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Discovery of Griffiths phase in itinerant magnetic semiconductor $Fe_{1-x}Co_xS_2$

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Abstract

Critical points that can be suppressed to zero temperature are interesting because quantum fluctuations have been shown to dramatically alter electron gas properties. Here, the metal formed by Co doping the paramagnetic insulator FeS_2, $Fe_{1-x}Co_xS_2$, is demonstrated to order ferromagnetically at $x > x_c = 0.01 \pm 0.005$ where we observe unusual transport, magnetic, and thermodynamic properties. We show that this magnetic semiconductor undergoes a percolative magnetic transition with distinct similarities to the Griffiths phase, including singular behavior at x_c and zero temperature.

The paramagnetic (PM) to ferromagnetic (FM) transition in magnetic semiconductors is a prominent topic in condensed matter physics because of efforts to discover materials useful for spintronics[1]. Magnetic semiconducting materials are considered essential for use as spin injectors in this nascent technology, yet single phase materials with Curie temperatures, T_C, well above 300 K that are compatible with today's technologies have not been identified. Problems encountered by efforts to increase T_C of Mn doped III-V semiconductors suggest that a deeper understanding is needed[2] and recent theoretical investigations have provided some progress[3, 4]. However, disorder and strong Coulomb interactions are both central issues in semiconductors with magnetic impurities and this makes modeling difficult. In Mn doped III-V semiconductors, Mn provides localized magnetic moments as well as a smaller number of hole carriers that couple the local moments via the RKKY interaction. Models based on a magnetic-polaron Hamiltonian with random arrangements of RKKY-coupled moments have predicted a zero-temperature, T, percolative transition at critical magnetic moment and charge carrier densities[3]. This critical point is governed by the competition between a nonmagnetic ground state and the magnetically ordered one and because of the doping induced disorder these materials are expected to display Griffiths phase singularities. Other than reports in doped $LaMnO_3$ and $LaCoO_4$ suggestive of Griffiths phase physics[5], there are no convincing demonstrations of Griffiths phases in magnetic semiconductors. A second class of materials predicted to display the Griffiths phase is the heavy fermion metals tuned by chemical substitution to be near a $T = 0$ quantum critical point (QCP)[6, 7, 8, 9]. In this case, rare clusters of strongly coupled magnetic moments are predicted to tunnel between magnetization states over classically forbidden regions resulting in non-analytic thermodynamic quantities at $T = 0$[8].

In this letter we report on a magnetic and semiconducting system which resembles (GaMn)As with the advantage that single crystals can easily be grown and characterized; Co doped iron pyrite or 'fools gold'. FeS_2 is an insulator with a ~ 1 eV band gap. It is isostructural to CoS_2, an itinerant ferromagnet with $T_C = 120$ K[10]. FeS_2 and CoS_2 form a continuous solid solution over the entire concentration range, x, in $Fe_{1-x}Co_xS_2$, where it is fully spin-polarized for $0.25 < x < 0.9$[11]. Previous magnetic susceptibility, χ, measurements found FM order at $T > 2$ K for $x \geq 0.05$[10]. Here, we discover metallic behavior for $x \geq 0.001$ with magnetic order at $x > x_c = 0.01 \pm 0.005$ consistent with earlier work. In addition, we observe an evolution from a partially Kondo screened metal at $x < x_c$ to

a ferromagnet characterized by a percolative transition for $x > x_c$. For $x \approx x_c$ we find a divergent Sommerfeld coefficient at low-T indicating non-Fermi liquid behavior along with a magnetic field H and T dependent magnetization M that suggests a critical transition to a Griffiths phase-like state. In metallic $Fe_{1-x}Co_xS_2$ we discover evidence for the unusual co-existence of magnetically ordered phases and partial Kondo screening of magnetic moments. In contrast the model[3] for (GaMn)As predicts a Griffiths phase under the conditions of localized electronic carriers where magnetic-polarons are important. In light of the inferred competition between the RKKY coupling and Kondo screening, as well as the divergent thermodynamic properties at x_c and $T \to 0$, this system may be more closely described by models of f-electron materials displaying quantum criticality[8].

