Metal-Insulator Transitions in the Kondo Insulator FeSi and Classic Semiconductors Are Similar

J. F. DiTusa,[1] K. Friemelt,[2] E. Bucher,[2] G. Aeppli,[3] and A. P. Ramirez[4]
[1]*Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803*
[2]*Fakultat für Physik, University of Konstanz, Postfach 5560, D-78434 Konstanz, Germany*
[3]*NEC, 4 Independence Way, Princeton, New Jersey 08540*
[4]*Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974*
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We have observed the metal-insulator transition in the strongly correlated insulator FeSi with the chemical substitution of Al at the Si site. The magnetic susceptibility, heat capacity, and field-dependent conductivity are measured for Al concentrations ranging from 0 to 0.08. For concentrations ≥ 0.01 we find metallic properties quantitatively similar to those measured in Si:P with the exception of a greatly enhanced quasiparticle mass. Below 2 K the temperature and field-dependent conductivity can be completely described by the theory of disordered Fermi liquids. [S0031-9007(97)02878-0]

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Lightly doped semiconductors and insulators lie at the heart of both microelectronic technologies and modern condensed matter physics. The most prevalent and best characterized of these systems continues to be carrier doped Si, a simple band insulator. The electronic and magnetic properties of carrier doped Si near the metal-insulator (MI) transition have been the subject of a large and growing literature where it is well established that these properties are determined by the disorder and electron-electron (*e-e*) interactions [1]. Investigations of the MI transition where the Coulomb interaction is more significant, such as the Mott-Hubbard systems $V_{2-x}O_3$, $La_{2-x}Sr_xCuO_4$, and $Ni(S, Se)_2$ [2] have revealed interesting magnetic and superconducting ground states. A key feature separating Si from the Mott-Hubbard insulators is that whereas Si is an insulator by virtue of its band structure, the latter are band metals which are insulating because of Coulomb interactions. Recently, another class of insulators has emerged, namely, insulators correctly predicted by band theory to be insulating [3] yet which also display optical and magnetic properties not understandable using band theory [4]. The extent to which such insulators, frequently labeled as "strongly correlated" or "Kondo" insulators, are fundamentally different from conventional insulators and semiconductors is unclear [5]. In the present Letter, we present strong evidence that one popular strongly correlated insulator, FeSi, is actually a renormalized version of Si in the same sense that the heavy fermion metals are Fermi liquids with vastly renormalized band masses. More specifically, we show that chemical doping by Al substitution onto the Si sites yields a metal which is very similar to Si doped just beyond its metal-insulator transition. The only obvious distinction is that in the metal derived from FeSi, the quasiparticle mass is greatly enhanced relative to that in doped Si. Thus we have carrier doped a strongly correlated insulator through the MI transition to obtain a disordered Fermi liquid ground state with a large carrier mass—a heavy fermion metal. Our data represent convincing support for the proposition that while heavy fermion metals and strongly correlated insulators have peculiar temperature-dependent properties, their ground states remain the well understood Fermi liquids and band insulators.

The samples were either polycrystalline pellets or small bars cut from large Czochralski grown single crystals [6]. Polycrystalline samples were produced from high purity starting materials by arc melting in an argon atmosphere. To improve sample homogeneity they were annealed for one week at 1000 °C in evacuated quartz ampoules. Powder x-ray spectra showed samples to be single phase with a lattice constant linearly dependent on Al concentration as can be seen in Fig. 1(a). The linearity demonstrates that Al successfully replaces Si in the concentration range investigated. Energy dispersive x-ray microanalysis yielded results consistent with the nominal Al concentration. The electrical conductivity was measured on rectangular samples with thin Pt wires attached to four contacts made with silver paste. We collected transverse magnetoconductance (MC) and Hall effect measurements at 19 Hz using lock-in techniques. Finally, magnetic susceptibility (χ) measurements were made between 1.7 and 400 K in fields of 0.1 T in a SQUID magnetometer and the specific heat was established using a standard semiadiabatic heat pulse technique.

