattering but it is consistent with several other mechanisms including localized-spin-fluctuation scattering, s - d scattering in a nonmagnetic model, scattering from tunneling states in the amorphous alloy, or quasi-liquid-metal-pseudopotential scattering. A recent theory due to Nagel and Tauc on the nearly-free-electron approach to metallic glass alloys is shown to be consistent with this last idea and also is used to account for other features exhibited by the amorphous Zr-Cu system. In the concentrated ($x > 6$) amorphous alloys, resistance maxima and magnetic hysteresis are seen at low temperatures. For $x = 12$ a random ferromagnetic state develops with $T_0 = 30$ K, which is some five times smaller than T_0 for the corresponding crystalline alloy. The saturation moment in the amorphous alloy is also considerably smaller than in the crystalline case. This behavior is similar to other systems in which the crystalline-to-amorphous transition greatly weakens the magnetism.

I. INTRODUCTION

Since the development of techniques for rapidly cooling liquids, a large number of amorphous structures have been discovered. These materials are providing new opportunities for studying the problem of electronic and magnetic states in disordered solids. The inherent interest in such studies is augmented by the fact that disordered materials have potential uses in a variety of technological applications.¹ In the class of amorphous solids which are metallic, many of the materials obtained thus far have been produced by splat cooling molten mixtures of transition metals and metalloids (P, Si, etc.).² However, Ray *et al.*³ have produced noncrystalline alloys in a system containing only transition metals, namely, Cu and Zr, which were shown to be amorphous in subsequent work.⁴

In this paper we present the results of magnetic susceptibility, high-field magnetization, and electrical-resistivity measurements on amorphous $\text{Zr}_{40}\text{Cu}_{60}$ alloys to which small amounts of Fe have been added. The study was motivated in general by interest in the electronic and magnetic properties of glassy metals containing no "glass formers." In particular, it was of interest to study the

influence of host disorder on the local-moment formation of the Fe atoms, on the coupling of the Fe moments as their concentration increases, and on the general nature of any low-temperature cooperative magnetic state. In addition, speculating that the Fe impurities in the ZrCu(Fe) alloys are randomly distributed and couple via the Ruderman-Kittel-Kasuya-Yosida interaction, the study of these alloys appeared to be ideal for testing theoretical work of Kok and Anderson⁵ on the effects of the amorphous nature of a host alloy on this coupling. In particular, the theory predicted that the paramagnetic Weiss temperature, often finite for a crystalline alloy, would tend towards zero in an amorphous alloy. It will be seen that the amorphous alloys exhibited some interesting properties, and for this reason we were led to crystallize a set of samples to further study the effects of the local environments of the Fe atoms on moment formation and magnetic interactions. Preliminary accounts of this work have appeared elsewhere.⁶

II. EXPERIMENTAL PROCEDURE

The amorphous samples were produced as follows: Buttons of $\text{Zr}_{40}\text{Cu}_{60}$ and $\text{Zr}_{40}\text{Cu}_{60-x}\text{Fe}_x$ with $x = 1, 3, 6, 8, 10$, and 12 were prepared by arc

melting, using high-purity Cu and iodide Zr (both better than 99.99% pure). The quenched samples were produced by melting 100–250 mg of alloy in a modified arc-melting furnace equipped with a copper plunger; they were then quenched into foils of $\approx 50\text{-}\mu\text{m}$ thickness by rapidly propelling the plunger onto the melted alloy. Cooling rates of $10^6\text{--}10^7\text{ K/sec}$ were achieved.

The nominal Fe concentrations of several alloys were verified with x-ray fluorescence techniques. The amorphous nature of the alloys was confirmed by x-ray diffraction and by measuring the heat of crystallization released upon heating the alloys through the crystallization temperature. The crystallization temperature measurements were made by means of differential thermal analysis (DTA).

The magnetic susceptibility χ was measured with a standard Faraday technique⁷ between 1.4 and 300 K. All amorphous-alloy data were taken at a field of 10.4 kOe, and the crystalline-alloy data were taken at various fields ranging from about 1 to 10.4 kOe. Electrical resistivity ρ was determined in the same temperature range by attaching current and potential leads to thin strips of the samples with Ag paint. A constant current was passed through the sample and the voltage determined with a Keithley Model 180 digital voltmeter. Temperature was measured in both the susceptibility and resistivity experiments with calibrated GaAs or Si diodes. Measurements of the magnetization were made on the $x = 12$ samples to 80 kOe in a superconducting solenoid. These measurements were made with a vibrating-sample magnetometer, in which the temperature was controlled by a Lakeshore Cryotronics capacitance controller. All the experiments utilized a digital data-acquisition system, which is described in detail elsewhere.⁸

The amorphous samples (with the exception of the $x = 12$ alloy) were quite flexible and could be cut with scissors. After crystallization, however, the samples were extremely brittle. This necessitated cutting the sample before crystallization and keeping it flat (between two microscope slides) during crystallization. The extreme fragility of the samples made it difficult to mount them on the apparatus without cracking them. In some cases, those that were mounted successfully cracked upon cooling to low temperatures. Therefore, it was possible to obtain only qualitative resistivity data on the crystallized samples.

III. RESULTS

Figure 1 shows a typical x-ray diffraction pattern for one of the amorphous samples. It is seen that there is only one strong peak and a weaker and broader second maximum, which is the typical

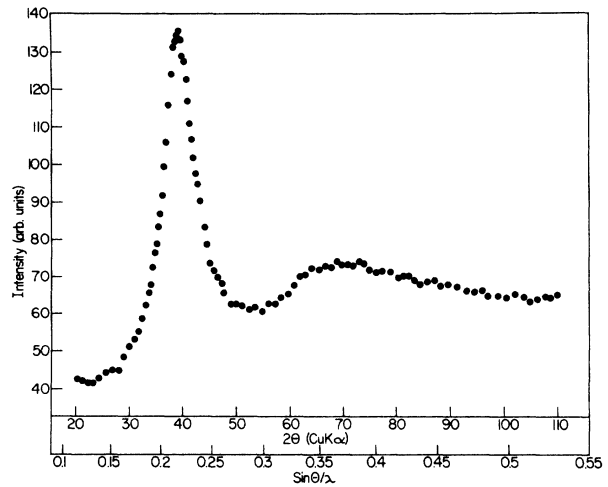


FIG. 1. X-ray diffraction pattern for amorphous $\text{Zr}_{40}\text{Cu}_{60}$. The radiation was $\text{CuK}\alpha$.

behavior of liquid or glassy metals. None of the amorphous samples showed any evidence of additional order.