Single crystals were synthesized by standard I_2 vapor techniques from high purity starting materials. Crystals were etched in HCl to remove any remaining flux and characterized by single crystal X-ray diffraction and energy dispersive X-ray microanalysis. The Co concentration of our crystals is consistent with the saturated M at 5 T and 1.8 K and is about 70% of the nominal concentration of our starting materials. M and χ were measured in a SQUID magnetometer for $T > 1.8$ K and a dilution refrigerator above 50 mK. The resistivity, ρ, and Hall effect were measured using four-probe lock-in techniques at 17 or 19Hz, with thin Pt wires attached using silver paste or silver epoxy. The specific heat was measured using a standard thermal relaxation method.

Our M measurements identify magnetically ordered states with T_Cs shown in Fig. 1a by way of a peak in the real part of the AC susceptibility, χ' (Fig. 2a), that is apparent in all of our samples with $x > x_C = 0.01 \pm 0.005$. We have checked that T_c signals a FM transition by comparing to a standard Arrott analysis of a dense set of $M(H,T)$ data for a few samples with $x \geq 0.05$[12]. A comparison is made in Fig. 1a between T_C and the Weiss temperature, θ_W, determined from the T-dependence of χ' at T's well above T_C, Fig. 2a, b. It is apparent that for $x > x_c$ a FM phase emerges and that T_C increases systematically with x. The scatter in these data is likely due to the variations in simultaneously grown crystals as is evident by the range of θ_W values for crystals of the same or similar x. In Fig. 1b the density of magnetic moments, n, determined from fits of the Curie-Weiss (CW) form (Fig. 2b) to $\chi(T)$ for $T >> T_C$ are displayed. We have assumed an effective moment of $J = 1/2$ and found n much larger than the high-H low-T saturated moment for $x > x_c$. This could indicate either a large Rhodes-Wohlfarth ratio as in itinerant ferromagnets (between 1.8 and

7 as compared to 3.5 in MnSi), or $J > 1/2$ local moments[13]. To investigate this we have measured the Hall effect to determine the carrier concentration, n_{Hall}, of our samples. n_{Hall} was determined at high-H to eliminate anomalous contributions. Fig. 1b shows that n_{Hall} ranges from 10 to 30% of x indicating that only a fraction of dopants donate electrons to a conducting band. Thus, it is likely that the difference between the Curie and saturated moments results from localized electrons with $J > 1/2$.

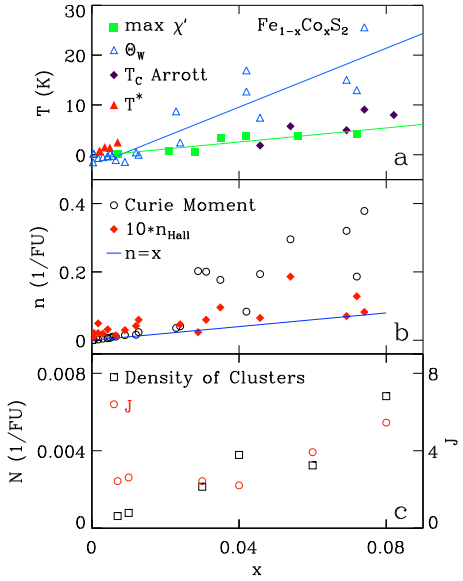

FIG. 1: (Color) Doping dependence (a) T_C from peak in AC susceptibility, χ' and from Arrott analysis [12], Weiss temperature, Θ_W, Kondo temperature, T^*. Lines are linear fits. (b) Curie moment per formula unit from Curie-Weiss analysis and Hall carrier density per formula unit, n_{Hall}, multiplied by ten. (c) Density, N, and J of spin clusters per formula unit.

To explore more fully the properties of $Fe_{1-x}Co_xS_2$, we have measured the specific heat, C, finding nearly identical C for all our crystals above 20 K since this region is dominated by phonons. However, at lower T's we find a contribution that grows with x shown in Fig. 2c. Samples that display a finite-T peak in χ also display a broad maximum in $C(T)/T$, albeit at a lower T. The idea of spin clusters suggested by $M(H,T)$ and $\chi'(T)$ was probed by comparing $C(T)$ and $\chi'(T)$ to determine J, the fluctuating moment above T_C. At $T > 2K$ we fit $C(T)$ by the sum of γT, a phonon term βT^3 ($\beta = 2.17 \times 10^{-5}$ J/mol K^4), and a Schottky term due to localized magnetic moments with $nJ(J+1)$ determined by fits of the CW form to $\chi'(T)$ (Fig. 2c). The best fit n and J are shown in Fig. 1c where we observe

