Metal-Insulator Transition and Giant Negative Magnetoresistance in Amorphous Magnetic Rare Earth Silicon Alloys

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Large negative magnetoresistance and anomalous magnetic properties are found in amorphous Si doped with magnetic rare earth ions near the metal-insulator transition. The resistivity below 50 K rises orders of magnitude above that of comparable composition nonmagnetic alloys and is strongly reduced by a magnetic field. Magnetization measurements show noninteracting moments at high temperature which develop antiferromagnetic interactions below 50 K. We suggest that these results are due to formation below 50 K of a dense concentration of magnetic polarons which localize conduction electrons. [S0031-9007(96)01722-X]

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In crystalline semiconductors, the presence of local magnetic moments and, in particular, the exchange interaction between carriers and local moments are known to dramatically modify carrier transport [1–8], especially near a metal-insulator (M-I) transition. In addition to magnetic scattering, there can be giant spin splitting of electronic bands, increased localization of carriers via the formation of magnetic polarons, and a consequent shift of the M-I transition to higher carrier concentrations. Previous work has involved chalcogenide compounds such as EuO or vacancy-dominated Gd_3S_4 [1,7] or Mn doped II-VI or III-V semiconductors [2,4,6,8]. In some of these, negative magnetoresistance (MR) as large as 6 orders of magnitude was observed [6,7]. More generally, somewhat complicated magnetoresistances (both positive and negative) [2,8] have led to theories for the formation of magnetic polarons [1,3,5]; these are ferromagnetic regions of local moments aligned with the spin of the carrier via the exchange interaction. They increase the carrier effective mass and hence tend to localize the carrier since the carrier is dressed with a polarization cloud.

Amorphous systems have provided a rich field for studies of the M-I transition in the presence of disorder [9–12]. For these samples in the vicinity of the M-I transition, the Fermi level E_F is near the mobility edge E_C; either just below (for the insulating samples) or just above (for the metallic samples). Alloys such as a-Nb-Si can be tuned through this transition by varying the metal (Nb) concentration, thereby varying the Fermi energy. Near the transition, electron correlation effects become important, causing a gap ("Coulomb gap") in the single particle density of states at the Fermi energy [9,10]. There have, however, to our knowledge been no studies of the effect of local magnetic moments on the M-I transition in amorphous systems. Studies of a-Fe-Ge, for example [11,12], were among those which showed the absence of a minimum metallic conductivity, but, at concentrations relevant to the M-I transition (below 20 at. %), Fe does not retain a magnetic moment in Si or Ge [13]. Studies of rare earth Si or Ge alloys have been either very dilute ($\leq$ 3 at. %) or at high concentrations ($\geq$ 18 at. %, well above the M-I transition) [14–16]. There are important differences in electrical conduction in amorphous and crystalline alloys: These include enormous differences in conduction electron elastic mean free path, magnitude of potential fluctuations, and separation of dopant atoms in materials at the M-I transition. For amorphous alloys, the concentration of dopant required to reach the M-I transition is orders of magnitude larger than that in crystalline materials ($\approx 4 \times 10^{21}$ versus 3×10^{17} cm^{-3} [2,11]). Thus, the usual notion for the crystalline dilute magnetic semiconductors of a bound magnetic polaron in which a single localized electron with a Bohr radius of many lattice constants polarizes the moments within its Bohr radius must be rethought in amorphous alloys where there are many overlapping and yet (nearly) localized electronic states and where Coulomb interactions between the electrons are crucial.

We present here results on a new class of dilute magnetic semiconductor, amorphous rare earth silicon alloys (a-RE_xSi_{1-x}: RE = Gd, Tb, and the nonmagnetic analog Y) with composition x spanning the metal-insulator transition ($0.1 < x < 0.15$). Below 50 K, large negative magnetoresistance and magnetic susceptibility indicative of temperature-dependent antiferromagnetic interactions suggest the formation of a dense array of magnetic polarons which localize the conduction electrons. Gd and Tb ions retain a large local magnetic moment because of their compact $4f$ shells. The three ions are all expected to be trivalent with nearly the same electronic structure except for the presence or lack of f electrons. All three have approximately the same ionic radii. For similar x, their a-RE_xSi_{1-x} alloys are therefore expected to have similar bonding structures and electronic densities of states. 1100 Å thick samples were coevaporated from separate Si and Gd, Tb, or Y sources onto amorphous silicon nitride-coated Si substrates held near 300 K. Samples were lithographically patterned for four-lead conductivity measurements (geometry shown in Fig. 1 inset). Magnetization data were obtained with a Quantum Design SQUID