Figure 2 shows the results of the DTA measurements. Figure 2(a) shows consecutive DTA runs for 80 mg of host material. In run 1 the exothermic crystallization process is clearly in evidence at about 500 °C. Run 2 confirms that the phenomenon observed in run 1 was due to crystallization. All DTA runs were made with $dT/dt = +10\text{ }^\circ\text{C/min}$ using powdered alumina as a reference material. The $\alpha\text{-}\beta$ transition of quartz at 573 °C was used as

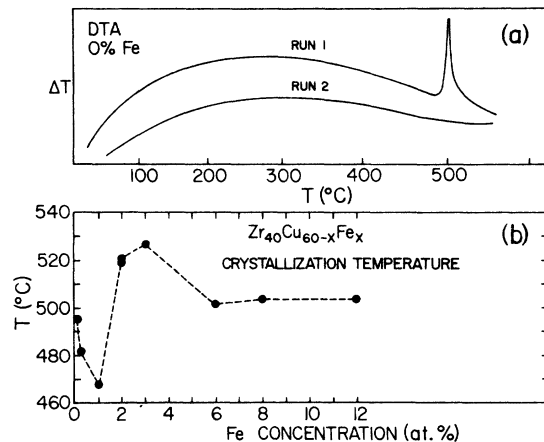


FIG. 2.(a) Differential thermal analysis scans for $\text{Zr}_{40}\text{Cu}_{60}$ in the amorphous state (run 1) and for the same sample (run 2) after being crystallized. (b) Crystallization temperature determined from the peak in the DTA runs. The value at $x = 0$ is the average of six measurements with T_C values ranging from 490 to 500 °C. The point at $x = 0$ was confirmed by independent measurements of A. Kerns (Ref. 9).

a temperature calibration check. The DTA results for several other samples are indicated in Fig. 2(b). The line is simply to connect the points in order of ascending Fe concentration. The full width at half-maximum of the exothermic peak is also dependent on the Fe concentration, but no attempt at a quantitative analysis was made.

X-ray diffraction analysis on the crystallized alloys showed many lines characteristic of the crystalline state. The phase diagram¹⁰ of Zr-Cu shows the existence of a congruently melting intermetallic compound Zr_2Cu_3 at the composition of our amorphous host alloy. Recent work¹¹ indicates that, in fact, a compound with a fairly complex orthorhombic structure exists with the composition Zr_7Cu_{10} . Since this corresponds to 41.2% Zr, our host alloy in the crystalline state may contain a small fraction of second phase; as we shall see later, this would not affect the general conclusions reached in connection with local-moment properties associated with doping the crystalline compound with small amounts of Fe.

The general behavior of χ for selected amorphous samples in the field-cooled state is shown in Fig. 3. As a test of the effect of field cooling, measurements at 1.5 kOe were made on the $x = 12$ sample cooled in zero field. No qualitative differences from Fig. 3 were observed in the low-temperature behavior. Except for a small upturn at the lowest temperatures, the host susceptibility shows very little temperature dependence. The addition of iron clearly increases the temperature dependence of the susceptibility at low tempera-

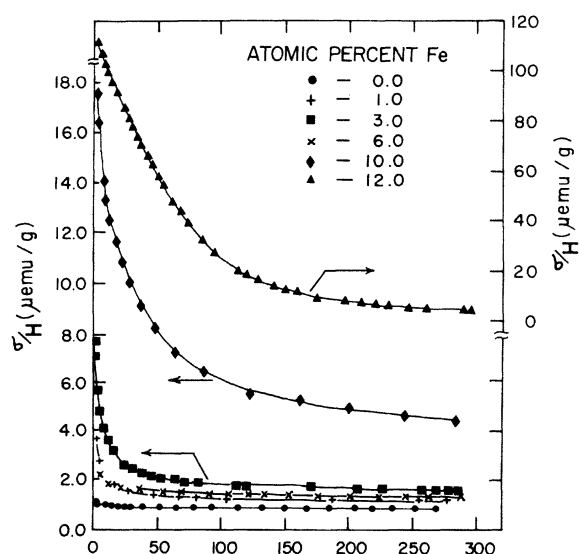


FIG. 3. Magnetic susceptibility σ/H for selected amorphous alloys, where σ is the moment per unit mass and H is the applied field (see text).

tures in such a way as to be indicative of local moments associated with at least some of the Fe atoms. There is one puzzling aspect of Fig. 3 that should be emphasized. This is that the susceptibility does not increase monotonically with the Fe concentration, that is, $\chi(x=3) > \chi(x=6)$. In addition, measurements were made on a few other samples at selected temperatures, and these measurements also showed that $\chi(x)$ was not a monotonically increasing function of x . It should be emphasized that all of the samples were checked with x rays to confirm that they were amorphous. Also, there were no gross inhomogeneities in Fe composition in a single specimen since x-ray fluorescence measurements on several portions of the same sample gave essentially identical results. A possible reason for complex concentration dependence of the susceptibility is that because of the difficulty in reproducing exactly the quench rate in the splat-cooling technique, there may be differences in the local environment of the Fe atoms, affecting, for example, the short-range Fe-Fe correlation functions in the various samples. Other workers have commented upon the same feature seen in structural¹² and magnetic-susceptibility data¹³ of other glassy metal systems.

