Electronic Griffiths Phase in the Te-Doped Semiconductor FeSb$_2$

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We report on the emergence of an electronic Griffiths phase in the doped semiconductor FeSb$_2$, predicted for disordered insulators with random localized moments in the vicinity of a metal-insulator transition. Magnetic, transport, and thermodynamic measurements of Fe(Sb$_{1-x}$Te$_x$)$_2$ single crystals show signatures of disorder-induced non-Fermi liquid behavior and a Wilson ratio expected for strong electronic correlations. The electronic Griffiths phase states are found on the metallic boundary between the insulating state ($x = 0$) and a long-range albeit weak magnetic order ($x \geq 0.075$).

The coupling of disorder to strong correlations remains one of the most interesting frontiers in physics [1]. One of the key issues is the mechanism of disorder-induced quantum Griffiths phases in metals. Magnetic quantum Griffiths phases (MGP) found in insulators host rare magnetic clusters with large susceptibilities [2]. They arise in the proximity to magnetic phase transitions and have been advocated recently to be the correct framework for the understanding of the non-Fermi-liquid behavior even in metallic heavy-fermion compounds [3,4]. Yet, it was pointed out that in such systems quantum tunneling will be suppressed, leading to superparamagnetic classical instead of quantum Griffiths behavior [5,6]. The quantum Griffiths singularities can only be observed in the temperature region $T^* < T < T_F$, where T_F is the Fermi temperature, whereas below T^*, the clusters are frozen and electronic heat capacity $\gamma \sim \ln T$ and magnetic susceptibility $\chi \sim 1/T$ [4,7]. However, the crossover temperature to the paramagnetic phase T^* and the temperature window where Griffiths phases can be observed in heavy-fermion metals remain controversial [8–10]. On the other hand, electronic Griffiths phases (EGPs) in metals are found close to a disorder-driven Mott-Anderson transition where the number of unscreened local spins rises with the increase in disorder strength [11–13]. Nevertheless, the Kondo or magnetic materials where EGP has been unambiguously observed remain elusive due to the stability of competing ground states such as MGP or Kondo-cluster-glass [14–17].

FeSb$_2$ is an example of a nearly magnetic (Kondo insulatorlike) semiconductor, similar to FeSi [18–20]. It exhibits a large Seebeck coefficient S and the highest known thermoelectric power factor $S^2\sigma$ [21]. The electronic system in Fe(Sb$_{1-x}$Te$_x$)$_2$ shows a high sensitivity to substitutions. A metal-insulator transition (MIT) is induced at the critical concentration $x_c = 0.001$ and a region of canted antiferromagnetism is observed for $0.1 \leq x \leq 0.4$ with an intermediate ferromagnetic phase for $x = 0.2$ [22].

We now focus on the paramagnetic metallic region in the vicinity of the MIT for $x_c < x < 0.1$ where we note that a canted antiferromagnetic state is induced already at $x = 0.075$. Below that concentration, both thermodynamics and electrical transport are consistent with the EGP predicted in disordered heavy-fermion metals.

Single crystals of Fe(Sb$_{1-x}$Te$_x$)$_2$ were prepared as described previously [22]. They were oriented using a Laue camera and polished along three principal crystal axes for four-probe resistivity measurements. Magnetic, thermal, and transport measurements were carried out in a Quantum Design MPMS-5, ^{3}He inserts of PPMS-9, PPMS-14, and in an Oxford ^{3}He insert equipped with an 18 Tesla magnet at NHMFL, Tallahassee.

