Large Magnetic Entropy in Giant Magnetoresistive Amorphous Gadolinium Silicon

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We report results of specific heat measurements from 5 to 70 K on thin films of the giant negative magnetoresistive spin glass a-Gd_xSi_{1-x} and its nonmagnetic analog a-Y_xSi_{1-x}. The specific heat of a-Gd_xSi_{1-x} samples is significantly greater than that of a-Y_xSi_{1-x} samples below 50 K. The resulting magnetic entropy of a-Gd_xSi_{1-x} exceeds the total calculated entropy available from Gd moments alone. We suggest that the additional entropy is provided by the interaction of barely localized electron spins with the Gd moments.

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A large and varied literature exists on the disorder- and Coulomb interaction-driven metal-insulator (MI) transition [1]. In a disordered electronic system the states with energy below the mobility edge, E_c, are localized within a localization length, ξ, which can be much greater than the interatomic spacing. The Fermi energy, E_F, can be changed by adding atoms that either donate or accept electrons. When $E_F < E_c$, ξ is finite, conductivity is zero at $T = 0$, and conduction can occur only by thermally activated hopping of electrons from one localized state to another. When $E_F > E_c$, ξ diverges and the resulting extended states allow metallic conduction. Therefore in theory the transition from insulator to metal occurs when E_F moves through E_c as the electronic content of the material is increased.

The effects of electron-electron interactions near the MI transition in transition metal doped amorphous semiconductors have proven especially interesting. The electron-electron interaction causes a gap in the single electron density of states centered around the Fermi energy which substantially modifies conductivity near the MI transition. Experimental evidence suggests that the transition is primarily driven by development of this Coulomb gap [2].

There are previously reported heat capacity studies of several disordered materials near their metal-insulator transitions: including Si:P [3–5], amorphous Mo_xGe_{1-x} [6], and disordered $C_{1-x}Cu_x$ and $Si_{1-x}Au_x$ [7]. These reports indicate a specific heat of the form $C = \gamma T + \beta T^3$ for compositions well on the metallic side of the transition. For samples near the MI transition, an additional contribution to the low temperature specific heat appears. This additional specific heat is evidence of electrons in localized states interacting as local spin $1/2$ magnetic moments. This localized electron contribution persists into the insulating side of the transition. The local moment nature of these localized electrons is elegantly demonstrated by the application of a magnetic field. The external field causes a Zeeman splitting of the localized electron spin state. This splitting is observed as a Schottky anomaly in the specific heat which shifts to higher temperature in larger fields [4,8].

The addition of magnetic ions (with local magnetic moments) to these disordered electron systems has dramatic consequences that are not yet well understood. Our previous work shows that the MI transition in a-Y_xSi_{1-x} occurs between $x = 0.12$ and $x = 0.14$, similar to that observed in a-Nb_xSi_{1-x} and related amorphous alloys [2]. However, in a-Gd_xSi_{1-x} with zero applied magnetic field the interaction of the $J = 7/2$ Gd moment with the conduction electrons dramatically decreases conductivity below 70 K, driving the MI transition to higher concentration [9]. This suggests that the electron-moment interaction enhances the localization of the conduction electrons. This electron-moment interaction also causes negative magnetoresistance which is measurable at 90 K and grows exponentially larger at lower temperatures, reaching 5 orders of magnitude at 1 K and becoming immeasurably large by 150 mK [10]. This magnetoresistance is evidence that alignment of the Gd moments by the applied field delocalizes the conduction electrons.