The gross features of the temperature dependence of χ for several crystalline samples are shown in Fig. 4. The ordinate of Fig. 4 is logarithmic while the ordinate of Fig. 3 is linear. In the crystalline state, χ increases as x increases from zero, which is typical of local-moment formation at impurity sites. The upturn at low temperatures for small x is also indicative of local moments. The susceptibility of the $x = 8$ and 12 samples is much larger in the crystalline state than in the amorphous state. It should be mentioned that we have not investigated the phase in which the iron atoms exist after crystallization. For example, they may be in a random solid solution in Zr_7Cu_{10} , or perhaps they could be a constituent of an equilibrium phase, such as $ZrFe_2$. Thus it is not possible to discuss the local-moment properties of the iron atoms in the crystalline state in terms of well-defined iron-atom local environments.

Resistivity data for the host and some low-concentration amorphous samples are shown in Fig. 5, where $r(T) \equiv [\rho(T)/\rho(296 \text{ K}) - 1]$. It is seen that $d\rho/dT$ is negative over the whole temperature range. The value of ρ for all the samples is approximately $350 \mu\Omega\text{cm}$. Except for the region below 20 K, all of the samples appear to contain a negative T^2 term in $r(T)$ to about 50 K; at high temperatures there is a tendency towards a linear behavior. As a test of the low- T behavior, $r(T)$ for the host sample is plotted versus T^2 in Fig. 6. If, for the moment, the upturn below 20 K is ignored, it is

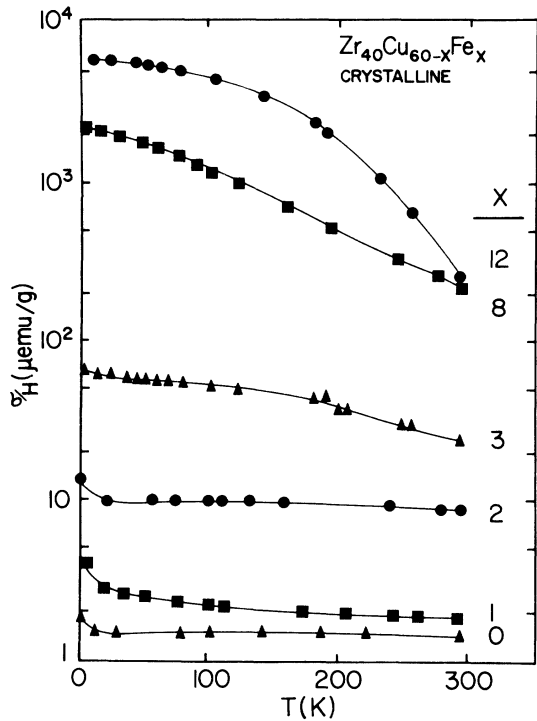


FIG. 4. Magnetic susceptibility σ/H for selected crystalline alloys, where σ is the moment per unit mass and H is the applied field (see text).

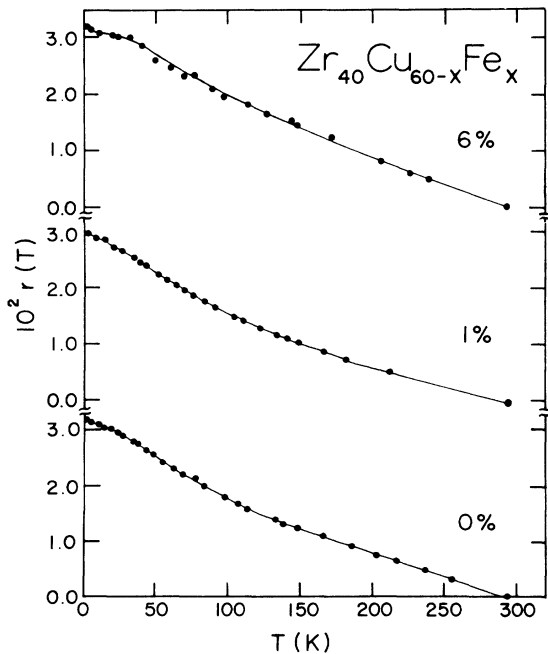


FIG. 5. Fractional change in the resistance of some low Fe-concentration amorphous alloys. $r(T) = [\rho(T) - \rho(296 \text{ K})] / \rho(296 \text{ K})$.

seen that $\rho(T)$ can be represented by

$$\rho(T)/\rho(0) = 1 - (T/\Theta')^2 \tag{1}$$

for $T < 50 \text{ K}$, with $\Theta' = 697 \text{ K}$. $\rho(T)$ vs T^2 plots for other samples ($x = 1, 3, 4, 5$) show behavior similar to Fig. 6, each with an upturn at low T and Θ' values between 700 and 840 K.

In the most concentrated amorphous alloys, the resistance-maximum phenomenon develops at a temperature T_{max} as is seen in Fig. 7. There are resistivity maxima at approximately the same T_{max} ($\approx 30 \text{ K}$) for $x = 10$ and 12, and no maxima above 4 K for $x = 8$. The occurrence of negative $d\rho/dT$ and resistance maxima are reminiscent of similar behavior often seen in crystalline spin glasses such as Cu(Mn). However, there are some important differences in the present amorphous alloys. In the first place, there are no corresponding susceptibility maxima near T_{max} as is seen in Fig. 3. Secondly, in crystalline spin glasses typically $T_{\text{max}} \propto x^m$, where $0.5 \leq m \leq 1$, and this behavior clearly is not present in our alloys.

Several attempts were made to measure $\rho(T)$ for the crystalline alloys, but reliable data could not be obtained over the whole temperature range for any sample because of the extreme brittleness of the samples. The data contained step functions which were not reproducible, presumably because of the development of tiny cracks in the samples. However, if we ignore these discontinuities, $d\rho/dT$ was zero, or positive for the $x = 0, 0.5, \text{ and } 1$ crystalline alloys over the whole temperature range. That is, if a resistance minimum were present in these samples at the lowest temperatures, it would have had to have been smaller than the precision of the measurements, i.e., about 0.1%.