The defining feature of an MI transition is the appearance of conduction at low temperatures. The carriers manifest themselves in a variety of standard quantities, including not only the temperature-dependent conductivity itself, but also the Hall effect, Pauli susceptibility, specific heat, and MC. Together, these quantities define the most fundamental parameters, namely, the carrier density (n), sign (hole or electron), effective mass (m^*), elastic scattering length, and *e-e* interaction strength, of the nascent metal. Arguably the most fundamental are the carrier density and sign. Our Hall effect data demonstrate that Al doping onto the Si sites in FeSi does what is naively

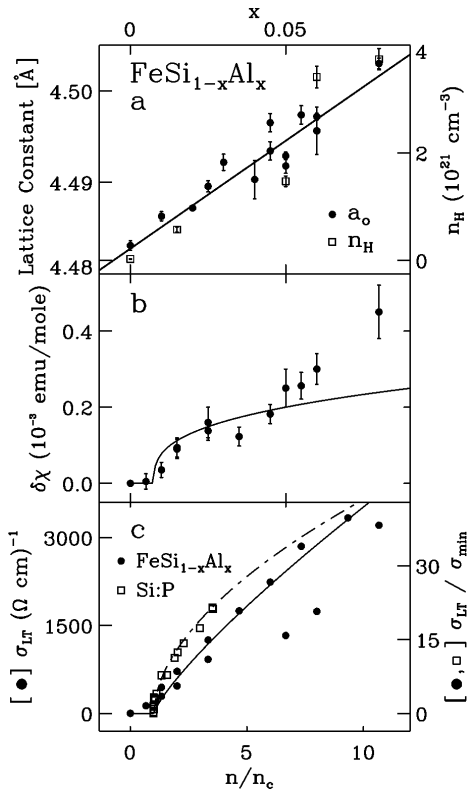

FIG. 1. (a) Lattice constant of $FeSi_{1-x}Al_x$ vs nominal Al concentration (• left axis) and nominal carrier concentration from measurements of Hall voltage (□ right axis). (b) change in χ with x, taken as the average χ between 80 and 120 K. Solid line is best fit to the form $\delta\chi = c(n - n_c)^{1/3}$ with $c = 1.44\mu_B^2\nu'^{2/3}m^*/\hbar^2\pi^{4/3}$, where ν' is the valley degeneracy taken as 8 [3]. The best fit corresponds to a carrier mass of $14m_e$. (c) The low temperature conductivity vs nominal Al concentration (•). Si:P data (□ left axis only) [16,18] is plotted for comparison with $n_c = 3.74 \times 10^{18}$. $\sigma_{\min}$ (left axis) is the Mott minimum conductivity defined as $\sigma_{\min} = 0.05e^2/\hbar d_c$ with $d_c = n_c^{-1/3}$. The solid line represents a fit of $FeSi_{1-x}Al_x$ data up to the concentration where the Ioffe-Regel condition is violated ($k_F\ell \sim 2, x \leq 0.045$) to $\sigma_{LT} = \sigma_0 * (n/n_c - 1)^\nu$ with best fit corresponding to $\nu = 0.9 \pm 0.1$ and $\sigma_0 = 190 \pm 40$. Dashed dotted line represents best fit of the Si:P data to the same form ($\nu = 0.55$).

expected and of course also happens when Al is added to pure Si, namely, donates one hole per added Al. Figure 1(a) shows the corresponding results for $T = 1.7$ K. Thermoelectric effects also depend on carrier sign, and we have accordingly measured the Seebeck coefficient for some samples. Doped samples display a positive coefficient over the entire 30 to 400 K measurement interval, while in agreement with Wolfe [7], pure samples yield two sign changes at temperatures above a maximum at 50 K.

After the carrier density and sign, the next basic information required about systems which undergo MI transitions is whether other types of order, e.g., superconducting, charge, or magnetic, appear nearby. If this were so, the associated fluctuations could contribute to scattering of the carriers and so affect all transport and thermodynamic properties. For $FeSi_{1-x}Al_x$, we have identified no finite temperature jumps or other singularities in any of our transport or thermodynamic data. In addition, we used low temperature specific heat and χ to search for unusual fluctuations at low temperatures. Of particular significance is that while there is generally a Curie-Weiss-like rise in χ' at low T, the amplitude of this rise appears uncorrelated with composition, and corresponds to 1% of $S = 1/2$ and $g = 2$ impurities per formula unit.

