Spin-Glass Freezing and RKKY Interactions near the Metal-Insulator Transition in Amorphous Gd-Si Alloys

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Magnetization measurements of giant negative magnetoresistive amorphous Gd_xSi_{1-x} ($0.04 < x < 0.19$) show strong mixed ferromagnetic and antiferromagnetic interactions and spin-glass freezing. The interactions appear to be an RKKY-like indirect exchange mediated by the conduction electrons, but are strikingly independent of their localization at the metal-insulator (MI) transition, presumably because the localization length exceeds the inter-Gd distance. The susceptibility per Gd atom in the paramagnetic state shows a nontrivial dependence on composition, with a maximum at the MI transition.

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Amorphous (a-)Gd_xSi_{1-x} for x near the metal-insulator (MI) transition possesses giant (many orders of magnitude) negative magnetoresistance (MR) at temperatures below 80 K [1,2]. Gd is a $4f^75d^16s^2$ atom, nearly always trivalent; the Gd^{3+} ion has a large moment $J = S = \frac{7}{2}$ and $L = 0$ due to the half-filled f shell. The enormous MR is presumably related to an exchange interaction J_{sf} between conduction electrons and local Gd magnetic moments, leading to increased electron localization when the moments are randomly oriented and (enormous) decreases in resistivity as they become aligned by an applied field. In metals such as crystalline Gd and $GdSi_2$, J_{sf} results in an indirect (RKKY) exchange interaction between the Gd ions. In Gd, the RKKY interaction is ferromagnetic, leading to a Curie temperature T_c of 293 K. In $GdSi_2$, it is antiferromagnetic and leads to a Néel temperature T_N of 27 K [3]. In a simple band insulator, the RKKY interaction cannot exist, hence insulating Gd compounds such as Gd_2Se_3 interact via a valence electron-mediated superexchange with $T_N = 5$ K [4]. Disorder alone does not appear to fundamentally alter the nature of the interactions; a-Gd_xGe_{1-x} for $x > 0.5$ is a ferromagnetic metal with T_c above 150 K [5]. Theoretical and experimental work on the RKKY interaction in a (weakly) disordered metal with elastic mean free path $l > 1/k_F$ and $< R$ (the intermoment spacing) shows that the interaction is *not* exponentially damped, as once supposed, but its sign is randomized [6].

The issue to be addressed in the present amorphous Gd_xSi_{1-x} alloys, near the MI transition, is the nature of an indirect RKKY-type interaction in a material where there is a high density of conduction electrons, but where these electrons are localized due to disorder, electron-electron, and electron-local moment interaction effects, with a localization length ξ much longer than R, the inter-Gd distance. ξ diverges at the MI transition and is strongly affected by magnetic field in these alloys [2]. The interactions between magnetic moments and itinerant electrons, and at a deeper level the interplay between localization, Coulomb, and magnetic interactions, are important in many materials of current interest, including the manganites, heavy fermion materials, diluted magnetic semiconductors (DMS), and the rare earth chalcogenides.

Near the MI transition, even nominally nonmagnetic doped semiconductors such as crystalline Si doped with P (Si:P) possess exotic and much-studied magnetic properties [7–9]. Localized conduction electrons singly occupy sites due to Coulomb correlation effects. The spin $\frac{1}{2}$ moments interact antiferromagnetically and form spin singlets [9]. The resulting magnetic susceptibility χ has been shown experimentally and theoretically modeled to depend on temperature as $T^{-\alpha}$, where α ranges from 1 in the insulating low-doping limit (Curie law) to 0 in the metallic high-doping limit (Pauli susceptibility) [7,9]. The MI transition has also been extensively studied in (nonmagnetic) amorphous semiconductor alloys such as a-T_xSi_{1-x} and a-T_xGe_{1-x} with T = Nb, Mo, Au, Cr, Y, and Fe (Fe does not have a magnetic moment in Si or Ge at this low concentration) [1,2,10,11]. The strong structural disorder here enormously increases the electron concentration at the MI transition compared to that of crystalline semiconductors.