In view of the observed resistance maxima which

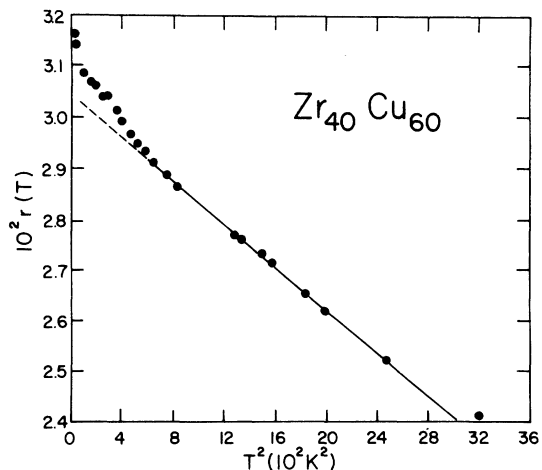


FIG. 6. $r(T)$ for the amorphous host alloy in the low-temperature region.

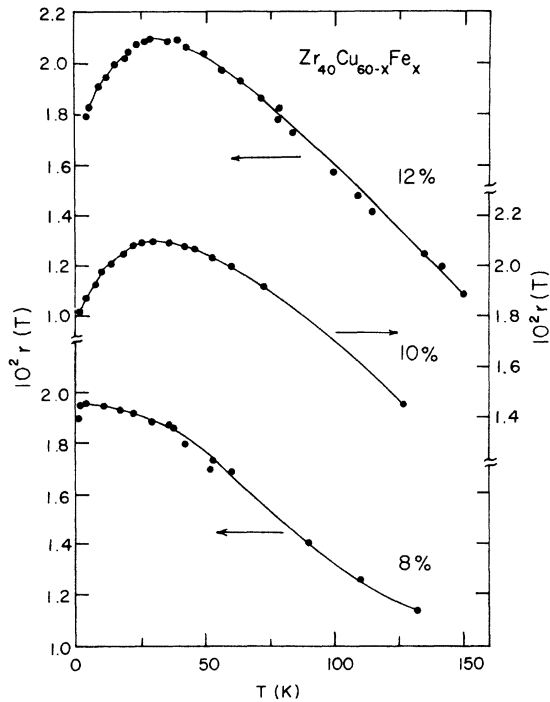


FIG. 7. $r(T)$ for several high Fe-concentration amorphous alloys.

are suggestive of a low-temperature ordered state similar to that seen in spin glasses, magnetization measurements were made with the $x = 12$ sample at low temperatures to detect the presence of hysteresis. Figure 8 shows hysteresis loops in the amorphous and crystalline $x = 12$ samples. In the amorphous state the hysteresis was absent when the sample was raised above T_{\max} . Cooling the sample in a high field had no measurable effect on the hysteresis loop. On the other hand, in the

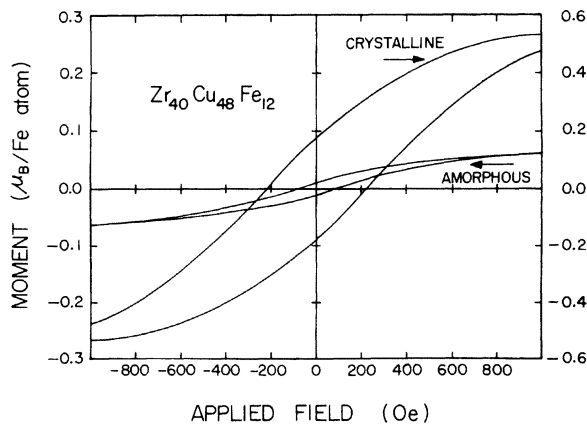


FIG. 8. Hysteresis loops for the amorphous and crystalline $Zr_{40}Cu_{48}Fe_{12}$ at 4.2 K. The applied field goes to 80 kOe.

crystalline state, the hysteresis remained up to 40 K, approximately the maximum temperature at which our vibrating-sample-magnetometer temperature controller operates; furthermore, Arrott plots determined from Faraday data on the $x = 12$ crystalline alloy showed that its magnetic ordering temperature was approximately 150 K.

Another significant difference between the amorphous and crystalline magnetic properties is illustrated in Fig. 9. It is seen that the crystalline alloy saturates at a low-field value, whereas the amorphous alloy approaches saturation only in fields of ~ 80 kOe. The moment values per Fe atom at 80 kOe are $0.66\mu_B$ and $0.18\mu_B$ for the crystalline and amorphous 12-at. % alloys, respectively.

IV. DISCUSSION

A. Host alloy: $Zr_{40}Cu_{60}$

There are several interesting aspects of the amorphous host alloy that must be discussed before considering localized moments and their interactions in the doped alloys. These include: (i) the origins of the negative $d\rho/dT$ and the $1-(T/\Theta)^2$ behavior in $\rho(T)$, and (ii) the origin of the upturn in $\rho(T)$ and $\chi(T)$ seen at the lowest temperatures ($T \lesssim 20$ K) in Figs. 3, 5, and 6.

There are several possible mechanisms which may be capable of explaining the temperature dependence of ρ in the host sample. These include: (1) localized-spin fluctuations (LSF),^{14,15} (2) Mott $s-d$ scattering,¹⁶ (3) tunneling-state scattering,¹⁷ (4) quasi-liquid-metal-pseudopotential scattering,¹² and (5) Kondo spin-flip scattering¹⁸ from unwanted magnetic impurities in the host sample. This last mechanism does not seem likely because the resistance behavior changes very little upon adding Fe impurities. Also, magnetoresistance measurements are not consistent with the Kondo mechanism.

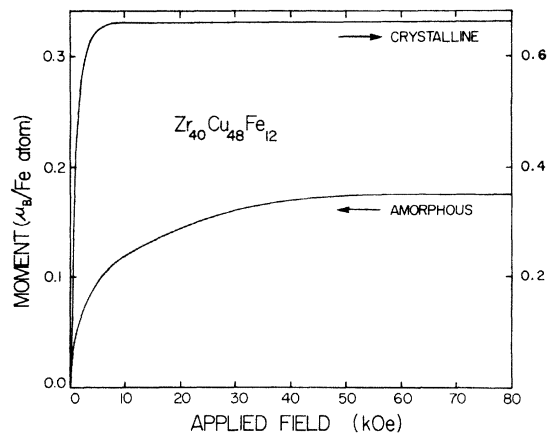


FIG. 9. High-field magnetization of amorphous and crystalline $Zr_{40}Cu_{48}Fe_{12}$ alloys.

ism. The magnetoresistance, defined as $[\rho(H) - \rho(0)]/\rho(0)$, was measured for $H = 10$ kOe on the $x = 10$ samples. The values at $T = 4.2$ and 296 K were approximately $+3 \times 10^{-4}$ and 0 , respectively, for both samples. If the increase in ρ as T decreased were due to ordinary spin-flip scattering, then one would expect a *negative* magnetoresistance since an increasing field freezes out the spin-flip scattering mechanism. Though it appears possible to rule out the Kondo effect, it is not easy to distinguish between the first four explanations mentioned above. We discuss these briefly in turn.

