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Magnetic properties of amorphous alloys of Fe with La, Lu, Y, and Zr

Neil Heiman and N. Kazama *
IBM Research Laboratory, San Jose, California 95193

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In order to study the systematics of the Fe-Fe exchange in amorphous rare-earth–Fe alloys, without the complications associated with the magnetic characteristics of the rare-earth elements, amorphous films of Fe alloyed with La, Lu, Y, and Zr have been prepared with a wide range of Fe concentrations. Magnetization and Mössbauer-effect measurements were made. The magnetic properties of the alloys depended critically on the choice of rare earth (or rare-earth-like element). YFe and LuFe alloys were found to have spin-glass characteristics while LaFe and ZrFe alloys were found to be ferromagnetic, but with evidence that exchange fluctuations were nearly as large as the average exchange. Thus the nature of the Fe-Fe exchange interaction depends critically upon the species of the rare earth. The most important parameter in determining the magnetic behavior of these alloys appears to be the size of the rare-earth atom, with large rare-earth atoms resulting in a smaller ratio of exchange fluctuations to exchange. The same dependence of the magnetic properties upon rare-earth size appears to be important in the case of magnetic-rare-earth atoms; however, the effect of rare-earth–Fe exchange also becomes important and these effects are discussed.

I. INTRODUCTION

Although some amorphous rare-earth (R)-Fe alloys were studied earlier,[1] strong interest in the subject began with the work of Rhyne *et al.*,[2] who showed that sputtered samples of $TbFe_2$ were structurally amorphous but magnetically ordered. They reported that both the magnetization and the critical temperature (T_c) were reduced in the amorphous state. Harris *et al.*[3] suggested the reduction in magnetization (M) and T_c was due to strong random local anisotropy. Systematic investigations[4-6] of amorphous R–transition-metal (TM) alloys have established that while the reduction in M can be attributed in a large measure to random local anisotropy, the reduced T_c is due for the most part to a reduced Fe-Fe exchange interaction. A number of researchers[5,7-10] have attempted to isolate the Fe-Fe interaction in these amorphous alloys by preparing samples of YFe or LuFe. In all cases the samples show complex magnetic behavior that has been characterized as spin glass or spin-glass-like. Heiman and Lee[11] prepared samples of amorphous LaFe and found that in contrast to YFe and LuFe the samples were ferromagnetic with T_c near room temperature. This suggested that the Fe-Fe exchange interaction somehow depends upon the size of the R because the most obvious difference be tween La and Y or Lu is that of size. The lanthanide contraction is a well-known feature of the R series of elements. The radius of the R atoms decreases with increasing atomic number from 1.87 Å for La to 1.74 Å for Lu (with the exception of multiple-valence elements). Because the R spin values or more correctly the de Gennes factor [DGF $=(g-1)^2J(J+1)$] varies systematically with atomic number, rising monotonically from La to Gd and then decreasing monotonically from Gd to Lu; it is possible to confuse effects due to DGF and atomic size. In the specific instance of the ordering temperatures of the amorphous heavy $R_{0.33}Fe_{0.67}$ alloys, both Heiman *et al.*[5] and Rhyne[6] attributed the systematic decrease of T_c with increasing atomic number to the decreasing value of the R DGF. Subsequent work by Heiman and Lee[11] involving the light $R_{0.33}Fe_{0.67}$ alloys (R =La and Nd), as well as the results of Taylor and McGuire[12] on amorphous NdFe, show that alloys with a larger light R have higher ordering temperatures than alloys with smaller heavy R even those having a much larger DGF (e.g., for $Nd_{0.33}Fe_{0.67}$ $T_c \simeq 375$K, $R = 1.82$ Å, the DGF is 1.84, while for $Dy_{0.33}Fe_{0.67}$ $T_c = 300$ K, $R = 1.77$ Å and the DGF is 7.08). But size cannot be the only consideration.

In the amorphous heavy R-Fe_2 alloys, T_c decreases monotonically with the increasing atomic number of the R from about 500 K for GdFe to an undefined value (spin glass?) for $LuFe_2$. As one proceeds through the heavy-R series, both the atomic radius and the de Gennes factor decrease monotonically. The extent to which each of these parameters contributes to the systematic decrease in T_c has not yet been established. Heiman and Lee[11] presented magnetization and Mössbauer-effect data that suggested the R size to be an important factor. More recently Cullen[13] had introduced a model in which the magnetic interaction of the R atom aligns nearest-neighbor Fe atoms, leaving non-nearest-neighbor Fe atoms in a spin-glass-like state. Support for this picture comes from neutron-diffraction studies of Pickart,[14] as well as an extensive investigation of the amorphous TbFe alloy system.[15] Finally work by Coey *et al.*[10] on the amorphous YFe system suggests a local coordination model in which the moment on the Fe atom is a function of the number of Fe nearest neighbors, a result that is similar to the results of Marchal *et al.*[16] in the case of amorphous FeSi alloys. The evidence available thus far suggests that features of all these models need to be accounted for in any comprehensive understanding of the amorphous RFe system.

Several complications which have arisen in recent studies of the magnetic properties of these amorphous R-iron alloys hinder the analysis of the data and make this comprehensive understanding difficult. First of all these materials are generally ferromagnetic so that M is the small difference between the two "sublattice" magnetizations (i.e., the R sublattice and the Fe sublattice). Thus any small uncertainty in composition gives rise to a very large uncertainty in M. Furthermore it appears that the spins within a given sublattice are not necessarily aligned. In the case of the non-S-state R elements, this nonalignment is due to local random anisotropy effects. In the case of Fe, the nonalignment apparently results from large exchange fluctuations. An additional complication is that the degree of nonalignment within the two sublattices is dependent upon the concentration and species of R. Whether this is due to the variation of the R-Fe exchange interaction or to electronic or structural effects has not been resolved.

Since there has been no systematic experimental investigation of the Fe-Fe interaction isolated from the effects of magnetic R elements, we have undertaken the task of examining this interaction by preparing amorphous Fe-based alloys containing Y, Lu, La, and Zr. The selection of these R and R-like elements allows us to isolate the effects of R size. The atomic radii (R_{at}) of Y, Lu, La, and Zr are 1.80, 1.74, 1.87, and 160 Å, respectively.

