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Magnetic properties of the rare-earth glasses $(R_{65}Fe_{35})_{100-x}B_x$*

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Results are reported on the magnetic properties of $(R_{65}Fe_{35})_{100-x}B_x$ glasses, where R denotes Y, Gd, and Er, and x is 10 or 20. Curie-Weiss fits were made to high temperature susceptibility data to determine average effective moments per magnetic ion and Weiss temperatures. Hysteresis loops and modified Arrott plots were used to determine the spontaneous magnetizations, coercive forces, and ordering temperatures. The effective moments and spontaneous moments are compared with those calculated on the assumption of local moments on both magnetic subnetworks, and assuming various spin structures. There is evidence for moment instabilities on Fe atoms in the Y-Fe-B glass, depending on local-environment effects. Local random anisotropy plays an important role in Er-Fe-B but not in Gd-Fe-B.

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INTRODUCTION

A fundamental description of the magnetic properties of magnetically concentrated rare earth-transition metal glasses is complicated by several issues [1-3]. For example, the magnetism associated with the transition-metal subnetwork could be described by either a local-moment or itinerant electron model. In addition, it is difficult to determine the relative influence of fluctuations in exchange (including negative values) as opposed to local random anisotropy (LRA); both effects can lead to a dispersion of the atomic moments in the magnetically ordered state, and to lack of saturation of the high-field magnetization. Previous studies of such concentrated magnetic glasses have emphasized concentrations rich in transition-metal [1,2]. Recently we nave studied the magnetic properties of glasses of the form $R_{65}Co_{35}$, with R denoting Nd, Gd, and Er [4]. Because of the anomalous properties of Fe in other metallic glasses [2], it was of interest to extend our previous study to alloys in which Co has been replaced by Fe. In particular, we wished to determine how this replacement affected (a) the local-moment or itinerant-electron nature of the transition-metal subnetwork, and (b) the strength of the local random anisotropy on the rare-earth subnetwork, as measured, for example, by the magnitude of the coercive force. Interestingly, attempts to produce $R_{65}Fe_{35}$ glasses by splat cooling techniques were not wholly successful; high resolution x-ray diffraction studies showed residual crystalline Bragg peaks on top of the normal, liquid-like, diffraction pattern observed in the $R_{65}Co_{35}$ glasses. For this reason we added boron, at the level of 10 or 20 atomic percent, which did enable us to prepare glassy alloys of the form $(R_{65}Fe_{35})_{100-x}B_x$.

EXPERIMENTAL

All the alloys were made by first arc melting the pure constituent elements several times. Then a small piece (approximately 0.1 g) was spark cut from the original button, remelted, and rapidly quenched from the liquid by a hammer-anvil technique. The resulting foils, including $(Nd_{65}Fe_{35})_{90}B_{10}$, $(Gd_{65}Fe_{35})_{90}B_{10}$, $(Er_{65}Fe_{35})_{90}B_{10}$, and $(Y_{65}Fe_{35})_{80}B_{20}$, were about 50 μm thick. In all cases except that of the Nd alloy, the diffraction pattern showed only two diffuse peaks indicating a glassy structure. In the Nd alloy, the first peak was actually a doublet, with some other resolvable peaks in addition to the two major, diffuse peaks. Apparently this Nd alloy was microcrystalline or perhaps a mixture of amorphous and crystalline phases. For this reason no magnetic properties are reported here for the Nd alloy. It is interesting and puzzling that with the same quench rate ($\sim 10^6$ - 10^7 K/s) [5], it is easily possible to prepare $R_{65}Co_{35}$ in the amorphous state, whereas if Co is replaced by Fe, 10 at. percent of the glass former boron must be added to obtain a glassy material. Also, it is not clear why, for example, it is much easier to make amorphous $(Er_{65}Fe_{35})_{90}B_{10}$ than it is $(Nd_{65}Fe_{35})_{90}B_{10}$.