A qualitative description of the field-dependent electron localization in a-Gd_xSi_{1-x} is that in zero applied magnetic field the conduction electrons interact with randomly oriented Gd spins. Electrons require less energy to hop to states with spins aligned to their own moment. High magnetic fields partially align the Gd spins, increasing the probability that electrons find states with compatible spins which increases the conductivity of the material. This effect is qualitatively similar to a bound magnetic polaron, although the high ratio of conduction electrons to local moments in a-Gd_xSi_{1-x} (of the order of 1), the high concentration of conduction electrons ($\approx 10^{22}$ cm^{-3}), and the strong disorder of the amorphous state are serious complications [9,11]. Bound magnetic polarons have been shown to give enormous magnetoresistance in dilute magnetic semiconductors [12] and chalcogenide compounds such as EuO or vacancy-doped Gd_3S_4 [11,13]. Specific heat measurements of these systems between 0.5–3 K are dominated by effects of Heisenberg interaction and crystal field splittings of the local moments and see little, if any, effect from the polarons [14,15].

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Recent ac and dc SQUID magnetometry measurements of a-Gd_xSi_{1-x} indicate spin glass behavior with a composition-dependent freezing temperature, T_f, of about 6 K [16]. Magnetoresistance measurements have as yet shown no clear evidence of spin freezing, though the focus of these measurements has been on the high field region where the interactions which cause the spin freezing would most likely be dominated by the large applied field. It is unclear what role, if any, the spin glass state and the magnetic interactions that cause it play in the magnetotransport in a-Gd_xSi_{1-x}.

The characteristic feature of the specific heat of a spin glass is a broad peak at about $T = 1.4 \times T_f$ [17]. Typical crystalline spin glass systems develop 22%–33% of the total available entropy below T_f [18]. Some amorphous spin glass systems tend to develop more entropy below T_f but most of the entropy still remains until significantly higher temperature [19,20]. This indicates that in spin glasses a considerable amount of short range magnetic order persists well above the freezing temperature.

The experimental evidence described above suggests that the a-Gd_xSi_{1-x} system combines the physics of a disordered electron system with the physics of a spin glass, with dramatic properties not seen in either system. We turn to specific heat measurements of a-Gd_xSi_{1-x} and a-Y_xSi_{1-x} to further investigate the effect of gadolinium magnetic moments on the disordered electron system and to explore the nature of the spin glass state.

These amorphous samples are currently available for study only in thin film form. The mass of such a film is typically several micrograms. Because traditional calorimetry is not possible on such tiny samples, our group designs and manufactures microcalorimeters optimized for the measurement of microgram samples [21]. The most important element of these calorimeters is an 1800 Å thick amorphous silicon-nitride (a-SiN) membrane. This free-standing membrane is supported by a silicon frame and allows thermal isolation of the sample. The resulting specific heat of the various contributions to the background is typically less than half the specific heat of the 3300–4000 Å thick films. We estimate an approximately 5% uncertainty in measured specific heat due to possible systematic error in the sample area and addenda determination.

The samples were electron beam coevaporated from elemental targets at base pressures of 10^{-8} Torr or lower. Films were deposited onto a 2000 Å thick aluminum layer centered on the a-SiN membrane of each microcalorimeter. This Al layer ensures high thermal conductivity between the sample and the device and allows measurement of the background specific heat [21]. We determined the composition and density of the films by Rutherford backscattering (RBS). Resulting compositions are accurate to $\approx 1\%$. Similar valences and ionic radii allow us to consider yttrium as the nonmagnetic analog to the spin 7/2 gadolinium. Therefore the magnetic contribution to the specific heat may be obtained by subtracting the specific heats of a-Y_xSi_{1-x} and a-Gd_xSi_{1-x} films with the comparable values of x. We measured two a-Gd_xSi_{1-x} samples (Gd1 and Gd2) and two a-Y_xSi_{1-x} samples (Y1 and Y2). Sample Y1 is a metallic sample with $x = 0.16$, while Y2 is insulating with $x = 0.14$. Sample Gd1 has $x = 0.15$ and $T_f = 6$ K, while Gd2 has $x = 0.12$ and $T_f = 5.2$ K.