The low-temperature heat capacity of Fe(Sb$_{1-x}$Te$_x$)$_2$ above 0.7 K is best described with a $C(T)/T = \beta T^2 + \delta T^4 + cT^{-1+\lambda_C}$ [Fig. 1(a)]. The first two terms are due to harmonic and anharmonic phonon contributions [23]. The last term is a disorder driven non-Fermi-liquid (NFL) electronic term with $\lambda_C < 1$, predicted for Griffiths phases in disordered paramagnetic metals [24]. Fits to our data (solid lines) are excellent down to 0.7 K and the fitted parameters are given in Table I. The phonon contribution remains nearly the same, as would be expected for such a low doping level. The difference in heat capacity below 10 K stems mainly from the electronic part. Below 0.7 K, $C(T)/T$ shows additional upturn. This cannot be described by a paramagnon model for spin fluctuations, $C(T)/T = \gamma_{\text{SF}} + \delta_{\text{SF}}T^2 \ln T/T_{\text{SF}}$ [25]. Moreover, the contribution due to spin fluctuations is generally sensitive to the magnetic field; i.e., such paramagnon fluctuations would be suppressed by the magnetic field and this is not observed. A power law, $C(T)/T \sim aT^{-3}$, (dashed line, Fig. 1) represents well the low-temperature heat-capacity increase below 0.7 K, suggesting a nuclear Schottky anomaly or a low lying magnetic ground state below 0.4 K similar to YbRh$_2$Si$_2$ or U$_x$Y$_{1-x}$Pd$_3$ [26,27].
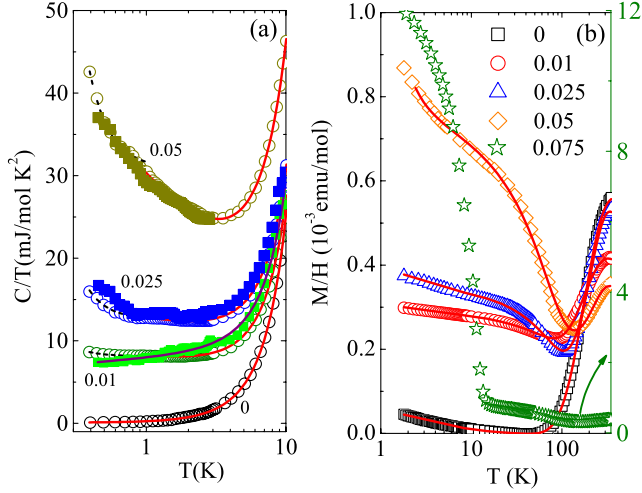
FIG. 1 (color online). (a) C_p/T versus T for $x \leq 0.05$ in $Fe(Sb_{1-x}Te_x)_2$. The $C(T) \sim T^{-2}$ dependence is represented by the dashed lines below 0.7 K. Closed symbols show data taken in $\mu_0 H = 9$ T. Solid lines are fits to the formula given in the text. (b) Polycrystalline average of the magnetic susceptibility of $Fe(Sb_{1-x}Te_x)$ as a function of temperature for $0 \leq x \leq 0.075$ in 1 kOe magnetic field. Solid lines are the best fits to the formula given in the text.

Deviation from the Fermi liquid behavior is often found near a magnetic instability. The local density approximation with on-site Coulomb repulsion correction (LDA + U) calculations have revealed that $FeSb_2$ is in the proximity to a magnetic ground state with an on-site Coulomb repulsion $U = 2.6$ eV [20]. As Te substitutes Sb in the lattice, the thermally activated susceptibility of $FeSb_2$ diminishes, accompanied by an increasing low-temperature tail [Fig. 1(b)]. The $\chi(T)$ data can be well described by

$$\chi(T) = \chi_{NB}(T) + \frac{C_1}{T - \Theta_1} + aT^{-1+\lambda_\chi}.$$

The first two terms are the narrow-band-gap [18,22,28] susceptibility $\chi_{NB}(T)$ (as described in Ref. [22]) and the impurity-related Curie-Weiss term whose Curie constant C_1 corresponds to the moment μ_1 ($C_1 = \mu_1^2/8$) and Weiss temperature θ_1. As small amounts of Te enter the lattice, the gap Δ and impurity moment related parameters μ_1 and θ_1 are approximately constant whereas the bandwidth W increases considerably (Table I) [22]. The additional term,

$\chi(T) \sim T^{-1+\lambda_\chi}$ corresponds to the magnetic susceptibility expected for Griffiths phases [24]. At $x = 0.075$, we observe signatures for magnetic order below 12 K, similar to what was earlier observed for $x = 0.1$ [22]. Fitted parameters are listed in Table I.