In the amorphous $Zr_{40}Cu_{60}$ alloy it does not seem unreasonable that on a local basis the filled Cu s and d levels will overlap the (mostly empty) d levels of the Zr atoms. Thus, there could be localized virtual d levels which could have LSF associated with them. On the other hand, if one adopts a spatially uniform collective-electron viewpoint, there could be a band of fairly immobile carriers based on Zr d states, and a band of mobile carriers based mainly on Cu s states. This is the Mott s - d scattering model in which the low-temperature resistivity behavior can be thought of simply as a temperature-dependent residual resistance.¹⁶ Both the LSF and s - d models predict low-temperatures resistivity behavior given by Eq. (1). In fact, Rivier and Zuckermann¹⁴ and Zuckermann¹⁵ have developed an LSF theory for dilute alloys which predicts $\rho(T)$ behavior quite similar to that which we observed over the whole temperature range. However, we obviously are not able to determine the phonon-scattering contribution to $\rho(T)$, which makes a quantitative comparison with the LSF theory impossible. Similarly, a calculation of Θ' values for each theory cannot be made because we have no knowledge of the electronic structure or of the density of states and its derivatives, which are necessary for such calculations. In general, the situation with respect to the LSF *versus* s - d models in amorphous $Zr_{40}Cu_{60}$ is similar to the controversial use of these same models in explaining the resistance minima observed in disordered Ag-Pd alloys near the equiatomic composition.¹⁹

The third and fourth mechanisms mentioned above were developed to deal specifically with amorphous metals. Tunneling-state scattering refers to recent theoretical work by Cochrane *et al.*¹⁷ These workers have shown that when electrons scatter from an atom which can tunnel from one site in the solid to another, the Hamiltonian describing the alloy can be put into the *form* of a Kondo-like anisotropic-exchange interaction which leads in third order to a resistivity varying as $\ln T$. This theory, which is completely nonmagnetic in origin, is consistent with the observation in our

alloys that there is little difference in $\rho(T)$ between the host alloy and the dilute Fe-doped samples.

The fourth possibility, that of quasi-liquid-metal-pseudopotential scattering, is also completely nonmagnetic in origin. This possibility, based upon theories²⁰ of electron scattering in liquid metals by Ziman and others, was suggested by Sinha¹² to explain negative $d\rho/dT$ measurements observed in some amorphous Ni-Pt-P alloys. In these theories the resistivity is obtained in the Born approximation and is given by

$$\rho \propto \int_0^{2k_F} S(q)v^2(q)q^3 dq, \quad (2)$$

where $v(q)$ is the pseudopotential form factor and $S(q)$ is the structure factor. Nagel and Tauc²¹ recently have given support to such nearly-free-electron ideas when applied to certain metallic glass alloys $M_{1-y}X_y$, where M is a transition or noble metal, and X is a metalloid. Their model shows that an alloy for which $2k_F = q_p$ should be more stable against crystallization than one for which $2k_F \neq q_p$; here q_p is that value of q for the first peak in $S(q)$. (Among other accomplishments their theory explains why the metal content for these metal-metalloid alloys is roughly 80%.) Because of the q^3 factor, the integral in Eq. (2) heavily weights those values of the integrand near $q = 2k_F$. Thus, the temperature dependence of ρ is expected to scale with the temperature dependence of $S(q)$ for q values near $2k_F$. Following the theory of Nagel and Tauc, we therefore expect the temperature dependence of ρ for the metal-metalloid alloys to scale with $S(q_p)$. This gives $d\rho/dT < 0$ if one assumes that $dS(q_p)/dT < 0$, which is not unreasonable in light of experimental work on liquid metals.¹² It is interesting to apply these ideas to the present system. For $Zr_{60}Cu_{40}$, Fig. 1 gives $q_p = 2.78 \text{ \AA}^{-1}$. Taking a density²² of 7.01 g/cm^3 and free-electron contributions of one from each Cu atom and four from each Zr atom, one finds $2k_F = 3.08 \text{ \AA}^{-1}$, which may be close enough to $q_p = 2.78 \text{ \AA}^{-1}$ to be consistent with an increasing $S(q_p)$ as T decreases. Of course, this calculation relies on the nearly-free-electron model, and for a transition-metal alloy such as $Zr_{40}Cu_{60}$, it is by no means clear that such a model is valid. There are, however, additional data which are consistent with the application of the Nagel-Tauc nearly-free-electron theory to the Zr-Cu system. Nagel and Tauc show that the maximum stability condition $2k_F = q_p$ occurs when the Fermi level E_F lies at a minimum of the density of states. As $2k_F$ begins to move away from q_p , E_F will move away from E_{\min} , that energy giving the minimum in the den-

sity of states. Consequently, the system becomes less stable against crystallization and will therefore have a lower glass transition temperature T_g . Measurements of T_g in Zr_yCu_{1-y} amorphous alloys for $0.32 \leq y \leq 0.5$ have been made⁹ and show that as y increases from 0.32 to 0.5, T_g decreases. This is entirely consistent with the idea that $2k_F$ is moving away from q_p , so that E_F is moving away from E_{min} , thereby decreasing the alloys' stability against crystallization. This reasoning assumes that the effect of alloying can be treated as a rigid shift of E_F with respect to the density-of-states curve and of $2k_F$ with respect to the structure-factor curve.

In the above we have presented several of the most obvious possibilities for explaining the $\rho(T)$ behavior of $Zr_{40}Cu_{60}$. Clearly we cannot state unequivocally which one is correct for our system. However, we feel that the quasi-liquid-metal idea strongly suggests that measurements of the temperature dependence of $S(q)$ in this and other amorphous alloys would be quite valuable.