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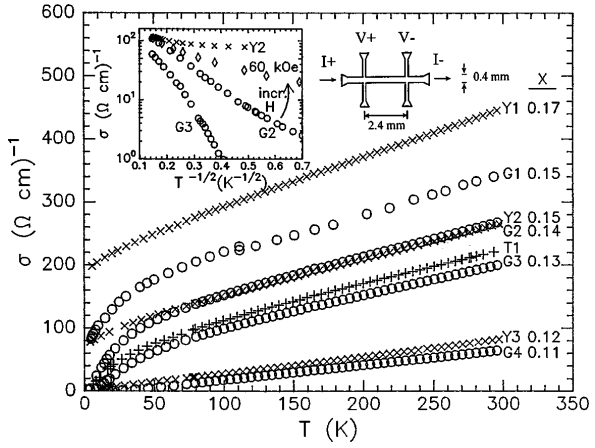

FIG. 1. Temperature dependence of conductivity for a-Gd_xSi_{1-x} (samples G1–G4: ◯), a-Y_xSi_{1-x} (Y1–Y3: ×), and a-Tb_xSi_{1-x} (T1: +). Composition x is shown for each: uncertainty in x is ±0.01. Inset: $\log_{10}(\sigma)$ vs $T^{-1/2}$.

magnetometer, and compositions determined by Rutherford backscattering.

The temperature dependence of the conductivity $\sigma(T)$ for $2 < T < 300$ K is shown in Fig. 1. In amorphous materials without local magnetic moments, on the metallic side of the M-I transition, $\sigma(T) = \sigma_0 + aT^{1/2} + bT^{p/2}$ where σ_0 is the conductivity at $T = 0$ (= 0 at and below the M-I transition), the second term is due to the Coulomb correlation gap and the third due to weak localization plus inelastic scattering; the power p depends on scattering mechanism and equals 2 for electron-electron scattering in 3D [10]. Figure 1 inset shows $\log_{10}(\sigma)$ plotted against $T^{-1/2}$. Amorphous materials on the insulating side of the M-I transition show variable range hopping and strong Coulomb correlations; $\sigma(T)$ is thermally activated and would be linear on this plot. $\sigma(T)$ for a-YSi alloys is very similar to the much-studied a-NbSi and related alloys [10,11]; with a similar dependence of $\sigma(T)$ on composition x. In the temperature range above 50 K, Coulomb gap effects are negligible, and hence the observed linear $\sigma(T)$ is reasonable. At lower temperature, $\sigma(T)$ for Y2 and Y1 show $\sigma_0 + aT^{1/2}$ dependence; as $T \to 0$, σ remains finite indicating the presence of extended states at the Fermi level. $\sigma(T)$ for Y3 has an activated temperature dependence which goes to zero as $T \to 0$, indicating only localized states. The M-I transition in a-Y_xSi_{1-x} thus occurs for x between that of Y2 and Y3: 0.15 and 0.12.