Above the critical concentration ($x_c = 0.001$), the anisotropy is greatly reduced and the electrical resistivity is metallic for current applied along all 3 axes of the orthorhombic unit cell [Figs. 2(a)–2(c)] for $0.01 \leq x \leq 0.05$ [22]. This is in line with isotropic $\chi(T)$ in the same temperature region. For $0.075 \leq x \leq 0.2$, $\rho(T)$ is similar to $x = 0.1$ and $x = 0.2$ [22] and the semiconducting gaps from fits to the activated behavior are less than 1 K, suggesting that the ground state is semimetallic. The metallic $\rho(T)$ in the paramagnetic region ($0.01 \leq x \leq 0.05$) is characterized by a power-law temperature dependence $\rho \sim T^n$, where ($1 \leq n \leq 2$) for current applied along all 3 principal axes of the orthorhombic structure. The exponent n diminishes as more Te enters the lattice [Fig. 2(d)] and the electronic system is tuned from Kondo-insulatorlike nonmagnetic towards a weak magnetic ground state. However, even a modest magnetic field $\mu_0 H = 2$ T induces a Fermi-liquidlike resistivity $\rho \sim AT^2$ in a crystal with $x = 0.01$ [Fig. 3(a)]. The low-temperature resistivity is quadratic up to 18 T and we plot the coefficient A as a function of field in Fig. 3(b). As opposed to the divergence in A near a magnetic-field-induced quantum critical point, we observe only modest increase [29,30]. Examination of C/T data in $\mu_0 H = 9$ T shows a field independence for $x = 0.05$ and $x = 0.025$ [31], whereas for $x = 0.01$, there is also a small change in the fitting parameters β, δ, and c: ($\beta = 0.12(2)$, $\delta = 0.0008(2)$, $c = 7.9(1)$, $\gamma_0 = 7.4(2)$ mJ/mol K^2). However, for $x = 0.01$, $\lambda = 1.07(2)$, suggesting that the electronic system has been tuned away from the NFL behavior (λ_C, $\lambda_\chi < 1$) [13].

The zero-temperature electronic heat capacity γ_0 (Table I) was obtained by extrapolation of the curves in Fig. 1 to $T = 0$ with the upturn below 0.7 K subtracted. The γ_0 values increase monotonically from nearly zero for $x = 0$ to $\gamma = 39.2$ mJ/mol K^2 for $x = 0.05$. By making a coarse estimate that the Fermi surface in $Fe(Sb_{1-x}Te_x)_2$ is spherical and counting one itinerant electron per Te, we may estimate the electron-mass enhancement due to electronic correlations. The quasiparticle effective masses are moderately renormalized and reach a maximum of 56 m_e for

TABLE I. Fitting parameters of the magnetic susceptibility and heat capacity. W is the bandwidth and $N(E_F)$ is in unit of state/eV F.U. $FeSb_2$ has negligible γ_0. The impurity terms μ_1 and θ_1 are observed already in the pure material and remain similar in the entire investigated doping range.

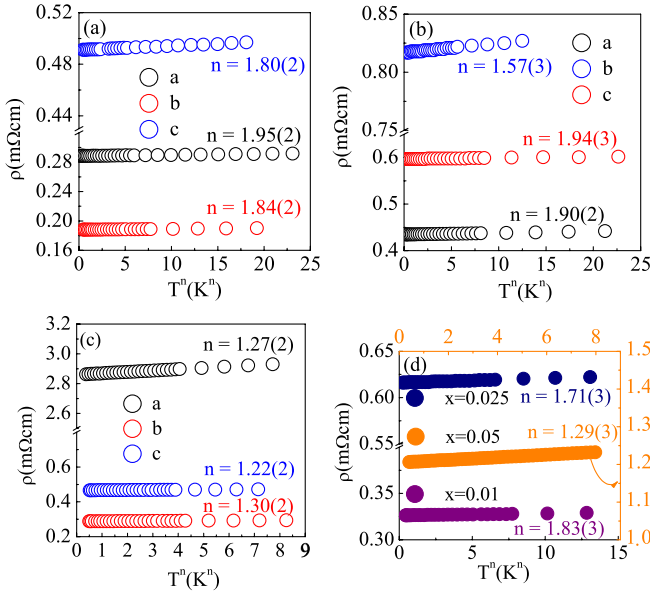| x	$\Delta(K)$	$W(K)$	$\mu_1(\mu_B)$	Θ_1 (K)	a	λ_χ	λ_C	γ_0 (mJ/mol K^2)	β	δ	c	$N(E_F)$	$m^*(m_e)$	R_W
0	425(9)	310(8)	0.030(2)	0.8(2)				$\sim$0	0.16(1)	0.0008(9)		0.0039(4)		
0.01	436(7)	451(6)	0.035(3)	1.6(3)	856(9)	0.86(3)	0.91(7)	8.7(2)	0.12(7)	0.0007(6)	8.1(8)	3.7(2)	21(1)	2.7
0.025	448(4)	525(9)	0.036(1)	3.7(3)	1117(3)	0.84(2)	0.87(5)	13.9(3)	0.15(9)	0.0005(9)	12.8(9)	5.9(3)	25(1)	2.1
0.05	453(5)	525(9)	0.039(2)	1.8(5)	1078(9)	0.89(4)	0.72(3)	39.2(3)	0.27(3)	0.0002(1)	30.2(8)	16.7(4)	56(2)	2.3