The final properties of the host alloy that must be discussed are the low-temperature upturns seen in both $\rho(T)$ and $\chi(T)$ below 20 K. The most likely explanation of these upturns is that they result from a small amount of magnetic impurity in the nominally pure host. It is clear in Fig. 3, for example, that introducing 1, 3, and 6-at. % Fe into the amorphous host leads to a Curie-like upturn in χ at low temperatures, which grows as x increases. This implies an impurity contribution to ρ and χ which becomes effective for $T \leq 20$ K. An analogous situation is observed in Cu(Fe), in which upturns due to Fe pairs are observed in both $\chi(T)$ ²³ and $\rho(T)$ ²⁴ below the "isolated-atom" Kondo temperature of, say, 10 K. In view of this hypothesis, a measurement of the Fe concentration was made in our nominally pure host and the result was of the order of 2000 ppm. $\rho(T)$ behavior very similar to that seen in our host sample has been reported for amorphous $(V_3Ni_{27}Pt_{70})_{75}P_{25}$ by Hasegawa.²⁵ In this latter alloy, the low-temperature upturn in $\rho(T)$ was attributed to scattering from local moments on V atoms superimposed on a $1 - (T/\theta)^2$ spin-fluctuation background.

In summary, the amorphous host alloy has magnetic properties consistent with temperature-independent Pauli paramagnetism, with the negative $d\rho/dT$ due either to LSF, Mott $s-d$ scattering, scattering from amorphous alloy tunneling states, or to quasi-liquid-metal-pseudopotential scattering. On the other hand, the crystalline host behaves like a normal metal; namely, $d\rho/dT$ is positive over the whole temperature range and $\chi(T)$ is essentially flat except for $T \leq 20$ K, behavior which again is reasonably associated with a small con-

centration of unwanted magnetic impurities in the undoped sample.

B. Dilute alloys: $0 < x \leq 6$

The susceptibility data for the dilute amorphous alloys clearly suggest a local-moment contribution from the Fe atoms. The data were fitted to the usual Curie-Weiss expression

$$\chi(T) = \chi_0 + C(T - \Theta)^{-1}, \quad (3)$$

where χ_0 is the temperature-independent contribution and C is the Curie constant. The data can be made to fit this expression within experimental error over the whole temperature range, and the fit for the $x = 3$ sample is shown in Fig. 10. Values of χ_0 , θ , p_{eff} , and S for the $x = 1, 3$, and 6 samples are shown in Table I. Here $p_{eff} = (3kC/N_i)^{1/2} \mu_B^{-1}$, where k is the Boltzmann constant, μ_B is the Bohr magneton, and N_i is the number of impurity atoms per unit mass of alloy. S is calculated with $p_{eff} = g[S(S+1)]^{1/2}$ assuming a g of 2. The spin values obtained (~ 0.1) are much smaller than those often found for Fe atoms in dilute crystalline alloys ($\sim \frac{3}{2}$). There are several possible reasons for the small spin values. For example, if one ignores any local-environment effects and adopts the Friedel-Anderson picture of local-moment formation,¹⁸ it could be that the intra-atomic exchange is so small and the $s-d$ mixing so large that the localized states are broad and overlap the Fermi

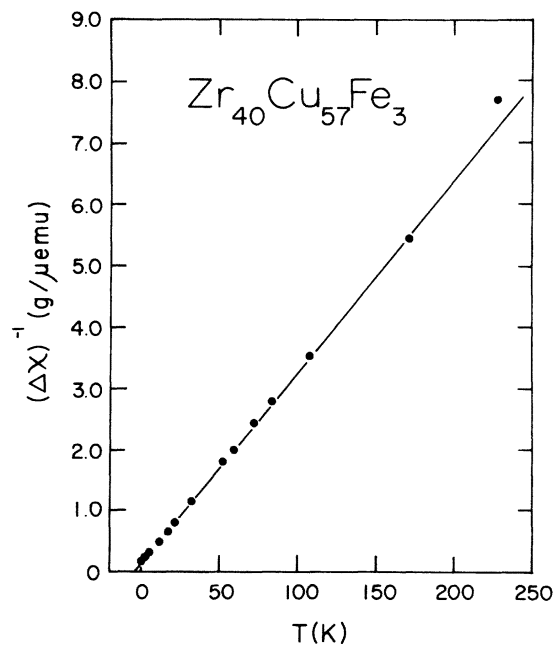


FIG. 10. Fit of amorphous $Zr_{40}Cu_{57}Fe_3$ susceptibility data to a Curie-Weiss law.

TABLE I. Curie-Weiss parameters for dilute $Zr_{40}Cu_{60-x}Fe_x$ amorphous alloys.

x (at.%)	χ_0 (emu/G)	Θ (K)	p_{eff}	S
1	1.23	-2.2	0.77	0.13
3	1.51	-3.9	0.81	0.14
6	1.41	-4.5	0.57	0.076

level in a way that leads to a very small spin value. On the other hand, it is known that Fe does have a moment in Cu, but does not have one in Zr,¹⁸ so that only a fraction of the Fe atoms in amorphous Zr-Cu may have a moment, depending on the local environments. A third possibility, again involving a local-environment effect, is that a given Fe atom may have a moment, irrespective of its Cu and Zr nearest neighbors, only if it has a certain minimum number of Fe atoms as nearest or near neighbors. Examples of such "cluster" models have already been applied to dilute crystalline alloys such as Au(Co) and Cu(Co).²⁶ The nonmonotonic dependence of χ on the Fe concentration, in fact, suggests that this cluster model, involving nonrandom Fe-Fe correlation functions in the various samples, may well be the most likely candidate. In this connection, some recent work²⁷ by Mizoguchi and Kudo should be mentioned. These workers studied the magnetic properties of $M_x(Cu_{57}Zr_{43})_{1-x}$, where M represents various $3d$ metals such as Fe and Mn. They found that Mn carries a well-defined local moment with $p_{\text{eff}} = 1.6$, but that Fe carried *no* local moment in a 2.1-at. % Fe sample. Their susceptibility data above ~ 60 K is flat and similar to our 1-at. % Fe data. However, below 60 K, it is not clear from the Mizoguchi-Kudo data whether or not a significant increase in $\chi(T)$ occurs. Thus, there is no convincing evidence on the question of whether an *isolated* Fe atom, in any of the possible environments in amorphous Zr-Cu, does or does not have a localized moment. Certainly our higher-concentration alloys exhibit local-moment behavior which can be associated only with single Fe or clusters of Fe atoms.