Figure 1 shows the specific heat vs temperature for all four samples from 5 to 70 K. The room temperature conductivity of Gd1 and Y1 and of Gd2 and Y2 are similar and agree with previously measured values [9]. The two a-Y_xSi_{1-x} curves are identical below approximately 18 K. The enhancement in the a-Gd_xSi_{1-x} curves relative to the a-Y_xSi_{1-x} curves is clear. Also note that the specific heats of samples with similar values of x converge as the temperature increases.

Figure 2 includes two plots of C/T vs T^2 which compare the data for the a-Gd_xSi_{1-x} and a-Y_xSi_{1-x} samples of similar composition up to $T = 60$ K. A standard specific heat curve for a metal, $C = \gamma T + \beta T^3$, appears as a straight line on such a plot. Both a-Y_xSi_{1-x} curves are approximately straight lines below 20 K (400 K^2). Data down to 5 K are not sufficient for accurate determination of γ, but do set an upper limit of $\gamma \approx 3 \frac{\text{mJ}}{\text{g-at. K}^2}$ with $\Theta_D \approx 300$ K. From 60 to 20 K the a-Gd_xSi_{1-x} curves are larger than the a-Y_xSi_{1-x} curves but have a similar shape. However, below 20 K we see a dramatic upturn in the a-Gd_xSi_{1-x} data.

Figure 3 shows the result of subtracting the a-Y_xSi_{1-x} data from the a-Gd_xSi_{1-x} data. This magnetic specific heat is plotted as C/T vs T. The area under these curves is the magnetic entropy developed over the measured temperature range,

$$\Delta S_{\text{mag}} = \int_{T_{\text{min}}}^{T_{\text{max}}} \frac{C_{\text{mag}}}{T}\, dT\,. \tag{1}$$

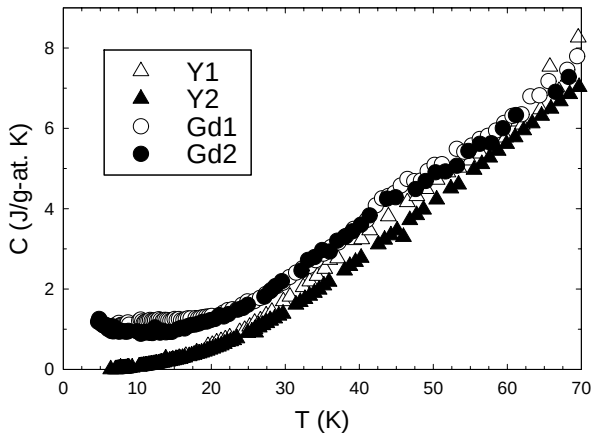

FIG. 1. Specific heat in zero magnetic field for a-Gd_xSi_{1-x} and a-Y_xSi_{1-x} samples. Note that samples with similar values of x (Y1 and Gd1, Y2 and Gd2) have similar C at higher T and that Gd samples have larger C than Y samples at low T.