Having established that Al doping introduces carriers into $FeSi_{1-x}Al_x$ while not leading to any instability such as magnetic order, we turn to a direct search for the MI transition in $FeSi_{1-x}Al_x$. Figure 2(b) shows σ of pure and Al doped samples. From 250 to 100 K a thermally activated form, $\sigma = \sigma_a e^{-\Delta_g/2k_BT}$ with $\Delta_g = 680$ K, characterizes the pure sample. For temperatures between 4 and 100 K, a variable range hopping form describes the data well [8,9]. Comparison of the data above 200 K for the pure and doped materials reveals only a slight change with Al doping. Thus the thermally activated carriers from the FeSi valence band dominate the transport here. Furthermore, the small change in room temperature σ is consistent with only a small loss of carrier mobility. In contrast, the low temperature σ [Fig. 1(c)] shows a dramatic change with Al substitution, including metallic behavior for $x \geq 0.01$. Assuming that every Al dopant creates one carrier, the critical concentration (n_c) is between 2.2×10^{20} and 4.4×10^{20} cm^{-3} [$n_c = 3.3(\pm 1.1) \times 10^{20}$ cm^{-3}].

Figure 2(c) shows that the effect of doping on χ mirrors the effect of doping on σ. Specifically, $\chi(T)$, like $\sigma(T)$ is the superposition of a contribution inherited from the insulator, and a doping-induced contribution. The most prominent feature of χ' for the insulator is the well-known hump above room temperature. The hump is due to the appearance of magnetic moments on warming and can be described using the activated form, $[\chi(T) = (C/T)e^{-\Delta_\chi/k_BT}]$ with a Curie constant $C = 1.9$, which is that associated with $g = 2$ and $s = 3/2$, and—most importantly—a gap $\Delta_\chi = 680$ K identical to the transport (conductivity) gap [4]. Figure 2(c) also shows clearly the Curie-Weiss-like low temperature term which was discussed above and which is common to all of our samples, doped and undoped. What is not common to all samples, and indeed grows with doping, is an essentially T-independent offset ($\delta\chi$) which is most likely the Pauli term derived from hole doping. Figure 1(b) shows how doping causes the amplitude of this term to rise from a value consistent with zero in the pure compound.

If our interpretation of the doping-induced T-independent offset as a Pauli term is correct, there should also be a linear-in-T (γT) contribution to the specific heat. We have checked this for some of our doped samples. The inset to Fig. 2(c) shows that γ is much larger in two doped boules than the $\gamma = 1.8 \times 10^{-4}$ J/mole Fe K^2 found in a nominally pure crystal [9]. The corresponding effective mass (m^*) of the carriers calculated from free electron