It is hard to understand the complex concentration dependence of χ and the previously mentioned variation of χ in different samples of the sample composition. A possible explanation of this complex concentration dependence displayed by the dilute amorphous alloys may be that separate amorphous samples of identical composition could have different degrees of structural and chemical disorder, particularly, the Fe-Fe short-range-order parameters. In this connection it is interesting to consider Fig. 2(b), which also shows a complex

concentration dependence of the crystallization temperature for $0 \leq x \leq 6$. At present, it is not clear whether both the complex concentration dependences of χ and T_C are intrinsic properties of this amorphous alloy system or whether, as speculated above, they might be due to subtle variations in the amorphous structure caused perhaps by fluctuations in the quench rate. One of the aspects of this alloy system that is worthy of additional study is to determine how the magnetic and other properties vary with quench rate. Unfortunately, however, it is by no means easy to vary the quench rate in the splat-cooling technique in a *controlled* way, let alone to *measure* it. Another experiment that suggests itself is to perform some annealing experiments at room temperature and above, to see whether diffusion could be producing varying amounts of clustering, depending on the age of the sample.

For the dilute crystalline alloys, where a more classical local-moment situation exists, values for Θ were found to be in the neighborhood of -100 K, and those for S about unity. The Curie-Weiss fit for the 1% crystalline sample is shown in Fig. 11. Since in other hosts spin values for Fe are often observed to be $\frac{3}{2} \pm \frac{1}{2}$, a spin value of unity is reasonable. Following the empirical rule²⁸ that $\Theta \approx 4.5T_K$, Fig. 11 suggests a Kondo temperature of about 25 K for dilute ZrCu(Fe) alloys.

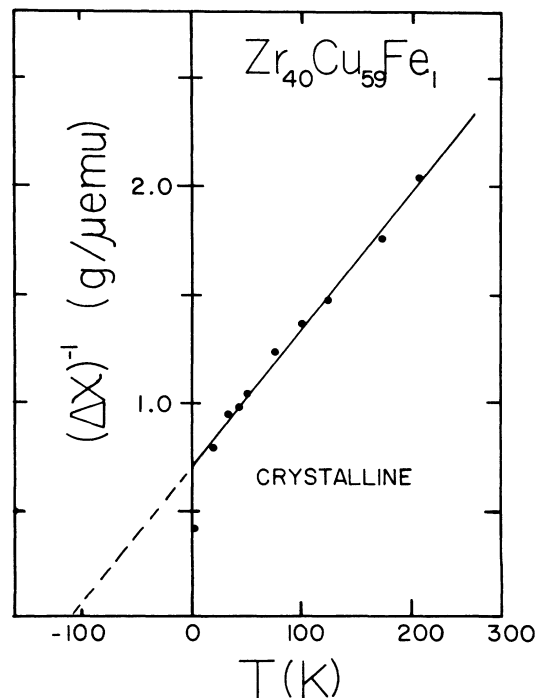


FIG. 11. Fit of crystalline $Zr_{40}Cu_{59}Fe_1$ susceptibility data to a Curie-Weiss law.

C. Concentrated alloys: $x > 6$

For the $x = 10$ and 12 amorphous alloys, we have the remarkable fact that there are resistivity maxima (Fig. 7), but the susceptibilities of these samples (Fig. 3) show no anomalies. (In fact, the data for the $x = 10$ sample fit a Curie-Weiss law over the *entire* temperature range with $\Theta = -18.9$ K, $S = 0.33$, and $\chi_0 = 3.63$ $\mu\text{emu/g.}$) This behavior is exactly the converse of that observed in amorphous $\text{Cr}_5\text{Pd}_{75}\text{Si}_{20}$ alloys where susceptibility maxima were seen but the resistivity showed no anomaly.²⁹ The data for the $x = 12$ amorphous and crystalline alloys did not fit a Curie-Weiss law for reasonable parameters, even at high temperatures. Vibrating-sample-magnetometer measurements at 4.2 K on the $x = 12$ amorphous alloy (Fig. 8) show that after exposure to an 80-kOe field the remanent magnetization corresponds to a moment of not more than $0.008\mu_B$ per Fe atom. Saturation of this alloy is essentially complete at 80 kOe (Fig. 9) for which there is a moment of $0.18\mu_B$ per Fe atom; assuming $g = 2$, this corresponds to $S = 0.092$. The small values of S for this and the $x = 10$ amorphous alloy may indicate, as already suggested in the previous section on the dilute alloys, that local-environment effects are preventing every Fe atom from bearing its "full" moment.

The microscopic nature of the magnetic order developed in the $x = 10$ and 12 amorphous alloys is difficult to determine from bulk measurements such as we have performed. The two most obvious possibilities are an amorphous spin-glass state and an amorphous ferromagnetic state. The amorphous spin-glass state is analogous to the crystalline spin-glass state which is found, for example, in dilute Cu(Mn) and Au(Fe) alloys at low temperatures. In the spin-glass state one imagines that the local moments are coupled by a *long-range* indirect interaction (e.g., Ruderman-Kittel-Kasuya-Yosida) that oscillates in sign depending on the distance between the impurities. The characteristic properties of the spin glass are that below a certain temperature the spin orientations freeze leading to susceptibility maxima and resistivity maxima at a temperature $T_{\text{max}} = Kc^m$, where K is a constant and $0.5 \leq m \leq 1$. Since the indirect interaction is long range, the ordering temperature follows $T_{\text{max}} = Kc^m$ for *arbitrarily* small values of c . That is, one does not have to exceed a certain critical concentration to produce the ordered spin-glass state. The oscillatory nature of the interaction implies that susceptibility peaks also are a general feature of the freezing in of the spin-glass state. The lack of susceptibility maxima in any of our amorphous alloys, and the fact that T_{max} (for the resistivity) does not follow the c^m law, indicates that the $\text{Zr}_{40}\text{Cu}_{60-x}\text{Fe}_x$ system is not a normal