The results are discussed in Sec. IV. In Sec. IV A we note that our data demonstrate that the Fe-Fe exchange interaction is small and that the ratio (δ) of exchange fluctuations to the strength of the exchange interaction is large. In Sec. IV B we review existing data on the structure of amorphous R-Fe alloys and present arguments that the correlation between structural and magnetic properties are consistent with the Bethe curve dependence of the Fe-Fe exchange interaction. In Sec. IV C we note that our results are consistent with an interpretation that larger R atoms produce smaller δ via the Bethe curve dependence of the exchange interaction. It is also shown that the same size dependence is seen for alloys containing magnetic R elements. Further discussion points out that other parameters, particularly the magnetic hyperfine field, also depend on R size. Comparison of results for amorphous YFe with those of GdFe in Sec. IV D make it clear that the spin of the R also plays a key role. It is argued that when the R has a spin, δ is reduced because the total exchange interaction is increased by the addition of the R-Fe exchange interaction. This effect is then calculated within the context of a mean-field model, and it is shown that such calculations are in good qualitative agreement with the data. Finally in Sec. IV E the additional complications of local anisotropy are assessed.

II. EXPERIMENTS

The amorphous films were prepared by two-source coevaporation of the elements. The elemental rates were controlled and feedback stabilized with ionization type rate monitors. The vacuum system operated with a base pressure of about 7×10^{-9} Torr, and pressure during deposition was maintained at less than 9×10^{-8} Torr.

Films were approximately 5000 Å thick. Thicknesses were determined by microtopographic and interferometric techniques.

Substrates were either 0.64-cm-diam fused-quartz disks (for magnetization measurements) or larger sheets of polyparabanic acid, a temperature-stable polymer (used for Mössbauer spectroscopy). Samples for Mössbauer spectroscopy were prepared by punching out and stacking up several disk-shaped samples in order to increase the absorber thickness.

The chemical compositions of all films were determined by x-ray fluorescence. The accuracy of the results is expected to be better than 3 at.% relative. In actual practice, the fluorescence results agreed with the rate-monitor determinations to within 2 at.%.

All films were examined by x-ray diffraction. All films containing less than 80-at.% Fe were found to be amorphous. LaFe films containing more than 80-at.% Fe tended to be partially crystalline. Films with Y, Lu or Zr were generally amorphous up to 88-at.% Fe or more.

Magnetization measurements were carried out from 4.2 to 300 K on a vibrating sample magnetometer in fields up to 20 kOe.

Mössbauer-effect measurements were made with a conventional constant acceleration-type spectrometer in zero applied field. The temperature was varied with a liquid-He flow cryostat from 5 up to 300 K.

III. RESULTS

A. YFe

Amorphous films of $Y_{1-x}Fe_x$ were prepared with $x = 0.70$, 0.75, 0.83. Whereas the crystalline YFe alloys are normal ferromagnets, the M vs H curves of the amorphous samples failed to saturate even in high fields. Figure 1 shows the low-field magnetization isotherms for various temperatures. The sample was cooled to 4.2 K in zero field, and the isotherms shown in Fig. 1 were collected with increasing applied field in order of increasing temperature. No significant variation was observed when the order of data collection was altered, although possibly some thermal hysteresis was present. The results shown in Fig. 1 are similar to those of Rhyne *et al.*[7] for a bulk amorphous YFe_2 sample. One interesting feature is the crossing of isotherms. The same feature occurs in the data of Rhyne *et al.*[7] but is less apparent because the 4.2-K data are plotted on a separate figure. This crossing is due to a coercive-force-type behavior appearing below $T \approx 75$ K. Hysteresis occurs at low temperatures, also as observed by Rhyne *et al.*[7] The appearance of this coercive force is likely due to a freezing in of the spin clusters below the spin-glass-ordering temperature. The magnetizations were also measured in a superconducting solenoid at 70 kOe but only at 4.2 K. The results are the same as reported by Coey.[10] If one attempts to plot the data in Fig. 1 in the form M vs T, it is found that these curves are field dependent, and that no transition temperature can be defined. This is suggestive of spin-glass behavior. The usual test for true spin-glass behavior is the cusp in the low-field susceptibility. This defining cusp is difficult to observe in thin films but has been reported by Forester *et al.*[8] for a bulk sample of amorphous YFe_2. The cusp occurs at ≈ 60 K.

We can assign an average Z component for the moment of the atom from M at $T = 4.2$ K by assuming the alloy density is a linear combination of the elemental densities in proportion to the elemental concentrations, i.e.,

$$\rho_{\text{alloy}} = x\rho_{\text{Fe}} + (1-x)\rho_Y \ .$$

For $H = 12.5$ kOe such a procedure yields $\mu_Z \simeq 0.9\mu_B$ with little dependence on concentration. If we use the 70-kOe data to extrapolate μ_Z to $H = \infty$, we find only a slight increase to $\mu_Z \simeq 1.05\mu_B$.

Mössbauer spectra at 4.2 K show a broad six-line pattern as shown in Fig. 2 for the $Y_{0.30}Fe_{0.70}$ sample. No attempt was made to deconvolute the spectrum into a distribution of magnetic hyperfine fields H_{hf} in the manner of Sharon and Tsuei[17] or Mangin *et al.*[18] The spectrum could be fit quite well with an average $\overline{H}_{\text{hf}}$ and lines broadened in proportion to the Zeeman energies (the solid line in Fig. 2). The resulting $\overline{H}_{\text{hf}}$ values obtained at 4.2 K were 235, 253, and 273 kOe for $x = 0.70$, 0.75, 0.83, respectively. Pala *et al.*[19] report $\overline{H}_{\text{hf}} = 233$ kOe for $x = 0.67$ in good agreement with our results.