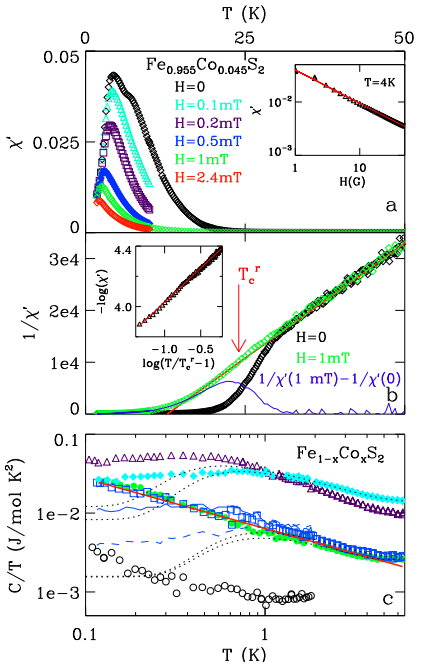

FIG. 2: (Color) Susceptibility and Specific heat. (a) Temperature T dependence of real part of AC susceptibility, χ'. Inset: $\chi'(H)$ at 4 K with power law fit (red line). (b) T dependence of $1/\chi'$ at 0 and 1 mT. Red line is fit of Curie-Weiss form at high-T. Inset: $1/\chi'(0)$ vs. reduced T, $(T/T_C^r - 1)$. Red line is $1/\chi' = a(T - T_C^r)^\delta$ with $\delta = 0.45 \pm 0.04$ and $T_C^r = 24 \pm 0.5$ K. (c) Specific heat, C divided by T, vs. T for $x = 0.002$ (circles), 0.005 (bullets), 0.007 at $H = 0$ (blue squares), $H = 1$ T (solid line), and $H = 3$ T (dashed line), 0.03 (FM) (triangles), and 0.045 (FM) (diamonds). Red line is fit of the form $aT^{-\alpha}$ with $\alpha = 0.69 \pm 0.05$, for $x = 0.005$. Dotted lines are fits of a Sommerfeld plus Schottky model to the data at $T > 2$ K.

that $J > 1/2$, $n < x$, and that both grow with x. Thus, spin clusters are consistent with both $C(T)$ above 2 K and $\chi'(T)$.

The magnetic transitions were explored in detail by measuring the low-H $\chi'(H,T)$ as in Fig. 2a, b. What is interesting is that both the T and magnitude of the χ' maxima are significantly suppressed by very small H. $\chi'(H)$ at 4 K is displayed in the inset to Fig. 2a where a power law form $\chi'(H) = bH^{-\beta}$ with $\beta = 0.62 \pm 0.03$ describes the data well. In addition to this extreme field sensitivity we have observed deviations from CW behavior. In Fig. 2b we plot $1/\chi'$ at DC fields of 0 and 1 mT with dramatic changes evident below 30 K. The 1 mT data follow a CW form, $\chi' \propto (T - \theta_W)^{-1}$ with $\theta_W = 13$ K for $T > \theta_W$. In contrast, the $H = 0$ data cannot be described by a CW form to much higher Ts and the

deviation is in the direction of *smaller* $1/\chi'$. The growth of χ' beyond the CW form is an indication of short range FM correlations [See e.g.[9]] as spin clusters imply larger χ'. In the inset of Fig. 2b we display a fit of the form $1/\chi' = (T - T_C^r)^\delta$ to the data, $T_C^r = 24 \pm 0.5$ K $\approx 2\Theta_W$ the critical T for the largest clusters and $\delta = 0.45 \pm 0.04$, suggestive of Griffiths phase formation.