FIG. 2 (color online).   (a)–(c) Anisotropic $\rho(T)$ for $x = 0.01$,
0.025, and 0.05 in $Fe(Sb_{1-x}Te_x)_2$. (d) Polycrystalline resistivity
of samples as a function of T^n for different Te concentrations.

$x = 0.05$, reminiscent of the heavy-fermion state induced in
$FeSi_{1-x}Al_x$ (Table I) [32]. This is in agreement with the
Wilson ratio $[R_W = 4\pi^2 k_B^2/(g3\mu_B^2)(\chi/\gamma)]$ which is a stan-
dard measure of electronic correlations in metals (Table I)
[33]. R_W is expected to be unity for a free electron gas and it
is about 2 if strong electronic correlations are present.

In metals, conductivity arises due to electron diffusion
and the Seebeck coefficient can be described as $S = \frac{\pi^2 k_B^2}{2e} \times$
$\frac{T}{T_F} = \frac{\gamma T}{ne}$, where γ is given by $\gamma = \frac{C_{el}}{T} = \frac{\pi^2}{2} \frac{nk_B}{T_F}$, with C_{el} the
electronic specific heat and n the carrier density [34]. The
correlation between $\frac{S}{T}$ and γ in the zero-temperature limit
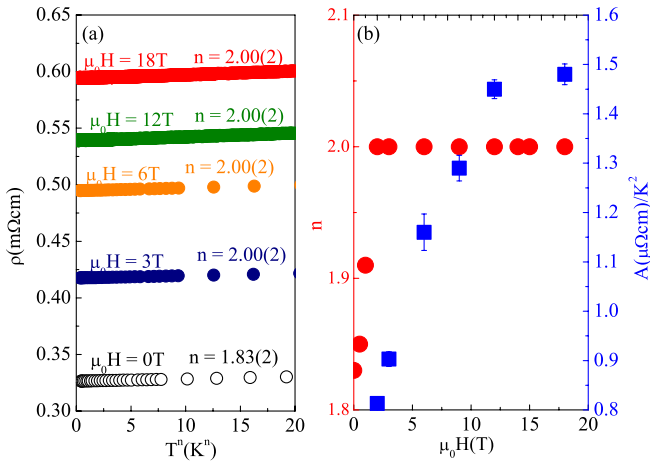gives a scaling in metals as $q = \frac{SN_{av}e}{T\gamma} = \pm 1$ where N_{av} is

Avogadro's constant [35]. This quasiuniversal ratio is valid
if the relevant scattering arises from impurities but not from
the mutual scattering of quasiparticles [36]. In order to shed
more light onto the nature of correlations in our crystals, we
performed Seebeck-coefficient measurements at ~2 K.
Figure 4 shows the power-law dependence of $\frac{S}{T}$ on γ for
$Fe(Sb_{1-x}Te_x)_2$ with $x = 0$, 0.01, 0.025, and 0.05. The solid
line is the power-law fit to the data for metallic samples
(excluding $x = 0$). $FeSb_2$ ($x = 0$) is a Kondo-insulatorlike
narrow-gap semiconductor with extremely low carrier den-
sity. Hence, a very large magnitude of $q \sim 663$ correspond-
ing to a small but finite carrier density of 0.0015 electrons
per unit cell ($\sim 1.25 \times 10^{19}$ cm^{-3}) is obtained. A similar
effect was discovered in CeNiSn [35]. The doped samples
exhibit a power-law dependence of S/T on γ with an
exponent $\sim -1.7 \pm 0.4$ (Fig. 4), contradicting the quasiu-
niversal ratio in a Fermi liquid and implying very strong
electron-electron scattering and intersite magnetic correla-
tions. The power-law dependence of S/T on γ is expected
for metals near a MIT, as seen in $FeSi_{1-x}Al_x$ [37]. This
shows that the proximity to a MIT has substantial effects on
thermodynamics and, as we discuss below, on the mecha-
nism of the Griffiths phase.