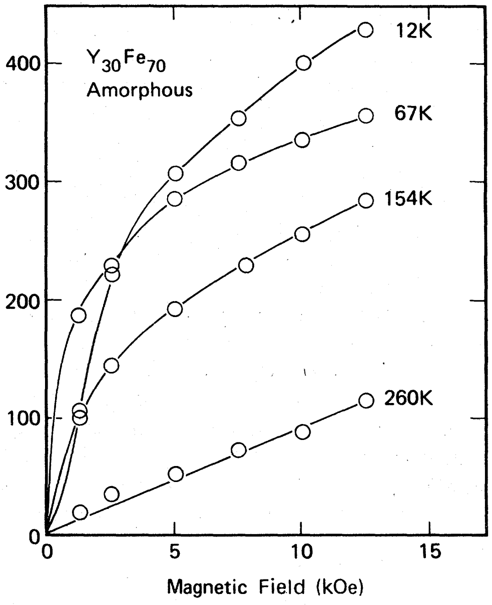

FIG. 1. Field dependence of the magnetization at several temperatures for a sample of amorphous $Y_{0.30}Fe_{0.70}$. Note the lack of saturation.

It is enlightening to plot $\overline{H}_{\text{hf}}$ and μ_{Fe} for the amorphous alloys on a figure along with data for crystalline YFe alloys. This is done in Fig. 3. The crystalline data is that of Gubbens *et al.*,[20] who established a firm correlation between H_{hf} and μ_{Fe} for the crystalline YFe alloys. They found that for all compositions and crystallographic sites the relation between H_{hf} and μ_{Fe} could be generally represented by

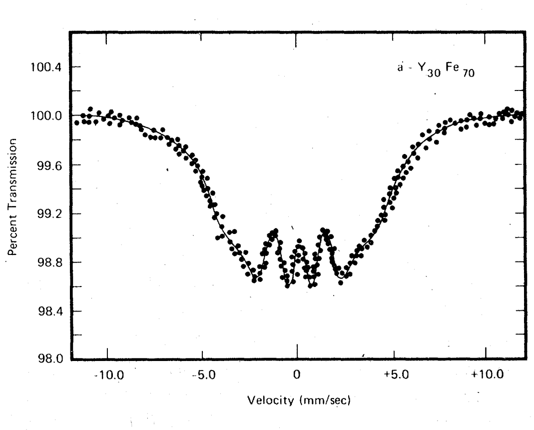

FIG. 2. Mössbauer spectrum of the same amorphous $Y_{0.30}Fe_{0.70}$ sample. The solid line is a fit assuming line broadening proportional to the Zeeman energy.

$$\mu_{\rm Fe} = (1\mu_B/147\ {\rm kOe})H_{\rm hf}\ .$$

It is clearly seen that $\bar{H}_{\rm hf}$ for the amorphous alloys is nearly identical to that of the crystalline alloys. This suggests strongly that the atomic moments are the same in the crystalline and amorphous alloys. On the other hand, $\mu_{\rm Fe}$ obtained from magnetization data above show a value that is considerably reduced. The combined results show that in the amorphous alloys, the atomic moments are the same as in the crystalline materials, but are unable to align parallel to one another. The most likely reason for this is large fluctuations in the value of the exchange interactions.

The temperature dependence of $\bar{H}_{\rm hf}$ for a-$Y_{0.30}Fe_{0.70}$ is shown in Fig. 4. The solid line is the $S=1$ Weiss–molecular-field-model calculation with $T_c=73$ K. This result is consistent with the observations of Forester *et al.*[8] for a-$Y_{0.33}Fe_{0.67}$. Forester *et al.*[8] also report temperature hysteresis in the zero-velocity absorption. Similar hysteresis is observed in the temperature dependence of the zero-velocity absorption for all three of our samples. T_c values obtained for a-$Y_{0.25}Fe_{0.75}$ and a-$Y_{0.17}Fe_{0.83}$ were 98 and 128 K, respectively.

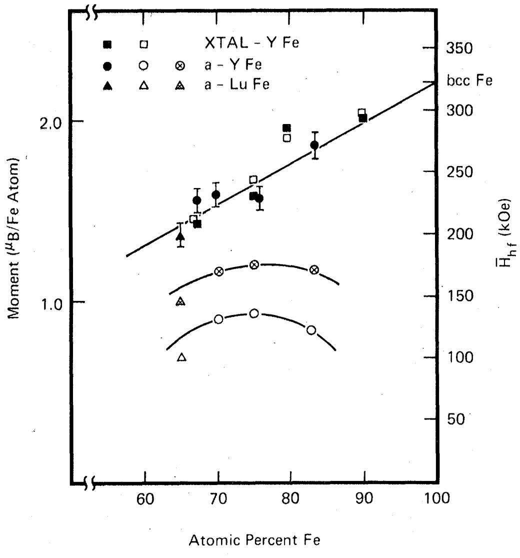

FIG. 3. Average hyperfine field ($\bar{H}_{\rm hf}$) and moment per Fe atom obtained from magnetization measurements for both crystalline and amorphous YFe alloys. The solid symbols refer to $\bar{H}_{\rm hf}$. The open symbols are from magnetization measurements at 12.5 kOe, and the crossed symbols are from magnetization data extrapolated to $H=\infty$. Note that for the amorphous alloys, the moments per Fe atom obtained from $\bar{H}_{\rm hf}$ are comparable to those for crystalline YFe alloys (whether obtained by $\bar{H}_{\rm hf}$ or magnetization measurements). However, the moments per Fe atom for the amorphous alloys obtained by magnetization measurements are much less. This suggests that the average Fe moments are the same in crystalline and amorphous alloys, but are not aligned in the amorphous state (spin glass).