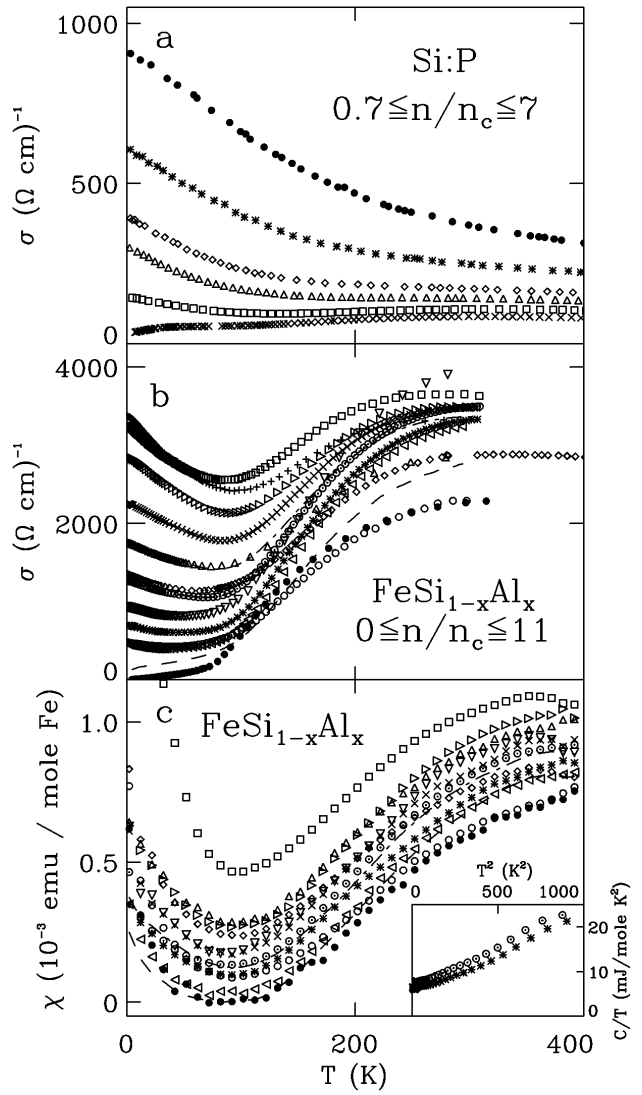

FIG. 2. (a) $\sigma(T)$ for Si:P with P concentrations of 2.7×10^{19} (•), 1.6×10^{19} (∗), 1.1×10^{19} (⋄), 7.8×10^{18} (△), 4.9×10^{18} (□), 2.8×10^{18} (×) data of Chapman *et al.* [11]. (b) $\sigma(T)$ for $FeSi_{1-x}Al_x$ with x of 0.0 single crystal (•), 0.0 (solid line), 0.005 (dashed line), 0.01 (◁), 0.015 (○), 0.015 (∗), 0.025 single crystal (▽), 0.025 (⊙), 0.035 (dashed dotted line), 0.045 (×), 0.05 (⋄), 0.055 (▷), 0.06 (△), 0.07 (+), 0.08 (□). (c) $\chi(T)$ for $FeSi_{1-x}Al_x$ with symbols same as in (b). Inset: $C(T)/T$ plotted as a function of T^2 for $x = 0.015$ (∗) and $x = 0.025$ (⊙).

theory is 55 ± 5 times the bare electron mass, which is reduced to $(14 \pm 2)m_e$ when the band degeneracy ($\nu' = 8$) is taken into account [3]. A similar analysis for an $x = 0.05$ sample prepared at a different time yields $m^* = (17 \pm 2)m_e$ or $(4.25 \pm 1)m_e$ with $\nu' = 8$. For comparison m^* from χ is $(54 \pm 5)m_e$ which is reduced to $(14 \pm 2)m_e$ by the band degeneracy. This mass, together with the free electron theory for a parabolic band which begins to be filled at n_c, yields the solid line in Fig. 1(b) and so provides a good description of how $\delta\chi$ varies with x.

Thus far we have focused on the gross features of the MI transition visible at relatively high temperatures. Because we are dealing with a disordered alloy derived from an insulator with strong correlation effects, we expect significant correlation effects to be visible also in the low-T σ and MC. Figure 3 demonstrates that $FeSi_{1-x}Al_x$ is not disappointing in this regard. In particular, there is a large contribution to $\sigma(T, H)$ which is proportional to $\sqrt{T}$ and whose sign can be switched by a 16 T magnetic field. In addition, there is a large MC with a composition-dependent shape. The shape also varies among samples with the same composition, and seems more correlated with the apparent Curie-Weiss temperature than with any other parameter. Therefore, to understand the behavior of all samples, one needs to use the theory of Fermi liquids in the presence of ordinary localizing disorder as well as spin-flip (SF) and spin-orbit (SO) scattering terms [1,10]. We have applied this theory to calculate the lines through the data in Fig. 3, and will give further details elsewhere. What is most important, though, is that for one $x = 0.015$ sample, SF and SO processes could be ignored in a single consistent description of all of our T- and H-dependent data. Thus, the moments formed at high-T in $FeSi_{1-x}Al_x$ appear to be completely independent of the Fermi liquid of holes induced by Al doping.

We have shown that $FeSi_{1-x}Al_x$ undergoes a metal-insulator transition as a function of x. The transition is not accompanied by strongly enhanced magnetic fluctuations, as would be expressed by a high Wilson ratio ($\chi k_B^2 \pi^2 / 3\gamma\mu_B^2 \simeq 2$ for FeSi), and seems unexceptional in all but one respect, the relatively high effective mass of the carriers. How unexceptional is clear from Table I and Fig. 1(c), which summarize our results and compare them with those for other materials, especially Si:P, near their metal-insulator transitions. Even the magnitudes of the conductivities as a function of both reduced composition (n/n_c) and temperature, as expressed in the coefficient of $\sqrt{T}$ in the low temperature data, are similar in $FeSi_{1-x}Al_x$ and systems based on the classical semiconductors. Parallels exist not only for the low temperature limiting

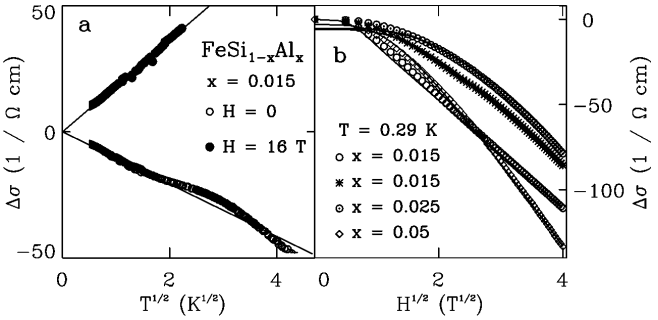

FIG. 3. (a) $\Delta\sigma$ vs $T^{1/2}$ for $FeSi_{0.985}Al_{0.015}$ in 0 and 16 T. Lines represent best fits to the low-T data to $\sigma(T) \propto T^{1/2}$. (b) Magnetoconductivity at 0.290 K for $FeSi_{1-x}Al_x$ with $x = 0.015$ (∘), $x = 0.015$ (∗), $x = 0.025$ (⊙), and $x = 0.05$ (⋄). Solid line through data in both (a) and (b) for $x = 0.015$ (∘) is calculated from theory [10] with the gyromagnetic ratio for the carriers of 2.75. Other lines represent fits to theory which include effects of spin orbit or spin flip scattering.