Down to approximately 50 K, $\sigma(T)$ for a-Gd_xSi_{1-x} and a-Y_xSi_{1-x} alloys are nearly identical for comparable x (compare samples Y2 and G2 or Y3 and G4). However, below 50 K, $\sigma(T)$ for a-Gd-Si alloys decreases sharply below that of comparable composition a-Y-Si; $\sigma(T)$ for Y2 remains finite as $T \to 0$, while $\sigma(T)$ for G2 is activated, approaching zero as $T \to 0$. G2 is hence an insulator while Y2 is a metal. It appears, therefore, that at low temperatures Gd moments are capable of localizing electrons which would be in extended states in a-Y-Si alloys. The large effect of the Gd magnetic moments are evident also on the insulating side of the M-I transition. $\sigma(T)$ for G4 is comparable to Y3 above 50 K, while below, it is orders of magnitude less and $\log(\sigma)$ versus $T^{-1/2}$ exhibits a much steeper slope. $\sigma(T)$ for Y3, in fact, crosses $\sigma(T)$ for G3 at 6 K. Turning now to the Tb-based alloys, again at higher T, $\sigma(T)$ is comparable for all alloys of similar x. $\sigma(T)$ for sample T1 is comparable to Y2 and would appear to be on the metal side of the M-I transition. However, below approximately 30 K, $\sigma(T)$ for T1 drops sharply; it becomes activated and shows T1 to be an insulator. We note that the thermal activation coefficient (for variable range hopping) for T1 is less than that for G3 or even G2, suggesting that the carrier effective mass is less enhanced by Tb moments than by Gd.

The conductivity of all a-Gd-Si samples was found to increase strongly with applied magnetic field (negative MR) at temperatures up to approximately 50 K. Figure 1 inset shows this increase for G2. $\sigma(H)/\sigma(0)$ at various T for G3 is shown in Fig. 2 [$\sigma(0)$ is σ at $H = 0$ at temperature T]. We measured $\sigma(H)$ in increasing and decreasing H and for $\pm H$; $\sigma(H) = \sigma(-H)$ with no hysteresis. The field was applied in the sample plane. No detectable difference (to 1 part in 10^4) was observed for H parallel or perpendicular to the current. For samples G2-G4, $\sigma(H) - \sigma(0)$ is approximately proportional to H^2; for G1 it is closer to H. Sample G1 is also the only Gd-based sample which may still be on the metallic side of the M-I transition; although $\sigma(T)$ shows a steeper slope than either Y1 or Y2 below 50 K, it appears, at least down to 2 K, to have a finite value of σ_0. At the lowest temperature ($T = 2.4$ K), the field-induced increase of the conductivity

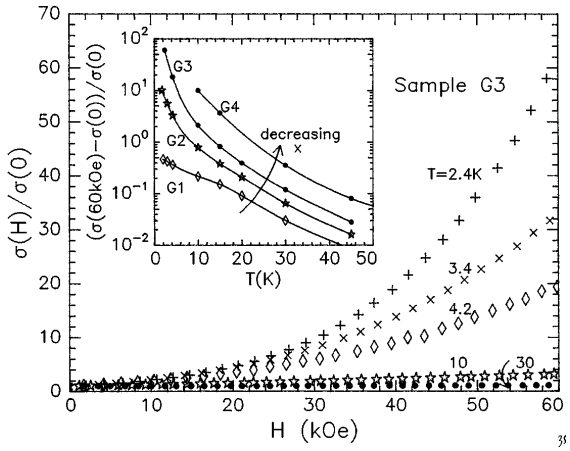

FIG. 2. Conductivity σ vs magnetic field for a-$Gd_{13}Si_{87}$ (G3) at different temperatures [normalized to $\sigma(0)$ = zero field value at each temperature]. Inset: σ at $H = 60$ kOe $- \sigma(0)$ normalized by $\sigma(0)$ (= −magnetoresistance) versus temperature for G1–G4.

is greatest, with $\sigma(60\ \text{kOe})/\sigma(0) = 60$ for sample G3, a significant negative MR. Figure 2 inset shows the MR ($[\sigma(60\ \text{kOe}) - \sigma(0)]/\sigma(0)$ is mathematically equal to the negative of the magnetoresistance, conventionally defined as $[\rho(60\ \text{kOe}) - \rho(0)]/\rho(60\ \text{kOe})$ where ρ is the resistivity) for all four Gd-based samples versus T; MR decreases with increasing T and disappears above 50 K, the temperature below which $\sigma(T)$ of a-Gd_xSi_{1-x} deviates from that of Y_xSi_{1-x}. Even larger negative magnetoresistance can presumably be obtained at lower temperatures and/or for samples of lower Gd concentrations. $\sigma(T)$ at $H = 60$ kOe for G2 is nearly metallic (see Fig. 1 inset) and approaches the value it would be expected to have based on comparable composition a-YSi data. The a-YSi samples show only a small, positive MR ($[\sigma(0) - \sigma(60\ \text{kOe})]/\sigma(0) \leq 0.4$ for Y1 and <0.01 for Y3).