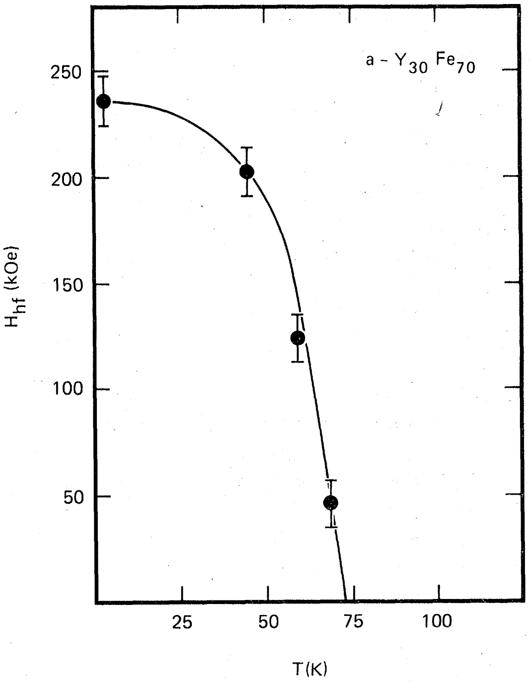

FIG. 4. Temperature dependence of $\bar{H}_{\rm hf}$ for amorphous $Y_{0.30}Fe_{0.70}$ shows normal $J=1$ mean-field behavior with $T_c \approx 73$ K.

The composition dependence of T_c thus determined can be seen in Fig. 5. For comparison we have included T_c for the crystalline alloys. (For crystalline Y_2Fe_{17} there are at least two values reported for T_c as indicated.) Values for T_c in the crystalline case are essentially the same whether obtained from magnetization measurements or from Mössbauer-effect determinations. This is not true for the amorphous YFe alloys. Rhyne *et al.*[7] first found that Arrott plots of the magnetization data for a sample of amorphous $Y_{0.33}Fe_{0.67}$ do not yield a critical temperature. The same is true for our data. The fact that Arrott plots and Mössbauer-effect yield different critical behavior should not be surprising for this class of materials. For example in the case of amorphous TbFe alloys, Alperin *et al.*[15,21] obtain a significantly lower T_c from Arrott plots than indicated by other techniques. The Arrott plots, it should be noted, also show a great deal of curvature. These differences are likely associated with cluster effects such as those reported by Pickart.[14] Thus the ordering temperature depends on the type of order and the time scale on which it is observed. It is interesting that T_c for amorphous YFe_2 as measured by Mössbauer effect agrees reasonably well with the cusp in the low-field susceptibility.[8] Attempts to determine a paramagnetic ordering temperature from the high-temperature susceptibility run into difficulty in that a Curie-Weiss-type behavior is not obeyed in the temperature regime that can be observed. One is restricted to $T < 500$ K by crystallization effects. The temperature dependence of the inverse susceptibility shows considerable curvature as one might expect if short-range correlations or clusters begin to form; but if one extrapolates the data to the high-temperature limit, they appear to indicate $200\ \mathrm{K} < \Theta_C < 300$ K. The result that Θ_C is higher than the spin-freezing temperature is common for spin-glass behavior.[22]

An interesting observation is that the extrapolation of T_c to 100% Fe yields $T_c \approx 200$ K for both the crystalline and amorphous systems. This extrapolation yields a slightly lower T_c value than previous extrapolations,[5] but is corroborated by data of Alperin *et al.*[15,21] which show a $T_c \approx 195$ K for a-$\mathrm{Tb_{0.02}Fe_{0.98}}$ obtained from Arrott plots, although the shape of the magnetization versus temperature curve appeared to indicate a higher value.

As we have seen, the complicated spin-glass-like magnetic behavior of these amorphous alloys makes it difficult to assign values to the usual magnetic parameters (e.g., spin T_c, etc.). In the case of the exchange constant J_{Fe}, this determination is doubly complicated. In spin-glass alloys an average exchange constant can often be determined from susceptibility measurements at temperatures far above T_c. As already noted for the a-YFe alloys this regime is not accessible due to crystallization problems. An alternative method is to use the mean-field formula

$$J_{\mathrm{Fe}} = 3KT_c/2ZxS(S+1) \ ,$$

where k is Boltzmann's constant, Z is the coordination number (we shall assume 12), and x is the Fe concentration. If one uses the values of T_c from the Mössbauer-effect data and values of S from H_{hf} and the formula of Gubbens *et al.* (assuming $g \approx 2.0$), one finds $J_{\mathrm{Fe}} \approx 1.7 \times 10^{-15}$ ergs for all values of x (i.e., J_{Fe} is independent of Fe concentration). This result is heartening because it is similar to the result reported by us for a-YCo alloys in which J_{Co} was independent of concentration.[23] We argued that such a result was evidence that long-range interactions and structure effects are absent in the amorphous material and that J depends only on pairwise nearest-neighbor exchange. We would suggest the same is

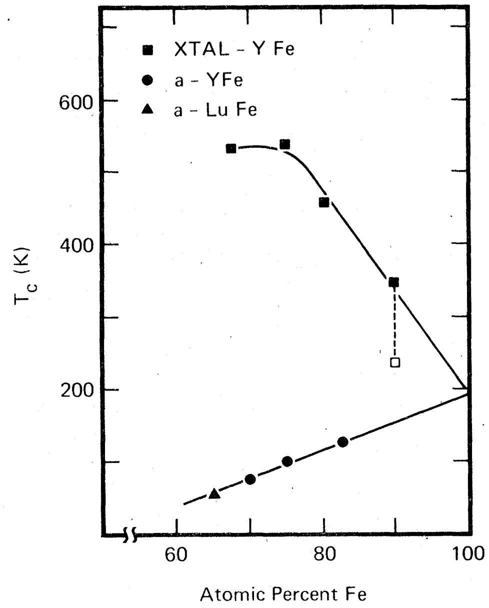

FIG. 5. Ordering temperature for amorphous and crystalline YFe alloys. The squares are the result for crystalline alloys. The circles are the result for the amorphous alloys obtained from Mössbauer-effect data. The triangles, the result for $\mathrm{Lu_{0.35}Fe_{0.65}}$, are included for comparison. The open square and dashed line are meant to represent the fact that for $\mathrm{Y_2Fe_{17}}$ at least two values for T_c have been reported.