In a-Gd_xSi_{1-x}, Gd introduces a fixed local moment, which is likely to interact with the conduction electrons. In recent specific heat experiments on a-Gd_xSi_{1-x} for x near the MI transition [12], we saw thermodynamic evidence of magnetic ordering at low temperature (<10 K). The entropy in this ordering is larger than can be attributed to Gd^{3+} moments, and was ascribed to a contribution from the magnetic moments of the localized conduction electrons. Magnetic measurements on these alloys are very limited, particularly near the MI transition. Our measurements of $M(H, T)$ on an $x = 0.13$ sample showed a lack of saturation at high fields and a susceptibility above 5 K that was close to the noninteracting Curie law dependence [1]. a-Gd_xGe_{1-x} (studied for $x = 0.18$ to 1, well above the MI transition) showed ferromagnetic ordering at high x with a Curie temperature which drops monotonically with decreasing x down to 0.5 [5]. For $x < 0.5$, T_c drops precipitously to zero and the induced magnetization at 4.2 K drops well below a simple local moment model [5]. Measurements of a-$Gd_{0.18}Si_{0.82}$ showed signs of antiferromagnetic

interactions at low temperature (a Curie-Weiss intercept of -10 K, and a large high field susceptibility), but no magnetic freezing was claimed [13].

In this paper, we present results of a magnetization study for 0.19 (well above the MI transition) $> x > 0.04$ (strongly localized). We find that these alloys are classical spin glasses, with strong mixed ferro- and antiferromagnetic Gd-Gd interactions. The interaction strength is similar to that in the crystalline metallic $GdSi_2$, consistent with calculations which suggest that the effect of disorder is to randomize the sign without changing the strength [6]. We also show an anomalous dependence of the magnetic susceptibility χ on composition, with a peak near the MI transition. This result is presumably related to the interactions of conduction electrons with Gd magnetic moments, and hence is qualitatively consistent with the enhanced entropy found in specific heat measurements [12].

Samples were made by electron beam coevaporation under UHV conditions onto amorphous Si-N coated Si substrates held near room temperature. TEM and x-ray characterization show the samples to be amorphous. Thickness is 4000 Å, measured by profilometry. Gd concentrations were determined by Rutherford backscattering (RBS). ac and dc susceptibility χ_{ac} and χ_{dc} and the dc magnetization $M(H,T)$ were measured using a SQUID magnetometer. $\chi_{substrate}$ was subtracted.

Figure 1 shows χ versus temperature T for $x = 0.14$. χ_{dc} is defined as the magnetization M measured at 100 Oe, divided by 100 Oe; data are shown for the zero field-cooled (ZFC) and 100 Oe field-cooled (FC) states. χ_{ac} was measured in an ac field of 4 Oe (fields from 1–5 Oe were tested for linearity of χ) at 135 Hz. A peak is seen in χ near 6 K, which sharpens for χ_{ac}, and a split between zero field cooling and field cooling is seen near 5 K, indicating a magnetic freezing, consistent with our specific heat measurements [12]. The fit shown is for a Curie-Weiss law from 6.5–300 K.

Figure 2 shows $\chi_{ac}(T)$ on an expanded scale for $x = 0.12$ for different measurement frequency f (15 to 950 Hz). The peak height increases and shifts to lower temperatures with decreasing frequency. Similar small yet clear shifts (of the order of 1%) are seen in the canonical spin glasses [14]. The inset shows the dependence of the freezing temperature T_f on f, with T_f defined as the peak in χ_{ac}. $\Delta T_f/T_f$ per decade $\omega = 0.04$, similar to many spin glasses [14]; this shows a dependence consistent with cooperative freezing of individual magnetic moments, rather than blocking of superparamagnetic particles or an antiferromagnetic phase transition.