Samples that remain PM down to our lowest T have a $C(T)/T$ that decreases with T and that can be accurately described by a $aT^{-\alpha}$ form with $\alpha < 1$. The red line in Fig. 2c represents this form with $\alpha = 0.69 \pm 0.03$. Application of $H > 0$ suppresses the low-T $C(T)/T$ of all of our samples and the PM samples display a $C(T)/T$ that resembles our FM samples. If we make the assumption that the conduction electron gas acts independently from a set of weakly interacting local moments, then $C(T)$ would be well fit by the sum of γT, βT^3 and a Schottky-like anomaly down to zero-T. At finite field, the anomaly would evolve into a Schottky peak. Although this description works well above 1 K, our low-T data does not conform to this simple picture. Interestingly, materials in proximity to metal-insulator transitions have a diverging $C(T)/T$ also described by a $T^{-\alpha}$ form. This is ascribed to the random position of local moments that are interacting antiferromagnetically leading to a singlet ground state[14]. However, since our samples are either FM or nearly FM, we do not consider this to be a likely explanation of our data. Instead, we suggest that the divergence of $C(T)/T$ for $x \sim x_c$ is indicative of Griffiths phase physics and/or to the proximity to a FM QCP. Magnetic fields or ordering return $C(T)/T$ to a Fermi liquid form at T's proportional to H or T_C.

The charge carrier transport properties of our crystals are presented in Fig. 3. While nominally pure FeS_2 displays insulating behavior, Co doping at a level of $x = 0.001$ is sufficient to create a metal (Fig. 3a). Larger x tends to increase n_{Hall} and decrease the resistivity, ρ. One interesting feature is that the T-dependence of ρ for $x \approx x_c$ closely follows a T^ξ form with $\xi = 1.6 \pm 0.1$ over a wide T-range similar to that found in MnSi near the critical pressure for suppression of ferromagnetism. It is also consistent with the spin fluctuation model of nearly FM metals where a $T^{5/3}$ dependence is predicted for itinerant magnets. However, as noted above, the magnetic moments are likely to result from localized electrons so it is not clear that this model is appropriate. Evidence for the importance of magnetic fluctuations[13, 15, 16] in determining $\rho(T)$ can be seen in Fig. 3b where the T-derivative of ρ normalized by $\rho_0 = \rho(4K)$, $d\rho/dT/\rho_0$, is displayed. The normalization

removes error in crystal geometry determination as well as changes due to variations in n_{Hall}. This quantity is strongly peaked near x_c. Thus, we observe a reduced power-law behavior of $\rho(T)$ along with an increased scattering rate over a wide T-range in proximity to the zero-T critical point for magnetism.

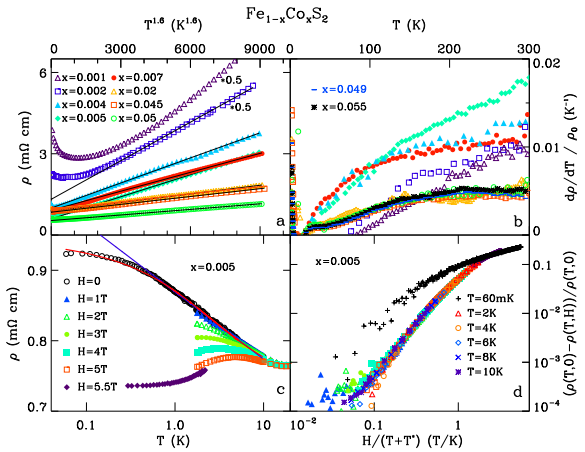

FIG. 3: (Color) Carrier Transport (a) Resistivity, ρ, vs. temperature to the 1.6 power, $T^{1.6}$, for a subset of our crystals. (b) T-derivative of ρ, $d\rho/dT$, normalized by $\rho(4\text{ K})$, ρ_0, vs T. (c) T dependence of ρ for $x = 0.005$ at magnetic fields, H, identified in the figure. Blue line is fit of a $\ln T$ behavior for $H = 0$ and red line is fit of Kondo theory[17]. (d) Scaling plot of magnetoresistance at Ts and Hs identified in (c) and (d).

In addition, a second contribution to ρ is apparent at $T < 20$ K as demonstrated for a PM sample in Fig. 3c. Here ρ increases with decreasing T in a manner that is well described by a logarithm over more than a decade in T with Kondo temperatures $T^* = 0.8$, 1.5, 1.4, and 2.5 K for x =0.002, 0.004, 0.005, and 0.007, Fig. 1a[17]. We have also measured a large negative magnetoresistance (MR) (Fig. 3c, d) that is identical in the transverse and longitudinal current directions. This indicates a spin, rather than orbital, mechanism for the MR consistent with a Kondo effect dominating $\rho(T, H)$. Furthermore, all of our T- and H-dependent data can be scaled by a single ion Kondo form; $\rho(T, H) - \rho(T, 0)/\rho(T, 0)$ scales as $H/(T + T^*)$ for $T \geq T^*$ as shown in Fig. 3d[18]. We conclude that a single energy scale, likely a Kondo coupling of conduction electrons with the local moments associated with the Co ions, determines the low-T ρ of $Fe_{1-x}Co_xS_2$.