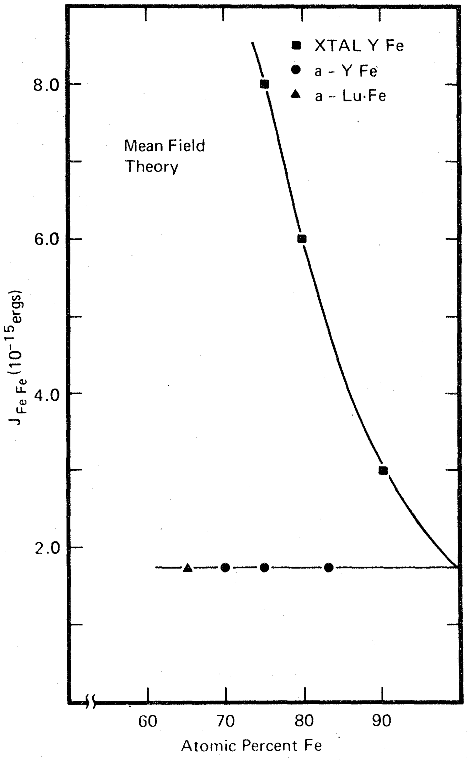

FIG. 6. Exchange constants for crystalline and amorphous YFe alloys as calculated in the text. Squares are the result for crystalline alloys. The circles are the result for the amorphous alloys obtained from Mössbauer-effect data. This is the most valid result. Note that J_{FeFe} is a constant. The result implies only nearest-neighbor interactions are important. Results for LuFe (triangles) are included for comparison.

true in the case of the Fe alloys. It is interesting to compare this result to the situation for crystalline YFe compounds, where J_{Fe} values determined in the same manner rise steeply with the addition of Y. The difference is strikingly evident in Fig. 6.

B. LuFe

We prepared thick samples at only one composition, $Lu_{0.38}Fe_{0.62}$. This is due to the expense of Lu. Only a small amount of Lu was purchased, and it was difficult to stabilize the evaporation rate with a small crucible charge.

The results for the magnetic properties of amorphous $Lu_{0.38}Fe_{0.62}$ were similar to and consistent with those for amorphous YFe, except that values for M, T_c, and $\overline{H}_{hf}$ were slightly lower. The results for LuFe are included in Figs. 3, 5, and 6. This suggests that exchange fluctuations are larger in LuFe than in YFe alloys.

C. LaFe

Amorphous films of $La_{1-x}Fe_x$ were prepared with $x=0.69$ and 0.76. Films with higher Fe content were also prepared, but films with $x \geqslant 0.81$ were found to precipitate crystalline Fe. The tendency of these alloys to precipitate Fe may be related to the fact that crystalline LaFe compounds do not form at all. This in turn may be due to the failure of LaFe complexes to form because of the large size of the La atom.

Unlike the results for the amorphous YFe alloys, the magnetizations of the amorphous LaFe alloys were easily saturated in modest applied fields. (See for example Fig. 7.) For T near T_c, saturation still occurs but higher fields are required. Also unlike the case for YFe, for fields sufficiently high to produce saturation, a field independent T_c can be defined. For the amorphous LaFe samples T_c was found to be about 275 and 300 K for $x=0.69$ and 0.76, respectively. For both samples the 4.2 K moment was well defined and found to be about $1.36\mu_B$. Although we find a well-defined T_c and μ_{Fe}, we find that $M(T)$ does not obey a simple molecular-field-model law. This is, however, not unexpected since such behavior is often observed in amorphous systems and is usually associated with exchange fluctuations. As will be pointed out in Sec. IV A, the $M(T)$ behavior of these alloys shows unusually large deviation from simple molecular-field theory, which indicates unusually large exchange fluctuations.

The chief difficulties encountered in designating these samples as simple ferromagnets occur when we compare the magnetization data to Mössbauer-effect data. First of all $\overline{H}_{hf}$ at 4.2 K is the same for both samples ($\overline{H}_{hf}=298$ kOe); however, if the Gubbens formula relating H_{hf} and μ_{Fe} is presumed to exist for LaFe as is the case for YFe, μ_{Fe} would be about $2.0\mu_B$. Thus the moment obtained from magnetization measurements is about 30% less than that implied by $\overline{H}_{hf}$ and the Gubbens formula. Thus either the formula, which was effective relating H_{hf} and μ_{Fe} for YFe is not valid for amorphous LaFe, or the Fe moments are not fully aligned. The latter seems unlikely in view of the ease with which the samples were saturated in low applied fields.

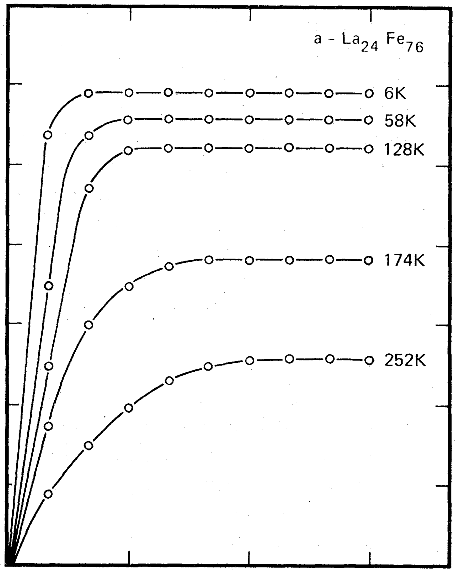

FIG. 7. Field dependence of the magnetization for amorphous $La_{0.31}Fe_{0.69}$. Note that the magnetization saturates at low fields, implying simple ferromagnetic behavior.

A complication which is more difficult to explain away is that T_c as obtained from the temperature dependence of H_{hf} is about 200 and 210 K for $x=0.69$ and 0.76, respectively. This is much lower than the 275 and 300 K one obtains from the magnetization data. Extrapolation of high-temperature susceptibility yields Θ_C in agreement with the Mössbauer-effect result. The reason for this disagreement in T_c values is not clear. Possible explanations include: (i) a small amount of a second amorphous phase with large μ_{Fe} and high T_c is present, or (ii) because of the large exchange fluctuations the T_c measured in the modest fields needed to saturate the samples is higher than would be observed at zero field.

One can compute J_{FeFe} in the same manner as for YFe. The result is that $J_{FeFe} \simeq 2.4\times10^{-15}$ erg for both samples. J_{FeFe} is thus about 50% larger for LaFe than for YFe.