Figure 3(a) shows the ac susceptibility measured at 135 Hz and 4 Oe for five samples with x from 0.036 to 0.19. For all x, above T_f, χ_{ac} and χ_{dc} agree within error bars. The inset shows T_f vs x, with T_f defined as the peak in χ_{ac} measured at 135 Hz; the $x = 0.036$ sample is shown with a downward arrow only as its freezing point if any is below our measurement range. Figure 3(b) shows the inverse dc susceptibility per Gd atom as a function of temperature above T_f for each sample. A temperature independent constant b due to core, substrate, and SQUID magnetometer background contributions has been subtracted from the raw data by extrapolating χ vs $1/T$ as $T \to \infty$. For simple interacting moments, a Curie-Weiss dependence $1/\chi = (T - \theta)/A$ gives a straight line on this plot with intercept θ and slope $1/A$. The Curie-Weiss constant $A = n_{Gd} p^2 \mu_B^2 / 3k_B$, where p is the effective moment, θ is their net interaction, and $n_{Gd} =$ Gd atoms/cm^3. For noninteracting $J = S = \frac{7}{2}$ moments, $p^2 = g^2 J(J+1) = 63$, where g is the Lande factor $= 2$, and $\theta = 0$, shown as a solid line. In the present samples, θ is less than 2.5 K for all samples, and there is *no* significant curvature in the $1/\chi$ data at any temperature; positive θ and/or curvature would indicate ferromagnetic clustering as is often seen in amorphous metallic Gd alloys. The random error in the data is relatively small at all T; the possible systematic error [error bars in Fig. 3(b)], due primarily to uncertainty in the constant b, becomes large above 50 K, particularly for the $x = 0.036$ sample. Table I shows data for θ, A, effective moment p, composition x, and n_{Gd} (from RBS measurements).

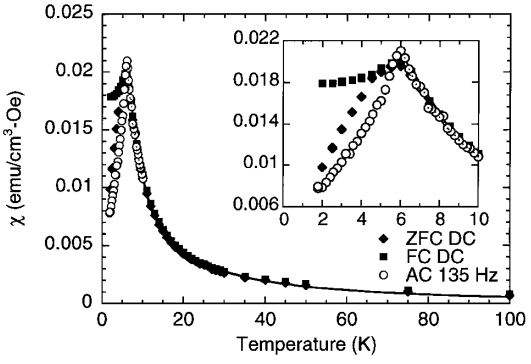

FIG. 1. χ for $x = 0.14$. χ_{dc} was measured in 100 Oe, applied either after cooling (zero field cooled) or at 300 K (field cooled). χ_{ac} was measured in 135 Hz 4 Oe, after cooling to 10 K in zero field. Line is a Curie-Weiss law, fit above T_f. Inset: same data on expanded scale.

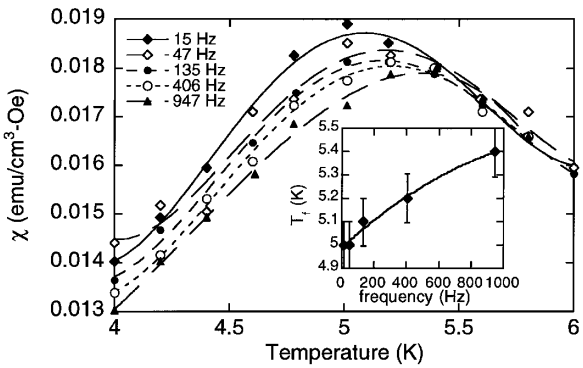

FIG. 2. χ_{ac} vs T for $x = 0.12$ measured at different frequencies f in 4 Oe field. Inset: T_f (from peak χ_{ac}) vs f. Lines are a guide to the eye.