Magnetization was measured for applied magnetic fields up to 80 kOe in the temperature range, $1.3\ K \leq T \leq 300\ K$, using a vibrating sample magnetometer. Susceptibility measurements were made with a Faraday balance for $4.2 \leq T \leq 300$ K and for applied magnetic fields, H, of $0 \leq H \leq 10$ kOe. ^{57}Fe Mössbauer measurements were made on certain of the alloys at temperatures between liquid helium and room temperatures.

RESULTS

In our earlier work on the $R_{65}Co_{35}$ glasses there was evidence in the paramagnetic susceptibility data for effective moments that were too large to be accounted for only on the basis of the R^{3+} ions [4]. Therefore, in the present work we have prepared the Y alloy in order to probe the presence of local moments on the Fe subnetwork; clearly the Y and B subnetworks are unlikely to contain local moments. Figure 1 shows the magnetization M for $(Y_{65}Fe_{35})_{80}B_{20}$. It is clear

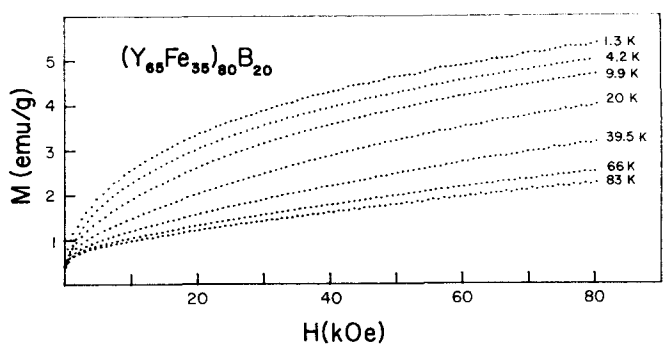

Fig. 1. Magnetization vs. applied field for $(Y_{65}Fe_{35})_{80}B_{20}$.

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that even for T = 83 K a remanent magnetization M_r exists. The magnitude M_r corresponds to 0.03 μ_B per average Fe atom. Susceptibility data at very low fields show a kink at 200 K which, when combined with the data of Fig. 1, suggest the presence of both ordered magnetic clusters and paramagnetic Fe atoms. Assuming saturated Fe atoms of 2 μ_B per atom in the clusters suggests that about 1.5% of all the Fe atoms are in clusters. By removing the cluster contribution to M it is possible to analyze the paramagnetic portion of M by means of a Curie-Weiss relation,

$$\chi = N\bar{p}^2\mu_B^2\,[3k_B(T-\theta)]^{-1}, \qquad (1)$$

where $\bar{p}$ is the effective moment per average magnetic atom and N is the number of magnetic atoms per unit mass. The result is $\bar{p}$ = 2.0 and θ = -17 K.

Figure 2 shows the high-field magnetization of the Gd alloy. It should be noted that at 4.2 K M(H) has essentially saturated. Figure 3 is an M^2 vs. H/M plot for the Gd alloy. The high-field portions of the curves contain nearly linear portions that can be extrapolated to obtain the spontaneous magnetization. The curves all converge to a point on the H/M axis where H_{int} = 0, because of the demagnetization factor. Figure 4 shows the square of the spontaneous magnetization and inverse susceptibility, as obtained from Fig. 3. $M^2(T)$ is plotted here since experience has shown that such plots are nearly linear and can be extrapolated to obtain an estimate of the ordering temperature T_c, in this case 263 ± 5 K. The coercive force for the Gd alloy at 4.2 K is very small, about 22 ± 5 Oe.

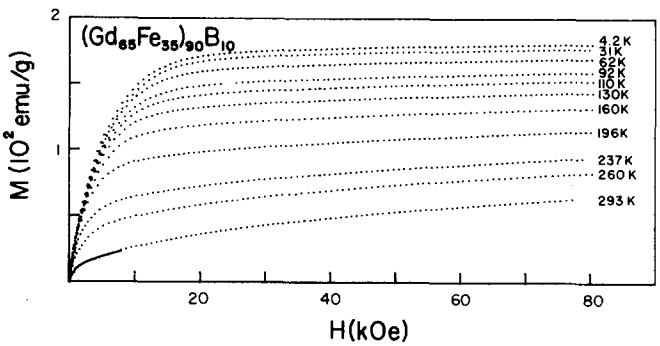

Fig. 2. Magnetization vs. applied field for $(Gd_{65}Fe_{35})_{90}B_{10}$.