Thus the amorphous LaFe samples are unlike amorphous YFe and LuFe in that either the magnetization data or the Mössbauer-effect data when taken by themselves indicate ferromagnetic behavior, but with large exchange fluctuations. A difficulty with the amorphous LaFe samples is that T_c obtained by Mössbauer spectra is less than T_c obtained from magnetization measurements while μ_{Fe} obtained from Mössbauer spectra is larger than that obtained from magnetization data. However, because the amorphous LaFe samples are so easily saturated, it does not appear that the explanation in this case is a nonalignment of the Fe moments.

D. ZrFe

Amorphous films of $\mathrm{Zr}_{1-x}\mathrm{Fe}_x$ were prepared with $x=0.65$, 0.76, and 0.80. The magnetizations of all samples saturated easily in low applied fields. The data is very similar to that for the LaFe alloys shown in Fig. 7. Also like the case of LaFe, T_c is easily defined. Values of T_c were found to be 255, 265, and 255 K, and unlike the results for LaFe, T_c was the same whether obtained from Mössbauer-effect data or magnetization data. In the case of these ZrFe samples, high-temperature susceptibility measurements can be made over a small range in temperature and approximate Θ_C values could be obtained. They tended to be somewhat lower than T_c, i.e., $\Theta_C \simeq 220-230$ K.

4.2 K moments were calculated from magnetization data and were found to be $1.14\mu_B$, $1.12\mu_B$, and $1.12\mu_B$, respectively.

$\bar{H}_{\mathrm{hf}}$ values were 165, 182, and 201 kOe, respectively. Unlike the spectra of other systems investigated, the spectra of ZrFe samples appeared to contain a small amount of intensity associated with Fe sites with no hyperfine splitting. If the relationship between $\bar{H}_{\mathrm{hf}}$ and μ_{Fe} that exists for the YFe series is equally valid for ZrFe, we obtain $\mu_{\mathrm{Fe}}=1.03$, 1.14, and $1.26\mu_B$, respectively. The agreement between μ_{Fe} from magnetization data and that from Mössbauer effect is approximate. The data are summarized in Fig. 8.

IV. DISCUSSION

A. Magnitude of exchange fluctuation

It is clear from our results, coupled with those of Forester *et al.*,[8] that amorphous YFe and LuFe alloys are spin glasses. The amorphous LaFe and ZrFe alloys appear to be ferromagnets but with complications that are likely due to large exchange fluctuations, resulting from structure variations. An estimate of the size of the exchange fluctuations can be obtained by comparing the temperature dependence of the magnetization to the theory of Handrich.[24] This is shown in Fig. 9. It is seen that the ratio of exchange fluctuations (ΔJ) to strength of the exchange interactions (J) for LaFe and ZrFe is on the order of $\delta=\Delta J/J \simeq 0.6$ or 0.7. Thus these materials are themselves borderline spin glasses, in that in most models[25] the value of δ dividing ferromagnetic from spin-glass behavior, though not well defined, is on the order of $\delta \simeq 0.8$. In view of the fact that the value of δ close to the critical value, it is not surprising that the magnetic properties are very sensitive to variations in composition or R species. For example, J_{FeFe} is about 50% larger for LaFe alloys than for

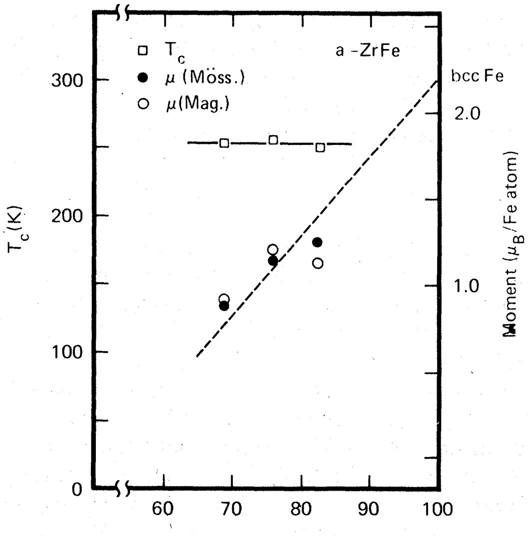

FIG. 8. Magnetic moment per Fe atom and T_c for amorphous ZrFe alloys. Note approximate agreement between Mössbauer-effect result and magnetization result. T_c was also the same by both methods. Note also that extrapolation of T_c to $x=0$ yields similar result as Fig. 5.

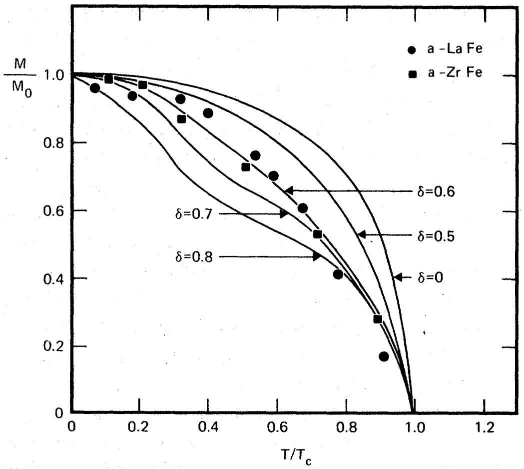

FIG. 9. Normalized magnetization vs temperature behavior according to Handrich model (Ref. 24) for various ratios of exchange fluctuations to exchange i.e., $\delta=\Delta J/J$. Note the data for amorphous LaFe and ZrFe yields $\delta \simeq 0.6$.

YFe. If one assumes ΔJ is about the same for both alloys, one finds $\delta \simeq 0.9$ for YFe, i.e., in the region of spin-glass behavior.