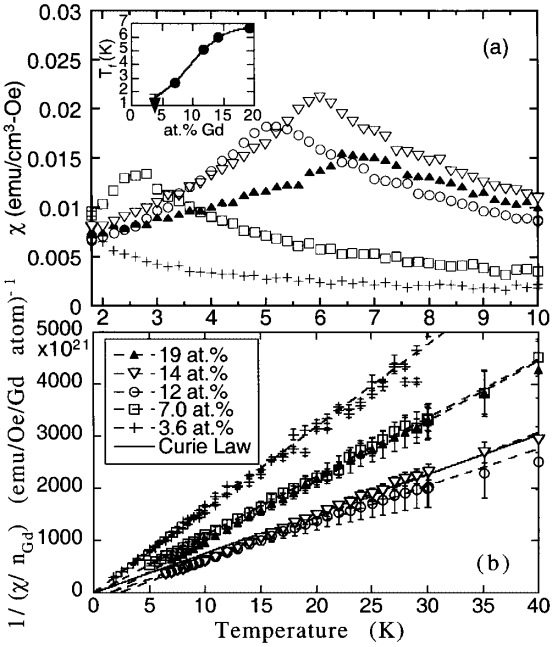

FIG. 3. (a) χ_{ac} vs T for $x = 0.036$ to 0.19 measured at 135 Hz in 4 Oe field. Inset shows T_f (from peak χ_{ac}) vs at. % Gd. Line is a guide to the eye. (b) Inverse χ_{dc} (measured in 100 Oe) per Gd atom $1/(\chi_{dc}/n_{Gd})$ vs T. Dashed lines are Curie-Weiss fits; fit parameters are in Table I. Solid line in (b) is the Curie law for noninteracting Gd^{3+} moments. Error bars shown include both random and *possible* systematic errors for $x = 0.7$ to 0.19; for $x = 0.036$, only the random error is shown.

Figure 4 shows the high field data $M(H)$ for $x = 0.036$ at various temperatures. As was previously seen for $x = 0.13$ [1], $M(H)$ does not saturate in fields up to 60 kOe. For both compositions, M is $\sim\frac{1}{2}$ the expected saturation magnetization, with a large high field susceptibility. At 6 K, in 60 kOe, the Brillouin function for $J = \frac{7}{2}$ Gd^{3+} is saturated if the moments are isolated ($\sim$0.9 of full value) or ferromagnetically interacting. Since the Gd^{3+} ion is an $L = 0$ state, anisotropy is not likely to play a significant role. Thus there must be strong antiferromagnetic interactions suppressing the magnetization. Similar results are seen in all the canonical spin-glass materials [14].

Table I shows that the effective moment p and θ are largest for samples near the MI transition ($x = 0.12$ and 0.14), and drop significantly for $x = 0.07$ and 0.036, which are strongly insulating. p is also suppressed for $x = 0.19$, consistent with the results reported in the literature of reduced moments at this composition [5,13]. This nontrivial dependence of χ on composition is easily seen in $1/(\chi_{dc}/n_{Gd})$ in Fig. 3(b), but is also visible in χ_{ac} in Fig. 3(a), where $x = 0.19$ has *lower* susceptibility than $x = 0.14$, despite a higher T_f. An effective moment of 7.6 or 8.2 is within error bars of the isolated Gd^{3+} value (7.9), but the values for the strongly insulating samples (as low as 5.5) are significantly less, suggesting an effect of the localized conduction electron moments, similar to what is seen in Si:P [7–9]. It thus seems likely that the magnetic state of relatively dilute Gd (<20 at. %) in amorphous Si is not as simple as a trivalent $4f^7(J = \frac{7}{2}, g = 2)$ state. This is perhaps not surprising since the conduction electrons originate from s and d electrons of the Gd atom and are localized (or nearly localized) in part due to an exchange interaction with the $4f$ core electrons. There is only one reported case of Gd in a nontrivalent state, where an altered value for p is expected; in SmB_6, Gd was reported to be in a divalent $4f^7 5d^1$ state, with $S = 4$ and reduced g value [15].

Amorphous metallic Gd alloys (with Ag, Au, Al) are ferromagnets for $x > 0.4$, true spin glasses for $x < 0.01$, and cluster glasses with positive Curie-Weiss constant θ in the paramagnetic state for $0.01 < x < 0.25$ [16]. For x comparable to the present work, θ is much larger than we find (>20 K), while T_f values are nearly the same. This suggests that here, even nearest neighbor interactions are of random sign, unlike the ferromagnetic clusters in metallic Gd alloys of comparable x, and are strong evidence against Gd clustering.