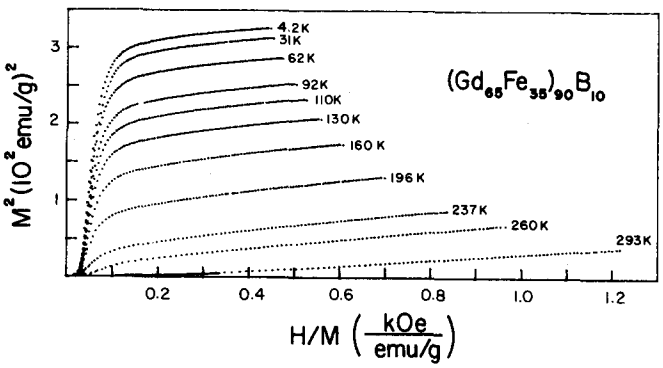

Fig. 3. M^2 vs. H/M for $(Gd_{65}Fe_{35})_{90}B_{10}$.

Figures 5 and 6 show $M^2(H/M)$, $M^2(T)$, and $\chi^{-1}(T)$ for $(Er_{65}Fe_{35})_{90}B_{10}$. It should be noted that the character of Fig. 5 is quite different from Fig. 3; as seen in Fig. 7, M(H) for the Er glass does not approach saturation in fields of 80 kOe so there is no quasi-linear region of the modified Arrott plott. As discussed in our paper on $R_{65}Co_{35}$ [4], this difference between glasses containing Er (or Nd) and Gd is that the former ions possess considerable local random anisotropy whereas for Gd, an S-state ion, the LRA is negligible. Although it is not obvious from Fig. 5, extrapolations based on Fig. 5 (see Fig. 6), as well as direct measurements of the remanent magnetization, indicate that T_c for the Er glass is 37 ± 3 K. Hysteresis loops for the Er glass are shown in Fig. 7 for 1.3 and 4.2 K. At 1.3 K the coercive force is about 10 kOe and there are magnetization jumps indicative of rapid domain-wall motions.

Preliminary ^{57}Fe Mössbauer measurements were made on the Er glass, at temperatures of 11 K, 77 K, and 300 K. At 300 K the data show a doublet consistent with the presence of an electric field gradiant (EFG) at the Fe sites. At 11 K, however, far below T_c, the spectrum consists of a considerably broadened line (by a factor of 1.5) with no resolvable doublet and also no resolvable magnetic hyperfine lines. This is consistent with a relatively small internal field in the ordered state, and with a quadrupole term that vanishes due to an EFG axis which varies from site to site [3].

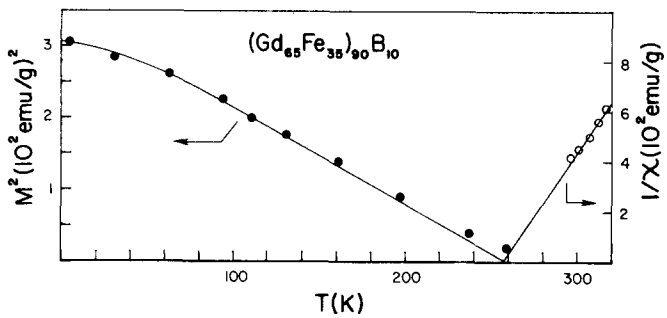

Fig. 4. Square of spontaneous magnetization and inverse susceptiblity vs. temperature for $(Gd_{65}Fe_{35})_{90}B_{10}$.