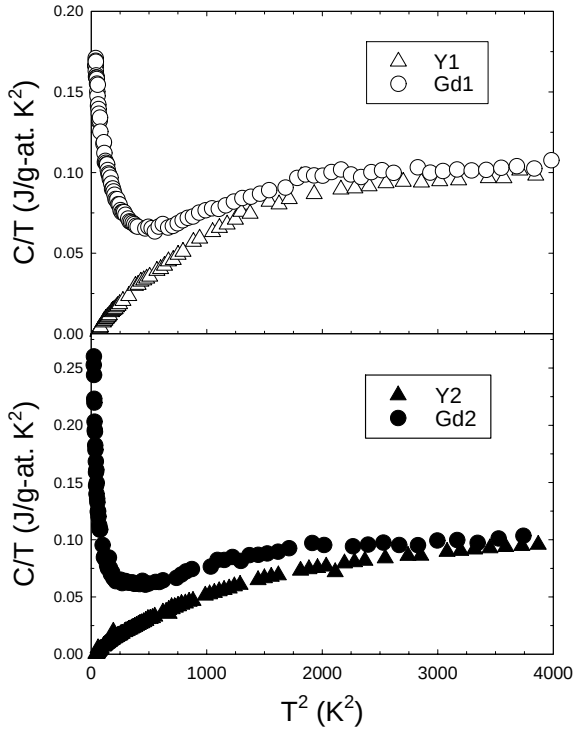

FIG. 2. C/T vs T^2 plotted for a-Gd_xSi_{1-x} and a-Y_xSi_{1-x}. As T decreases a-Gd_xSi_{1-x} samples show an upturn while the a-Y_xSi_{1-x} samples become approximately straight lines.

Sample Gd1 was measured from 6.1 to 69.4 K, with $\Delta S_{\mathrm{mag}} = 14.5 \frac{J}{\mathrm{mol(Gd)\,K}}$. Sample Gd2 was measured from 4.7 K to 68.3 K, with $\Delta S_{\mathrm{mag}} = 18.2 \frac{J}{\mathrm{mol(Gd)\,K}}$. The total magnetic entropy of a collection of Gd^{3+} ions ($S_{\mathrm{Gd}} = 7/2$) is $\Delta S = R \ln(2S_{\mathrm{Gd}} + 1) = 17.3 \frac{J}{\mathrm{mol(Gd)\,K}}$. ΔS_{mag} for both samples is thus comparable to or exceeds the total available from gadolinium moments and is only a lower limit. Data below T_{min} would clearly contribute significantly more entropy for any reasonable temperature dependence of C/T.

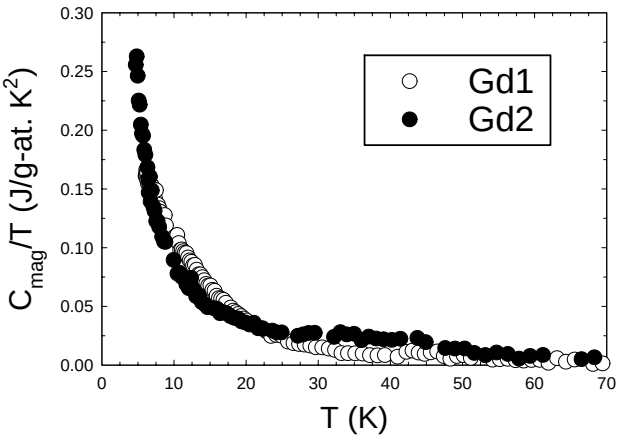

FIG. 3. C_{mag}/T vs T for the two Gd samples. The specific heat of nonmagnetic samples Y1 and Y2 are subtracted from the Gd1 and Gd2 curves to obtain C_{mag}. The area under the curves is the magnetic entropy in the system.

The inset in Fig. 4 is a plot of C_{mag} vs T for sample Gd2, with a cautious and unrealistically simple extrapolation shown as a dashed line. This extrapolation is made by drawing a straight line from the lowest temperature data point to $C = 0, T = 0$ (this would be a horizontal line on the C/T plot in Fig. 3). A plot of ΔS_{mag} vs T appears in the main part of Fig. 4. The dashed line represents the portion of the entropy contributed by the extrapolated C_{mag}. The entropy develops smoothly through the spin glass transition as is seen in canonical spin glass systems [17,18], and at 70 K is much larger than $R \ln(2S_{\mathrm{Gd}} + 1)$.