spin-glass in the above sense. The most likely breakdown of the usual spin-glass model as applied to our system is that the electron mean free paths are rather short in these alloys. Thus, the spin-spin interactions in a system of this type are predominantly direct $d-d$ interactions of near or close neighbors. The average distance between Fe atoms in a 12-at. % alloy is only of the order of a few atomic diameters, so that such direct interactions are quite probable. The question then becomes one of the sign (ferromagnetic versus antiferromagnetic) of these close-neighbor interactions. If these interactions were mainly antiferromagnetic, one might expect a susceptibility maximum at the ordering temperature, just as in the spin-glass case. Since we do not observe a susceptibility maximum but do see a hysteresis loop below the resistance maximum temperature, the indications are that the magnetic order is more likely to be some type of random ferromagnetic state, although we cannot say unequivocally that there are *no* close-neighbor antiferromagnetic Fe-Fe couplings. That the resistance maximum appears rather suddenly at $x = 10$, and that T_{max} increases very little, if at all, for $x = 12$, suggest that the ordering could perhaps be described by a percolation process.

The origin of the resistance maximum at the ordering temperature is not entirely clear. Since $d\rho/dT < 0$ for all the alloys at high temperatures, one must suppose that at the ordering temperature the presence of an internal field somehow suppresses or overpowers the mechanism which in all the samples leads to $d\rho/dT < 0$. It may also be possible, as discussed by Kim³⁰ and reviewed by Kawatra and Budnick,³¹ that there are critical fluctuations near the magnetic ordering temperature which lead to a resistance maximum. Kim's calculated curves are fairly sharply peaked near T_c , but in the case of an amorphous magnet like the present ones, it is perhaps reasonable that the sharp transition is smeared out in temperature.

The $x = 12$ crystalline alloy has a saturation moment of $0.66\mu_B$, almost four times that of its amorphous counterpart. Furthermore, it saturates at a much smaller field. The ordering temperature for this alloy is in the neighborhood of 150 K, which is about five times larger than that of the same alloy in the amorphous state. This increase of ordering temperature for crystalline as compared to amorphous alloys is seen also in the rare-earth (R) iron series $R\text{Fe}_2$.³² Theoretical explanations of this effect have been given by Madhukar³³ and Rhyne.³⁴

V. SUMMARY AND CONCLUSIONS

The major results and conclusions to be drawn from this study are as follows:

(i) The $Zr_{40}Cu_{60}$ amorphous host alloy exhibits a negative $d\rho/dT$ over the temperature range 1.4–300 K. This behavior appears to be consistent with the localized-spin-fluctuation picture, the essentially nonmagnetic Mott $s-d$ scattering model of temperature-dependent residual resistance, electron scattering from tunneling states in the amorphous metallic structure, or quasi-liquid-metal-pseudopotential scattering. Measurements such as the density of states at the Fermi energy, photoemission, and thermal properties at low temperatures will be important for clarifying this problem.

(ii) In amorphous alloys containing Fe impurities, local-moment behavior is observed. The average moment per Fe atom is quite small, and it is likely that local-environment effects are at work; these effects may depend upon either the type of Zr and Cu neighbors of a single Fe atom, or the type and number of Fe nearest neighbors of a given Fe atom.

(iii) In the dilute Fe-containing samples, the complex concentration dependence of the susceptibility suggests either that the Fe local environments are extremely sensitive to quench rate, or clustering effects occur from diffusion even at room temperature. It is conceivable that glassy metals like Zr-Cu, which contain no glass formers, are much more subject to such low-temperature annealing effects. Additional experimental work on these structural aspects certainly would be worthwhile.

(iv) When small concentrations of iron are added to the crystalline host alloy, normal local-moment behavior is observed with a spin value of about unity and with a Kondo temperature of about 25 K.

(v) The $x = 12$ amorphous alloy exhibits a resistance maximum and hysteresis below about 30 K. This is suggestive of some type of low-temperature ordered magnetic state, apparently a random ferromagnetic state, which allows for a saturation moment of only $0.18\mu_B$ per iron atom. The appearance of a resistance maximum in the $x = 10$ amorphous alloy seems to imply that it too is describable by this low-temperature ordered state. The fairly abrupt occurrence of these maxima at about 10 at.% suggests that a percolation process may be involved in the ordering.

(vi) On the other hand, the $x = 12$ crystalline alloy orders ferromagnetically at a much higher temper-

ature (150 K), and exhibits a much larger moment ($0.66\mu_B/\text{Fe atom}$). This behavior is similar to other systems in which the crystalline-to-amorphous transition greatly weakens the magnetism.

In the $x = 12$ amorphous alloy there exists a resistivity maximum but no susceptibility maximum at the ordering temperature. However, in the amorphous PdSi(Cr) system just the reverse is true. An interesting but purely speculative explanation for this behavior is as follows: Presumably, because of the disorder in these materials, the electron mean free paths will be much shorter in these alloys than in crystalline alloys. This will tend to emphasize the direct $d-d$ interactions at the expense of long-range Ruderman-Kittel-Kasuya-Yosida type interactions. If this is the case, it is possible that the susceptibility maximum seen in the PdSi(Cr) system, suggesting random antiferromagnetic order, results from the predominance of *antiferromagnetic* near-neighbor Cr-Cr interactions. However, in the ZrCu(Fe) system one would expect ferromagnetic order on the basis of the likelihood of *ferromagnetic* Fe-Fe near-neighbor interactions.

In conclusion, we regard this work as an initial exploratory study of an amorphous magnetic alloy. It is obvious that a number of interesting phenomena have been observed and at this stage our understanding is relatively primitive. In order to better understand the magnetic behavior of this system, some of us are planning further experiments on this and other systems in which the dissolved impurity is other than Fe.

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