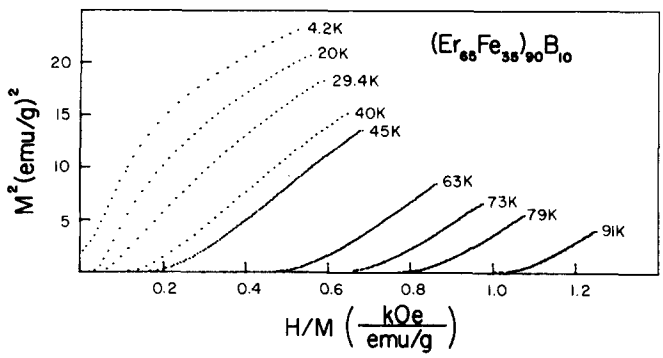

Fig. 5. M^2 vs. H/M for $(Er_{65}Fe_{35})_{90}B_{10}$.

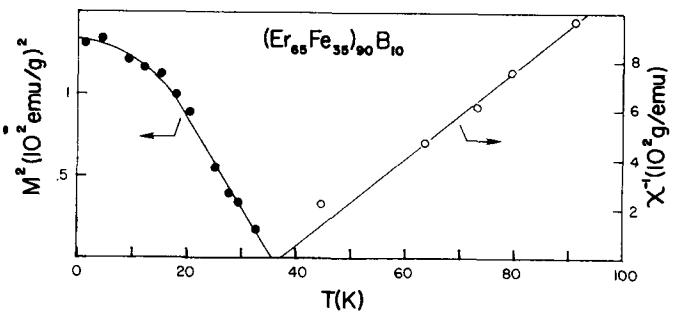

Fig. 6. Square of spontaneous magnetization and inverse susceptibility vs. temperature for $(Er_{65}Fe_{35})_{90}B_{10}$.

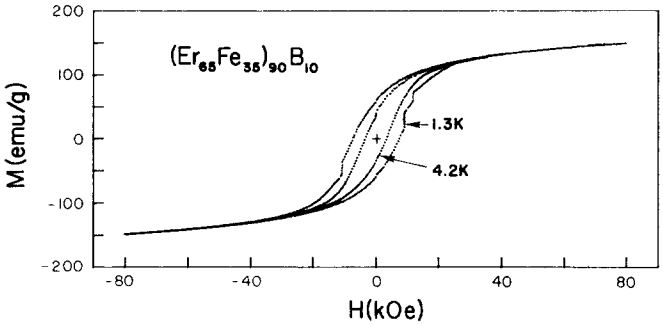

Fig. 7. Hysteresis loops, M(H), at 1.3 and 4.2 K for $(Er_{65}Fe_{35})_{90}B_{10}$.

DISCUSSION

As mentioned above, the purpose in measuring the Y-Fe-B alloy was to obtain information on the presence of local moments on the Fe subnetwork. The result of the analysis of Eq. (1) was that the effective moment per average Fe atom is $\bar{p} = 2.0$. However, recent Mössbauer work by Chappert et al. [6] has shown in amorphous $Y_{67}Fe_{33}$ that only 18% of the Fe atoms have a moment and that the data (as a function of composition) are consistent with a local-environment effect in which a given Fe atom must have at least six Fe nearest neighbors if it is to bear a moment. Our data is altogether consistent with this picture. If the above value of $\bar{p}$ is instead associated with only 15% of the Fe atoms (our Fe concentration is 28% of the total atoms), then for these magnetic Fe atoms $\bar{p}_{Fe} = 5.2$. This value is similar to that expected for a spin 2 particle (4.90). The demagnetization of most of the Fe atoms in $Y_{67}Fe_{33}$ presumably comes about because of hybridization of the Y(4d/5s) and Fe(3d) orbitals, with the latter broadened to the extent that they cannot support a moment [3]. The importance of this result for the alloys containing Gd or Er is that similar local environment effects should be present in the latter alloys.