The observed spin-glass freezing requires Gd-Gd magnetic interactions ($J_{Gd\text{-}Gd}$), and must include frustration and antiferromagnetic (AFM) interactions. Frustration of AFM interactions is natural in an amorphous structure since there are no distinct sublattices. The high field $M(H, T)$ data indicate that some $J_{Gd\text{-}Gd}$ AFM interactions are quite strong, since M is significantly suppressed below the Brillouin function. The net interaction $\sum J_{Gd\text{-}Gd}$ between a Gd moment and its neighbors is close to zero, as evidenced by the relatively small Curie-Weiss θ. There must therefore be a broad range of interactions, centered on zero, as in a classic spin glass [14]. As a crude estimate of their strength, the observed M/M_{sat} at 60 kOe and 6 K (4 K in Ref. [1]) requires an equivalent field of

TABLE I. Curie-Weiss fit parameters for dc susceptibility (FC or ZFC) above T_f.

Composition x[a]	n_{Gd} (No. Gd atoms/cm^3)[a]	θ(K)[b]	A (emu/cm^3 · Oe · K)[b]	p (Bohr magnetons)[c]
0.036	1.67×10^{21}	−0.08	0.011	5.5
0.07	3.5×10^{21}	0.23	0.031	6.5
0.12	5.7×10^{21}	1.3	0.080	8.2
0.14	6.8×10^{21}	2.4	0.083	7.6
0.19	9.5×10^{21}	1.5	0.082	6.4

[a]From RBS and profilometer. Values for x and n_{Gd} are ±5%.
[b]$\chi = A/(T - \theta) + b$; b is a temperature independent constant due to core, substrate, and magnetometer background contributions. Values for θ and A are ±5%.
[c]$A = n_{Gd} p^2 \mu_B^2 / 3k_B$. For isolated moments, $p^2 = g^2 J(J + 1) = 63$ for Gd^{3+}. g = Lande factor. Values for p are ±7%.

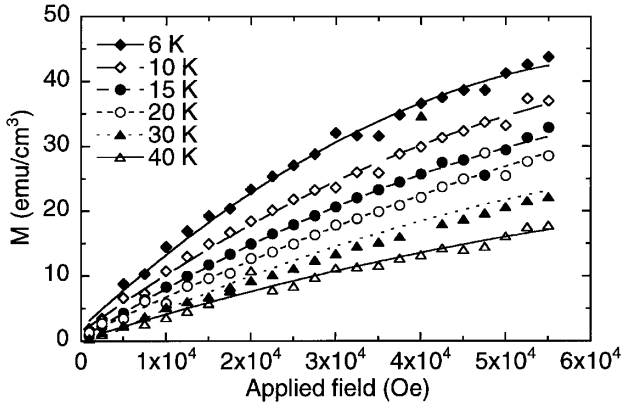

FIG. 4. $M(H,T)$ for $x = 0.036$. Saturation $M = 109$ emu/cm^3, assuming Gd^{3+} ions with $J = \frac{7}{2}$, $g = 2$. Lines are a guide to the eye.

less than 13 kOe, therefore AFM interactions of strength greater than 47 kOe, with equivalent temperature greater than 22 K, for $J = \frac{7}{2}$, must be present. It is common in spin glasses (probably essential) for the strength of the interactions to significantly exceed T_f.

The interaction strength here is thus comparable to that seen in the metallic crystalline $GdSi_2$ which has an antiferromagnetic RKKY-mediated ordering at 27 K [3]. Dipolar coupling, while large for $J = \frac{7}{2}$, is still quite small compared to T_f due to the large Gd-Gd spacing. The extremely local nature of Gd $4f$ levels means that direct exchange or conventional superexchange or double exchange are not likely contributions. The Kondo effect should play no role since J_{sf} for Gd should be ferromagnetic, although the sign of a J_{df} for a (partially) localized d level is not clear. The high electron/Gd moment ratio ($\sim$1) makes a magnetic polaron model as usually envisioned (e.g., Ref. [17]) not directly applicable, although probably still relevant. It is possible that the interaction could be a virtual d-level mediated superexchange, similar to Gd_2Se_3, but more likely (given the interaction strength and high electron concentration) is an indirect exchange, where the Gd-Gd interaction is mediated by J_{sf}-induced polarization of conduction electrons.