The observation of power-law divergent C and χ' for $x \sim x_c$ with similar exponents suggests that a single physical mechanism describes both. The sensitivity to magnetic fields

indicates that there is weak coupling between clusters creating a fragile magnetic order for small x. In Fig. 4 we summarize the evolution of $Fe_{1-x}Co_xS_2$ from a strongly PM low-carrier-density metal to a FM with increasing x. In Fig. 4a, for $x < x_c$ and $T = 0$, the system consists of a small density of magnetic moments localized on the Co impurity sites. The electron carriers screen only a portion of these moments via the Kondo coupling evident in the carrier transport. As x increases to x_c in Fig. 4b there is a percolative transition at $T = 0$ and we observe a divergent $C(T)/T$ at low-T. Clearly for a magnetic transition to occur at $x \sim 0.01$ long range interactions between moments is necessary. Thus, a percolative transition occurs at $x_c << 0.2$ required for a face-centered-cubic lattice with short range interactions[19]. At still larger x, Figs. 4c and d, the FM state is complete at low-T. For Ts above the critical point the system is dominated by super-paramagnetic regions where magnetic moments are correlated, but long range ordering is not apparent. The system consists of weakly coupled clusters that are easily modified by small H. In addition, the clusters have a finite probability to tunnel to nearly degenerate M states.

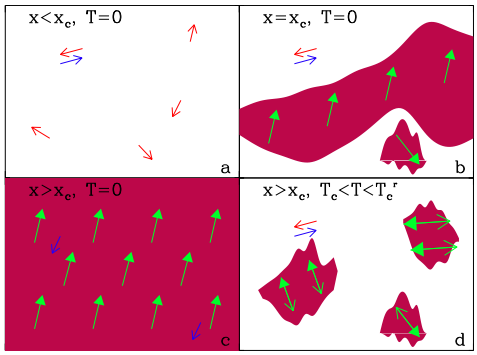

FIG. 4: (Color) Evolution. (a) Low Co concentration ($x < x_c$) with disperse local moments (red arrows) and low density of itinerant electrons (blue arrows). Electrons partially screen moments via Kondo coupling. (b) At $x = x_c$ a percolative magnetic transition occurs at $T = 0$. Ordered regions are red with magnetization, M, direction green. (c) Larger x, $x > x_c$, fully ordered at $T = 0$ with large M domains. (d) $T > T_C$, clusters of strongly coupled spins form for $T < T_C^r$. Tunneling of clusters indicated by the double-ended green arrows.

These features are described by Griffiths phase models [7, 8] where disorder is sufficient to cause clusters of localized short lived magnetic order at T's above the global ordering temperature. As the system is cooled toward T_C, these clusters grow and display switching

of M via tunneling. The consequence of this model is a power-law form, $1/(T - T_C^r)^{1-\lambda}$, with $\lambda < 1$, of the thermodynamic quantities above T_C that can be suppressed with small to moderate magnetic fields. For $Fe_{1-x}Co_xS_2$ $0.30 < \lambda < 0.55$. Griffiths phase physics has been suggested to explain the non-Fermi liquid behavior of heavy fermion antiferromagnets with Néel temperatures driven to zero by chemical substitution. However, Millis *et al.*[20] point out that the coupling of magnetic clusters to conduction electrons will suppress tunneling, removing the non-Fermi liquid response in the model. In contrast to well developed conductors, our materials are nascent metals with poor electrical screening formed by doping an insulator. Although $Fe_{1-x}Co_xS_2$ does not appear to be described by a magnetic-polaron Hamiltonian as in Ref. [3], our data suggest that Griffiths phase anomalies, likely influenced by Kondo screening, are in fact observable in magnetic semiconductors. The result is singular behavior at $T = 0$ similar to models of Griffiths phases in f-electron antiferromagnets.

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