An analysis of Eq. (1) for the Er-Fe-B glass leads to $\bar{p} = 7.5 \pm 0.2$. If there were no local moments associated with the Fe subnetwork, $\bar{p}$ would have the value 7.7, suggesting that there is very little moment to be associated with Fe. On the other hand an estimate of spontaneous moment per magnetic atom, $\bar{\mu}_s$, for Er-Fe-B, is 2.7. If one assumes zero Fe moment plus an asperomagnetic [1,2] structure for the Er subnetwork, with the Er moments dispersed in a cone of half angle $\phi = 90°$, then $\bar{\mu}_s$ would be 2.93. Altogether, these data are consistent with either: (a) no moment on the Fe subnetwork and ϕ somewhat greater than 90°, or (b) a small Fe moment coupled antiparallel to Er moments, which are themselves scattered into a cone of half angle 90°.

The near saturation of the magnetization of the Gd-Fe-B glass, plus the very small value of the coercive force, suggest a nearly collinear arrangement of the Gd spins, a structure permitted by a near absence of local random anisotropy. A Curie-Weiss analysis of the $\chi^{-1}(T)$ data of Fig. 4 leads to $\bar{p} = 9.7$ which is much larger than the expected value of 6.4 if there were no moment on the Fe subnetwork. If one adopts a simple local-moment model for both the Gd and Fe atoms in the paramagnetic state [4], $\bar{p} = 9.7$ leads to a very large value for the Fe spin, namely, $S_{Fe} \simeq 5$ (assuming $g_{Fe} = 2$). The $\bar{\mu}_s$ value obtained from Fig. 4 is $3.9 \pm 0.1\ \mu_B$. If all the Gd spins were perfectly aligned and if the Fe subnetwork possessed no moment, $\bar{\mu}_s$ would be $4.55\ \mu_B$. The assumption of a two subnetwork ferrimagnetic spin structure, for which

$$\bar{\mu}_s/\mu_B = 0.65(gJ)_{Gd} - 0.35(gJ)_{Fe}, \qquad (2)$$

leads to $(gJ)_{Fe} = 1.9$ and $J_{Fe} = S_{Fe} \simeq 0.9$. This value of S_{Fe} is not unreasonable but it does not agree with the very large value (~ 5) obtained from the local-moment model of the susceptibility mentioned above. These results suggest either that there is some dispersion of the moments on one or both of the subnetworks or perhaps that there is significant conduction electron polarization leading to a much enchanced susceptiblity in the paramagnetic state. In addition, these analyses are based on average values for the transition metal moments. As mentioned above, in connection with the Y-Fe-B results, it may well be that the situation is further complicated by local-environment effects so that any mean-field analysis [7] is a serious oversimplication.

CONCLUSIONS

The major conclusions to be drawn from this work are: (1) In Y-Fe-B the paramagnetic data are consistent with the local-environment model of Chappert et al. in which only Fe atoms with six or more Fe neighbors bear a moment. There is in addition a small cluster contribution to the magnetization whose properties may be intrinsic or extrinsic to those of an "ideal amorphous structure" of the same composition. (2) The Er-Fe-B glass shows magnetic properties readily explainable in terms of the LRA model of amorphous magnetism. The data are consistent with an asperomagnetic structure due to the Er moments, but the magnitude of any moments associated with the Fe subnetwork is too small to be detected. (3) The Gd-Fe-B glass shows no evidence for significant local random anisotropy as expected. The data for both the paramagnetic and ordered states suggest that there is a contribution of the Fe subnetwork to the magnetism. However, it is not possible to determine whether the local moment or itinerant model is more appropriate. The analysis is complicated by the possibility that local-environment effects, such as those seen in Y-Fe-B, may render mean-field-type models for the Fe subnetwork inadequate. (4) Replacing Co by Fe in glasses of the type under consideration increases the ordering temperatures and, in those cases for which local random anisotropy exists, the coercive force of the material. (5) Certain of these glasses show electrical resistivity anomalies at T_c. These and additional Mössbauer measurements are being pursued to further clarify the low temperature magnetic structures of these glasses rich in rare-earth.

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