Magnetic susceptibility has been measured for a-Gd_xSi_{1-x} and a-Y_xSi_{1-x}. We note that pure Gd metal is ferromagnetic with a Curie temperature of 293 K due to localized Gd moments interacting indirectly via conduction electrons; direct exchange interaction of even nearest neighbor Gd ions is negligible. In (nearly) insulating a-GdSi alloys, therefore, even with high Gd concentration, the Gd-Gd exchange interaction is expected to be weak. Figure 3 shows the induced magnetization M at $H = 100$ Oe for a-Gd-Si (sample G2) cooled in either zero field (ZFC) or in 100 Oe (FC). The two curves are identical, indicating no spin glass freezing down to at least 5 K. FC and ZFC data for 1000 Oe are similarly identical. The inset shows the inverse susceptibility $1/\chi = dH/dM$ at $H = 10^4$ Oe as a function of T for sample G3. For $T > 50$ K, χ follows a simple Curie law ($\chi = 0.06/T$), with no intercept, within error bars of that calculated for a sample containing 13 at.% Gd noninteracting moments. The data thus show no sign of any magnetic ordering: ferromagnetic, antiferromagnetic, or spin glass. χ for a-Y-Si is diamagnetic, temperature independent, and small compared to that of a-Gd-Si. Below 50 K, M for a-Gd-Si drops below that of isolated moments, indicating antiferromagnetic interactions. Figure 4 shows $M(H,T)$ below 50 K for sample G3. Samples displayed no measurable hysteresis [$M(H) = -M(-H)$]. At 4.2 K, in 60 kOe applied field, M for 13 at.% Gd ($J = 7/2$) isolated moments should be nearly saturated (at $\approx$300 emu/cm^3). The data are less than half of this and still show large susceptibility. The inset shows M versus normalized H/T. Data for different T do not collapse into a single curve, indicating that the sample is not simply paramagnetic (or superparamagnetic). The susceptibility is higher at lower temperatures, but not as high as it should be for a paramagnetic system: the $M(H/T)$ curve at 4.2 K is below the curve at 10 K, etc., consistent with antiferromagnetic interactions. Attempts to fit $M(H,T)$ with Brillouin functions (including an antiferromagnetic Θ) yield poor quality fits and strongly temperature-dependent quantities.

The suppression of the conductivity σ in zero field below approximately 50 K for a-Gd-Si and 30 K for a-Tb-Si relative to a-Y-Si and the large increase in σ with magnetic field is consistent with a strongly bound magnetic polaron picture. The exchange interaction between the carrier spin and the local moments causes the formation of magnetic polarons at temperatures below the polaron binding energy, increasing the effective mass, pushing the mobility edge E_c higher into the band, and converting some extended states into localized states. A magnetic field splits the electron band and aligns the Gd moments, reducing the effective mass and pushing E_c back down below the Fermi energy E_F. The polaron binding energy is proportional to the s-f exchange interaction energy which, in turn, is expected to be proportional to the de Gennes factor $(g-1)^2J(J+1)$ where g is the Lande factor and J the total angular momentum.

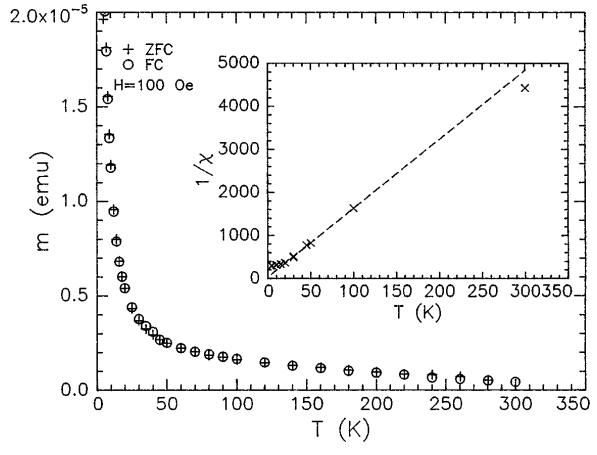

FIG. 3. Temperature dependence of induced magnetization at $H = 100$ Oe for sample G2 field cooled and zero field cooled. Inset: inverse differential susceptibility $1/\chi = dH/dM$ at $H = 10$ kOe vs T for G3. Dashed line: fit to Curie law $\chi = 0.06/T$.