An indirect RKKY exchange is usually considered in metals, while these materials are insulating or barely metallic. However, they are not simple band insulators but instead have a large electron concentration and are localized due to disorder, Coulomb and electron-Gd moment interactions, with localization length much greater than the Gd-Gd spacing R, at least for samples near the MI transition. The concentration of conduction electrons which might mediate an RKKY interaction is $\sim 10^4$ more than in DMS at the MI transition, $\sim$100 times more than in the chalcogenides at the MI transition ($Gd_{3-x}\upsilon_x S_4$; υ = vacancy, $x \sim 0.32$), and comparable to the colossal MR manganites or Gd_3S_4, a metallic ferromagnet.

We make two final observations: first, from MR measurements, spin-glass freezing is eliminated by fields $\sim$1000 Oe, consistent with $T_f \sim 6$ K, and thus plays little direct role in the high field MR. Even in zero field, the resistivity shows no obvious signature of the freezing. Second, in an applied field, the localization length of a-Gd_xSi_{1-x} increases, perhaps affecting the RKKY-type interaction.

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[1] F. Hellman, M. Q. Tran, A. E. Gebala, E. M. Wilcox, and R. C. Dynes, Phys. Rev. Lett. **77**, 4652 (1996).
[2] P. Xiong, B. L. Zink, S. I. Applebaum, F. Hellman, and R. C. Dynes, Phys. Rev. B **59**, R3929 (1999); W. Teizer, F. Hellman, and R. C. Dynes, Solid State Commun. **114**, 81 (2000).
[3] K. Sekizawa and K. Yasukochi, J. Phys. Soc. Jpn. **21**, 274 (1966).
[4] F. Holtzberg *et al.*, Phys. Rev. Lett. **13**, 18 (1964).
[5] R. J. Gambino and T. R. McGuire, IEEE Trans. Magn. **19**, 1952 (1983).
[6] P. F. de Chatel, J. Magn. Magn. Mater. **23**, 28 (1981); K. M. Wong and S. J. Poon, J. Magn. Magn. Mater. **42**, 130 (1984); D. C. Vier and S. Schultz, Phys. Rev. Lett. **54**, 150 (1985); A. Jagannathan, E. Abrahams, and M. J. Stephen, Phys. Rev. B **37**, 436 (1988).
[7] A. Roy and M. P. Sarachik, Phys. Rev. B **37**, 5531 (1988); A. Roy, M. Turner, and M. P. Sarachik, *ibid.* **37**, 5522 (1988).
[8] M. A. Paalanen, J. E. Graebner, R. N. Bhatt, and S. Sachdev, Phys. Rev. Lett. **61**, 597 (1988); M. Lakner and H. V. Lohneysen, Phys. Rev. Lett. **63**, 648 (1989); M. Lakner, H. V. Lohneysen, A. Langenfeld, and P. Wolfe, Phys. Rev. B **50**, 17 064 (1994).
[9] R. N. Bhatt and P. A. Lee, Phys. Rev. Lett. **48**, 344 (1982).
[10] For a review, see P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).
[11] A. Albers and D. S. McLachlan, J. Phys. Condens. Matter **5**, 6067 (1993); A. Heinrich *et al.*, J. Non-Cryst. Solids **164–166**, 513 (1993); S. Yoshizumi, T. H. Geballe, M. Kunchur, and W. L. McLean, Phys. Rev. B **37**, 7094 (1988); M. A. LaMadrid, W. Contrata, and J. M. Mochel, Phys. Rev. B **45**, 3870 (1992).
[12] B. L. Zink, E. Janod, K. Allen, and F. Hellman, Phys. Rev. Lett. **83**, 2266 (1999). More recent data show a broad bump in C_p centered near 6 K for $x = 0.12$.
[13] P. Simonnin *et al.*, Phys. Status Solidi **98**, 551 (1986).
[14] J. A. Mydosh, *Spin Glasses* (Taylor & Francis, London, 1993).
[15] G. Wiese, H. Schaffer, and B. Elschner, Europhys. Lett. **11**, 791 (1990).
[16] K. Moorjani and J. M. D. Coey, *Magnetic Glasses* (Elsevier, New York, 1984), p. 222; S. J. Poon and J. Durand, Phys. Rev. B **18**, 6253 (1978).
[17] T. Kasuya and A. Yanase, Rev. Mod. Phys. **40**, 684 (1968).