TABLE I. Values of the energy gap in the undoped systems (E_g), critical concentration n_c, the effective carrier mass m^*/m_e, the dimensionless diffusion constant $(k_F\ell/3)$ for $n = 2n_c$ calculated using the dopant density as the nominal carrier concentration, a valley degeneracy of 8 for FeSi, 6 for Si, and 4 for Ge, and the free electron formula for σ [1] (the value for $La_{2-x}Sr_xCuO_4$ was scaled from a high temperature estimate given in Ref. [13]), σ_0, and ν obtained from fits of the data to the form $\sigma = \sigma_0(n/n_c - 1)^\nu$, a from fits to the form $\sigma = \sigma_0(n) + aT^{1/2}$ to the low temperature conductivity at zero field, and the parameter b from fits to the linear temperature dependent conductivity to the form $\sigma(T, n) = \sigma_1(n) + bTn/n_c$. Data for Si:P were taken from Refs. [1,11,14], for Si:B from Refs. [1,11,14], for Si:As from Refs. [14,15], for Ge:Sb from Refs. [14,16], and for $La_{2-x}Sr_xCuO_4$ from Refs. [13,17].

E_g (eV)	n_c (10^{18} cm^{-3})	m^*/m_e	$k_F\ell/3$	σ_0 ($1/\Omega$ cm)	ν	a (Ω cm K$^{1/2}$)$^{-1}$	b (Ω cm K)
0.06	330 ± 110	14 ± 2	0.23	600 ± 150	0.85 ± 0.1	−10.0	−1.10 ± 0.2
1.17	3.74	0.26	0.46	260 ± 30	0.55 ± 0.1	−3.0	−0.41 ± 0.07
1.17	4.06	0.38	0.20	152 ± 18	0.65 ± 0.14	−7.0	−0.062 ± 0.005
1.17	8.2	0.31	0.34	381	0.64 ± 0.2	−11.0	−8 ± 2
0.75	0.15	0.22	0.51	26 ± 10	0.9 ± 0.1	−12.0	−0.073 ± 0.008
1.8	260	2	~3				−1.5 ± 0.3

properties but also for the crossover to the high temperature regime, which in the case of $FeSi_{1-x}Al_x$ is dominated by the small gap of the insulating parent. Specifically, Fig. 2(a) shows the conductivity of Si:P measured by Chapman *et al.* [11] up to 400 K for samples with n/n_c in the same range as in our measurements for $FeSi_{1-x}Al_x$. It is striking that for both Si:P and $FeSi_{1-x}Al_x$, the conductivity rises linearly with decreasing T over a large range of T, as of course it does for many high-T_c superconductors and certain rare earth intermetallics [12]. The associated slopes $d\sigma/dT$ appear to scale with distance from the MI transition, i.e., $\sigma(T, n) = \sigma_1(n) + bTn/n_c$ with a coefficient b which seems to be a property of the alloy series in question. From the last column in Table I, it is clear that b for $FeSi_{1-x}Al_x$ is of the same order as for the doped (band) semiconductors Si:P and Si:As. At the same time, it is substantially larger than for Si:B and Ge:Sb. What is perhaps most striking is that b for $FeSi_{1-x}Al_x$, Si:P, and Si:As is of the same order as b for the doped Mott-Hubbard insulator and high-T_c superconductor $La_{2-x}Sr_xCuO_4$, which is considerably more famous for its linearly T-dependent resistivity than the classic semiconductors.

In summary, we have shown how a heavy fermion metal emerges upon doping the strongly correlated insulator, FeSi. The resulting metals and associated insulator-metal transition bear an extraordinary and even quantitative resemblance to those near the classic metal-insulator transition in the more conventional insulator Si. Thus, the strong Coulomb effects present in insulating FeSi serve only to renormalize the critical concentration n_c and effective carrier masses in the metallic phase.

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