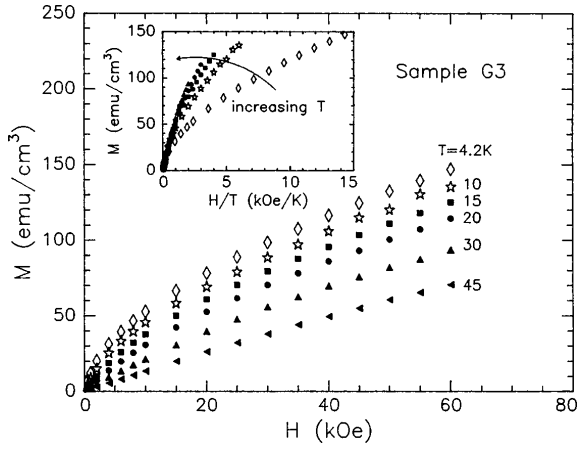

FIG. 4. $M(H)$ for G3 for $T < 50$ K. $M_{\text{sat}} \approx 300$ emu/cm^3. Inset: M vs field normalized by temperature (H/T).

50 K, the upper temperature of the effects described in this paper, is thus identified as the temperature at which the polaron binding energy $\approx k_B T$ for a-Gd-Si alloys, and 30 K for a-Tb-Si alloys, consistent with the 50% lower de Gennes factor of Tb than Gd. This binding energy is large, comparable to that of the most strongly bound p-type dilute magnetic semiconductors [6]. The large randomly oriented local magnetic anisotropy fields which act on the Tb ions (due to large orbital moment $L = 3$; Gd has $L = 0$) may also play a role in reducing the conduction electron/moment interaction and hence the effect of the Tb moments on the conductivity. The 50 K temperature may also be related to the energy associated with the Coulomb gap in amorphous materials; further theoretical analysis will be needed to separate out these effects.

Magnetic polarons are known to produce M which is not a simple function of (H/T) [3]. However, in the conventional crystalline systems, M for the polarons is *larger* at lower T for a given value of H/T, whereas here M is *smaller*. Also, in crystalline systems, the carrier concentration and hence the number of polarons is small, so that magnetization measurements are dominated by Mn^{2+} moments which have a direct exchange interaction not involving polarons. Here, the amorphous nature of these materials leads to a high concentration of carriers at the M-I transition. There are likely to be as many polarons as moments, hence the magnetization is dominated by the polarons. The interaction between conduction electron and local moment which leads to the polaron is almost certainly ferromagnetic; moreover, the interaction leads to a ferromagnetic alignment of the local moments *within* one polaron, independent of the sign of this interaction. The polarons, however, are likely to be overlapping with competing directions of polarization; antiferromagnetic interactions *between* the polarons causing a reduced susceptibility is thus perhaps not surprising. An intriguing remaining issue is the low temperature behavior of sample G1. Down to 2 K, it is still apparently metallic (with finite σ as $T \rightarrow 0$, and hence extended electron states) and yet shows signs of polarons (significant negative magnetoresistance). These would therefore be free magnetic polarons, a theoretically predicted but not yet observed entity [17].

In summary, we have studied the metal-insulator transition in amorphous rare earth-silicon alloys. The presence of magnetic moments completely changes the nature of electrical transport at low temperature, changing weakly localized metals into insulators. Below 50 K, a large negative magnetoresistance develops, reaching factors of 60 at 2 K and 60 kOe; it is likely that still larger values can be achieved. The conductivity, magnetoresistance, and magnetization data are consistent with the formation of magnetic polarons in this new dilute magnetic semiconductor, but its amorphous nature leads to striking and incompletely understood differences from the better-known crystalline systems.

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[17] In heavy fermion materials, there are extended state carriers with very large effective masses due to interactions with magnetic moments. These are not usually considered free magnetic polarons, however.