This should be contrasted with the results for amorphous Fe metalloid alloys, where all alloys are ferromagnetic with very little sensitivity to variations in composition. Data on these alloys show that δ is well into the ferromagnetic region. For example, Tsuei and Lilienthal[26] show that for $Fe_{75}P_{15}C_{10}$, $\delta \approx 0.3$, more than a factor of two less than typical for the amorphous R-Fe alloys. If one calculates J for $Fe_{75}P_{15}C_{10}$ in the same manner as we have done, one finds $J \approx 8.0 \times 10^{-15}$ erg which is a factor of 4 larger than that obtained for amorphous YFe. Thus, it seems that the increase in δ for amorphous YFe, LuFe, LaFe, and ZrFe is due to the small value of J rather than to an increase in ΔJ.

B. Structure of amorphous alloys

It has been demonstrated that the structure of the amorphous Fe metalloid alloys can be described in terms of a model such as the dense random packing of hard spheres (DRPHS) for the Fe atoms with the metalloid (P or C) occupying the larger holes inherent in such a structure. For the amorphous R-Fe alloys, the R is larger than the Fe atom and cannot occupy the holes which occur in a DRPHS arrangement of Fe atoms. Consequently Cargill[27] has suggested a binary DRPHS model in which there is an increased tendency to form Fe-Fe and R-R pairs. Another difference is that the interatomic Fe-Fe distance is 2.60 Å ± 0.05 Å in $Fe_{75}P_{15}C_{10}$,[28] and is 2.54 ± 0.05 Å in the R-Fe alloys.[27] While this difference in average interatomic distance is small, it is significant in terms of a Bethe curve argument. One expects the smaller interatomic Fe-Fe distance for the R-Fe alloys to shift the center of the distribution of J values to lower values, which of course agrees with the observed results. In addition as the distribution is shifted to lower-J values, fluctuations in interatomic distance gives rise to very large fluctuations in J. Thus an increase in δ is expected for at least two reasons. Furthermore, this argument can help explain the differences between amorphous and crystalline R-Fe alloys, because in the crystalline compound the interatomic Fe-Fe distance is larger (2.60 Å),[28] and of course does not fluctuate.

C. Effect on R size of magnetic properties

Y, La, and Lu are electronically very similar. The properties of crystalline alloys of Y, La, and Lu with transition metals are nearly identical. Even the magnetic properties of amorphous alloys of Co with Y or La are also essentially identical. The magnetic properties of the amorphous R-Fe alloys on the other hand depend critically upon whether Y, La, or Lu is used. The main difference between these elements is one of atomic size ($R_{La} = 1.87$ Å, $R_Y = 1.80$ Å, and $R_{Lu} = 1.74$ Å). Thus any explanation of these materials must be consistent with these facts. Though it may be simplistic, it appears that the results can be understood in terms of Bethe curve arguments through the effects of R size upon the Fe-Fe coordination and interatomic distances, because based on the arguments in Sec. IV B amorphous R-Fe alloys are sensitive to these parameters, whereas the crystalline alloys and the amorphous R-Co alloys and Fe-metalloid alloys are not.

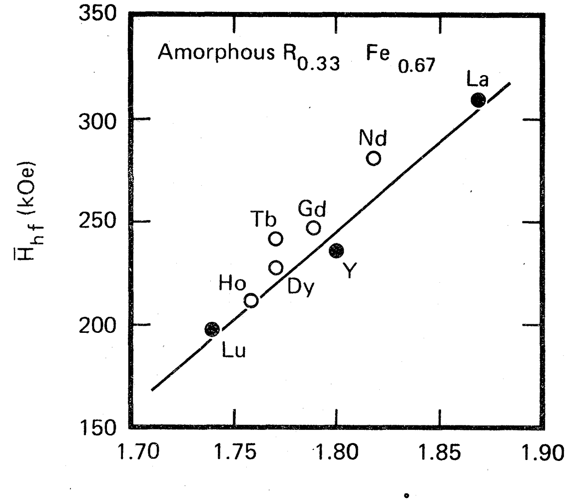

FIG. 10. Dependence of $\bar{H}_{hf}$ at the Fe site upon the size of the R. The solid circles are the results from this work. The open circles are the results for magnetic R.

One other specific characteristic of the amorphous R-Fe alloys which show a strong dependence on the size of the R constituent is $\bar{H}_{hf}$. Figure 10 shows $\bar{H}_{hf}$ as a function of the atomic radius of the R. The solid circles are data points taken from this work. Because in all three cases (Lu, Y, La) the DGF is zero, these three points represent the effect of size on $\bar{H}_{hf}$, uncomplicated by the magnetic characteristics of the R. The open circles are points for other R-Fe alloys. In these cases there may be contributions to $\bar{H}_{hf}$ from the magnetic nature of the R element— such as core polarization and dipolar terms. Nevertheless the trend is still obeyed by these alloys. It should be noted that this result does not necessarily imply that the Fe moment is a function of the size of the R element. In fact, it was noted earlier that magnetization data suggests that the Fe moment for $La_{0.3}Fe_{0.69}$ is of the order of $1.36\mu_B$, considerably less than that calculated from the relationship between $\bar{H}_{hf}$ and μ_{Fe} obtained by Gubbens *et al.*[20] for the case of crystalline YFe alloys. Thus one is led to suggest that the Fe moment is not a strong function of the atomic radius of the R but rather that the relationship between $\bar{H}_{\mathrm{hf}}$ and μ_{Fe} is.

D. Role of the R spin (DGF)

It is also clear that the DGF of the R also must play a role, because the ordering temperatures and $\bar{H}_{\mathrm{hf}}$ depend not only on the size of the R, but also upon the DGF. Perhaps this is nowhere more evident than when comparing the results for GdFe with those for YFe. The former is apparently a fine ferrimagnet with long-range magnetic order (in contrast to other ferrimagnetic amorphous R-Fe alloys which appear to have a finite size to the magnetic cluster[14]), while YFe is a spin glass. Yet the size of Gd and the size of Y are comparable (R_{Gd} = 1.79 Å, R_{Y} = 1.80 Å). In fact the similarity in size and electronic configuration is the reason that Y is usually selected as the nonmagnetic substitute for Gd. An explanation of this follows from a picture similar to that proposed by Cullen[13] for the case of the amorphous TbFe. If one starts from the YFe spin glass and begins replacing Y atoms with Gd atoms, because of the antiferromagnetic coupling between Fe and Gd, those Fe atoms nearest the Gd atom will align antiparallel to the Gd, and consequently parallel to one another. Thus the replacement of all the Y atoms with Gd atoms will have a strong aligning effect on the Fe atoms. Because the Fe atoms are coupled via a Gd atom, the total exchange energy is larger, since it now includes the R-Fe exchange energy. To our knowledge the effect of a second exchange interaction on the properties of a spin glass has never been treated; but it appears that this effect can be approximated rather easily. To calculate the effect of this upon δ (i.e., $\Delta J/J$) one needs either to recast δ in terms of exchange energy or to define an effective exchange constant (J_{eff}), which includes the effect of both Fe-Fe and R-Fe exchange. The latter approach is simpler since we can use the mean-field formula for the ordering temperature of a ferrimagnet (in which for simplicity we neglect the R-R exchange). In the case of YFe there is only one exchange constant:

$$J_0 = 3kT_c/xZ_0S(S+1) \ ,$$

where x is the Fe concentration, Z_0 is the Fe-Fe coordination number and S the Fe spin. With Gd present the formula for T_c becomes

$$3kT_c' = \tfrac{1}{2}xZ_0J_0S(S+1) + \tfrac{1}{2}\{[xZ_0J_0S(S+1)]^2 + 4(x)(1-x)Z_0Z_RJ_R^2(\mathrm{DGF})S(S+1)\}^{1/2} \ ,$$

where Z_R and J_R are the R-Fe coordination numbers and exchange constant and DGF is the R de Gennes factor. We can now define

$$J_{\mathrm{eff}} = 3kT_c'/xZ_0S(S+1) \ .$$

Carrying out the algebra, we find

$$\frac{J_{\mathrm{eff}}}{J_0} = \frac{1}{2} + \frac{1}{2}\left[1 + 4\frac{Z_R}{Z_0}\left(\frac{1-x}{x}\right)\frac{J_R^2}{J_0^2}\,(\mathrm{DGF})\right]^{1/2} \ .$$

We see immediately that the effective exchange is larger. To estimate the magnitude of the increase we need to know the ratio Z_R/Z_0 and J_R^2/J_0^2. We can assume, for simplicity, that $Z_R/Z_0 = 1$, and we can take the ratio J_R^2/J_0^2 from the mean-field model of amorphous GdFe of Heiman *et al.*,[29] who find for $x = 0.67$ that $J_R^2/J_0^2 \simeq 0.058$. Inserting these numbers along with the DGF (15.75) for Gd, we find $J_{\mathrm{eff}}/J_0 \simeq 1.34$. Thus the "effective" exchange between Fe atoms (including the coupling through Gd) is 34% higher than the bare Fe-Fe exchange. If we assume, as is reasonable, that the fluctuations in the exchange are not changed significantly by the replacement of Y with the similarly sized Gd, then the value of $\delta_0 = \Delta J/J_0$ becomes $\delta_{\mathrm{eff}} = \Delta J/J_{\mathrm{eff}}$ and is reduced considerably. Thus if $\mathrm{Y}_{0.33}\mathrm{Fe}_{0.67}$ is a spin glass with $\delta \simeq 0.9$, then amorphous $\mathrm{Gd}_{0.33}\mathrm{Fe}_{0.67}$ would be a ferromagnet with $\delta \simeq 0.6$. If we substitute the DGF for the other R elements, we can estimate δ_{eff} for those alloys. We find for example that for $\mathrm{Ho}_{0.63}\mathrm{Fe}_{0.67}$, $\delta_{\mathrm{eff}} \simeq 0.8$, approximately on the spin glass to ferromagnetic boundary. It is interesting that in proceeding through the R elements in the $R_{0.33}\mathrm{Fe}_{0.67}$ alloys, the behavior of the alloys begins to take on complicated magnetic behavior at Ho.

E. Effect of local anisotropy

In all this, the effect of local anisotropy has been ignored. That certainly is valid for alloys of Fe with Y, La, Lu, Zr, and Gd; however, these effects can become significant for other R-Fe alloys, as shown by Coey *et al.*[30] But while local anisotropy may inhibit collinear alignment of the R spins and thus plays some role, it does not seem to be a key parameter in the systematic variation of the exchange interactions, which seem much more dependent on the size and DGF of the R.

V. CONCLUSIONS

The magnetic properties of the amorphous R-Fe alloys are quite varied and are sensitive to the variation of composition and other parameters. Determining the basis for the systematics of these properties has been difficult because of several confusing complications (e.g., the alloys are *ferri*magnetic, exhibit effects of both anisotropy and large exchange fluctuations, and the R size and spin both contribute to the magnetic properties). We have simplified the problem by examining the Fe-Fe exchange, dealing only with nonmagnetic R and R substitutes (La, Y, Lu, Zr). We find the following:

(i) The Fe-Fe exchange constant J_0 is small in these alloys ($J_0 \approx 2 \times 10^{-15}$ erg).

(ii) Because of this, the ratio (δ) of exchange fluctuations to J_0 is large, $0.6 \leq \delta \leq 0.9$.

(iii) Since this range in δ spans the region of the magnetic phase diagram containing the ferromagnetic to spin-glass transition, the magnetic properties are especially sensitive to variations in material parameters.

(iv) For the La, Y, Lu alloys, the most important parameter appears to be the R size. δ is largest for LuFe alloys (spin glass) and smallest for LaFe alloys (ferromagnet). Ordering temperature (T_c) and $\overline{H}_{\text{hf}}$ increase with increasing R size.

(v) The same systematics occur for the amorphous alloys of Fe with magnetic R (Gd, Tb, Dy, Ho, Nd); however, the effect of R-Fe exchange becomes important. Because Fe spins are now coupled via a R spin, δ is decreased because of the increase in the total exchange energy, which is proportional to the R DGF.

(vi) Local anisotropy effects produces "sperimagnetic" spin structures, reduce the bulk magnetization and increase the coercive force but have only a small effect on the overall exchange energy or ordering temperature.

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[*] Permanent Address: Research Institute of Iron, Steel and Other Metals, Tohoku University, Sendai, Japan.

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