It is apparent that both a-Gd_xSi_{1-x} samples have magnetic contributions to the specific heat which remain up to 70 K. The magnetic specific heat of a-Gd_xSi_{1-x} is therefore measurable over a similar temperature range as the magnetoresistance. This indicates that the interactions responsible for the magnetic specific heat have the same energy scale as those which cause the magnetoresistance. Both of these effects are also larger for samples with smaller x [9]. The fact that the lower limit set on the total ΔS_{mag} is greater than $R \ln(2S_{\mathrm{Gd}} + 1)$ suggests that the gadolinium spin system is interacting with other spins that supply additional magnetic states. It seems a reasonable hypothesis that these additional spins are those of electrons in localized states interacting as local magnetic moments, as is observed in Si:P and other systems with nonmagnetic impurities. Comparison of these systems with previous results also suggests that localized electron spins in a-Y_xSi_{1-x} should contribute to the specific heat. Our data suggest that this contribution

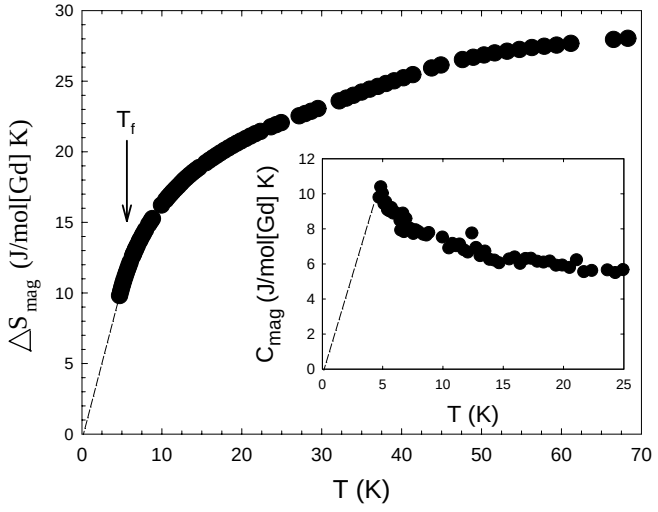

FIG. 4. Magnetic entropy developed vs T for sample Gd2. The dashed line is the entropy from the extrapolated C_{mag}. Inset: C_{mag} vs T for this sample with the extrapolation shown as a dashed line. $T_f = 5.2$ K for this sample, and $R \log(2S_{\mathrm{Gd}} + 1) = 17.3 \frac{J}{\mathrm{mol(Gd)\,K}}$.

is not significant above 5 K, which is consistent with reported measurements of Si:P [3–5].

The maximum magnetic entropy of a collection of Gd moments ($S_{\mathrm{Gd}} = 7/2$) and n localized electron moments per Gd ($s_e = 1/2$) is given by Eq. (2),

$$\Delta S_{\mathrm{mag}} = R[\ln(2S_{\mathrm{Gd}} + 1) + n\ln(2s_e + 1)]. \quad (2)$$

The total magnetic entropy of sample Gd2 determined from Fig. 4 is $\Delta S_{\mathrm{mag}} = 28\,\frac{J}{\mathrm{mol(Gd)\,K}}$. Application of Eq. (2) for this value gives $n = 1.9\,\frac{\mathrm{mol}(e^-)}{\mathrm{mol(Gd)}}$. This indicates that approximately two localized electron spins per gadolinium moment are cooperating in the magnetic interactions in this 12% Gd sample. We conclude that the spin glass state in a-$\mathrm{Gd}_x\mathrm{Si}_{1-x}$ is a disordered collection of misaligned gadolinium ion and localized electron magnetic moments.

In summary, we have used a-SiN membrane microcalorimeters to measure the specific heat of two a-$\mathrm{Gd}_x\mathrm{Si}_{1-x}$ and two a-$\mathrm{Y}_x\mathrm{Si}_{1-x}$ samples near the MI transition. In a-$\mathrm{Gd}_x\mathrm{Si}_{1-x}$ we observed an enhancement in specific heat which we believe is part of a broad peak centered just above the freezing temperature for these spin glasses. The associated magnetic entropy is greater than $R\ln(2S_{\mathrm{Gd}} + 1)$. We suggest that this large value of entropy is the result of interaction of Gd moments with localized electrons which behave as local spin $1/2$ magnetic moments. Measurements over a wider range of compositions, at lower and higher temperatures, and in high magnetic fields are underway in order to fully investigate this curious giant magnetorestive spin glass system.

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