The increase of disorder from a clean insulator will create
states in the gap in the EGP scenario, increasing the density of
states at the Fermi level until the gap is decreased to zero at
the MIT, giving rise to metallic states with disordered local
moments [12]. Even more disorder tunes the system again to
an insulating state due to localization effects [11,38].
Whereas the EGP formalism has been developed for disor-
dered Kondo systems, we note that the Hubbard U in the
strongly correlated electronic system of $FeSb_2$ is reduced
from the values common in lanthanide based heavy fermions
and Fe moments are not as localized [39–41]. Nevertheless,
the EGP predictions are in qualitative agreement with the
$Fe(Sb_{1-x}Te_x)_2$ phase diagram [22] and with the values we

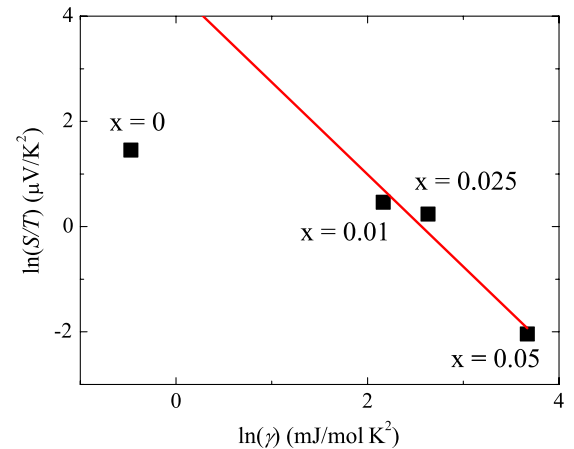FIG. 3 (color online).   (a) Low temperature resistivity of
$Fe(Sb_{1-x}Te_x)_2$ for $x = 0.01$ plotted vs T^n in magnetic fields
up to $\mu_0 H = 18$ T. Exponent n from (a) and coefficient A in
$\rho = \rho_0 + AT^2$ as a function of magnetic field (d).

FIG. 4 (color online).   Power-law dependence of $\frac{S}{T}$ on γ for
$Fe(Sb_{1-x}Te_x)_2$. The solid line is the fit to the data (excluding
$x = 0$ point) with an exponent of $-1.7(4)$. The direction of heat
current transport was along the crystallographic c axis.

obtained in Table I. Metallic conductivity with a characteristic non-Fermi-liquid temperature dependence for $x = 0.01$, 0.025, and 0.05 arises due to a bandwidth increase with Te substitution. The non-Fermi-liquid exponent n in $\rho(T) \sim T^n$ (Fig. 2) is close to $n = 3/2$, expected in metallic glasses [42] as well as for disordered heavy-fermion metals near an antiferromagnetic quantum critical point [43]. We note that the resistivity should evolve from $\rho \sim T^1$ to $\rho \sim T^{3/2}$ as the disorder is increased near a magnetic quantum critical point [43], in contrast to the decreasing n with x in $Fe(Sb_{1-x}Te_x)_2$ [Fig. 2(d)]. In addition, large values of the Wilson ratio ($R_W \sim 20$–700) are expected in MGP or in cluster-glass phases due to the existence of large-moment magnetically ordered clusters with a Griffiths exponent $\lambda \to 0$ as the system is tuned to the magnetic phase [10,17,44]. This is in contrast to our observations where $R_W \sim 2$ and $\lambda \sim (0.8$–$0.9)$ (Table I). This discussion suggests a considerable influence of the charge channel (MIT) in the underlying microscopic mechanism of the Griffiths phase. Spin fluctuations near a glassy state in the EGP are expected to lead to a marginal Fermi-liquid behavior [45] and a nearly logarithmic divergence of γ and χ ($\lambda \to 1$), all in much closer agreement with the parameters obtained here (Table I).

In summary, we have shown that a small amount of Te doping in $Fe(Sb_{1-x}Te_x)_2$ single-crystal alloys (up to $x \leq 0.05$) results in the non-Fermi-liquid Griffiths metallic state that primarily has an electronic origin. This highlights the importance of fluctuations in the conduction-electron local density of states. The EGP theoretical framework rests on the power-law distribution of the energy scale for the spin fluctuations, not necessarily of Kondo origin [1]. However, similarity with disordered Kondo or Anderson lattices is still significant since NFL divergences appear at rather weak randomness ($x = 0.01$) and are magnetic field tuned to a Fermi liquid.

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