First order transition from correlated electron semiconductor to ferromagnetic metal in single crystalline FeSi$_{1-x}$Ge$_x$

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The phase diagram of FeSi$_{1-x}$Ge$_x$, obtained from magnetic, thermal and transport measurements on single crystals, shows a first-order transition from a correlated electron semiconductor to a ferromagnetic metal at a critical concentration, $x_c \approx 0.25$. The gap of the insulating phase strongly decreases with $x$. The specific heat $\gamma$ coefficient appears to track the density of states of a Kondo insulator. The phase diagram is consistent with a correlation induced insulator-metal transition in conjunction with disorder on the Si/Ge ligand site.

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Kondo insulators (KIs) are Ce, Yb or U based small-gap semiconductors $^1$, e.g. CeNiSn, Ce$_3$Bi$_4$P$_3$ and YbB$_2$. Many KIs are nonmagnetic with a Van-Vleck-like low-$T$ susceptibility, but an exponentially activated low-$T$ resistivity and electronic specific heat. Most KIs are not perfect semiconductors, because the hybridization gap is frequently only a pseudogap and/or there are intrinsic or impurity states in the band gap $^2$. A magnetic field gradually closes the gap yielding a metallic state for fields larger than a critical one $^3$ $^4$.

FeSi is known as a correlated electron semiconductor $^5$ with an activation gap of about 0.05 eV and exhibits properties similar to those of KIs. Neutron scattering and Mössbauer experiments reveal no long-range magnetic order in FeSi $^5$ $^6$. FeGe, on the other hand, is a long-range spiral metallic ferromagnet (with period of 700Å below 280K) with a saturated magnetic moment of about 1 $\mu_B$ in a magnetic field larger than 0.3 T $^8$. By alloying these two systems it is then possible to study the transition from correlated electron semiconductor to ferromagnetic metal (FM), with the following unique advantages: (i) Both compounds form in the same slightly distorted rocksalt structure and are soluble over the entire concentration range. (ii) Single crystals can be grown for the two end-compounds and are available over the entire alloy range (previous studies were on polycrystalline samples and over a limited range of $x$ $^6$ $^7$). (iii) The substitution is on the sites of the ligand atoms, yielding a reduction of the gap, and not of the magnetically active ion (Fe), which would give rise to an impurity band in the gap $^{11}$. (iv) The Kondo gap is large (about 50 times larger than for other KIs) and therefore the system is less sensitive to internal strains and other impurities. (v) Since the spin-orbit coupling of Fe is much smaller than for rare earth and actinide ions, the orbital momentum is quenched and the magnetic susceptibility is exponentially activated, rather than Van-Vleck-like, and a useful tool to study the gap.

Optical conductivity measurements indicate that FeSi is a strongly correlated system $^{12}$, because (1) the gap disappears at unusually low $T$ (above 200K) relative to its magnitude, and (2) the conductivity displaced from the gap region at low $T$ does not appear just above the gap, but is spread over a wide energy range. The results are consistent with the usual KI picture. However, the gap is much larger than usual Kondo temperatures, so that FeSi could also be considered a mixed-valence insulator $^{14}$. Based on the spin-fluctuation theory, FeSi has been argued a nearly ferromagnetic semiconductor $^{14}$. LDA+$U$ band calculations $^{15}$ also suggest that FeSi is close to a magnetic instability. Increasing Hubbard $U$ leads to a first order transition from a strongly correlated semiconductor to a FM.

Similarly, as a function of $U/V$, the half-filled Anderson lattice undergoes a first order transition from KI to a FM ordered state $^{16}$. Here $V$ is the hybridization of the Fe 3d states with the ligand atoms. According to X-ray photoelectron spectroscopy (XPS) studies and band calculations $^{17}$, $V$ is smaller for FeGe than for FeSi. Alloying these two systems may then lead to a first order transition from KI to FM. Here we present magnetic, transport, and thermal properties of FeSi$_{1-x}$Ge$_x$ to study the evolution of this transition.

Single crystals were grown by vapor transport method described in Ref. $^{18}$. Polycrystalline samples prepared by arc-melting of the stoichiometric mixture of elements were sealed in an evacuated quartz tube with the chemical agent iodine and heated in a home made two zone furnace for a week. The temperature variations on both sides of the tube were measured with a commercial thermometer and found to be less than 5K. The Ge/Si concentration was determined by Energy Dispersive X-ray analysis (the uncertainty is $\pm 5\%$).

All measurements were performed using the same set of crystals. The DC susceptibility was obtained with a Quantum Design MPMS between 2 K and 350 K, the resistivity with a standard four-probe technique in the
temperature range from 2 K to 300 K, and the specific heat $C_p(T)$ with a relaxation method down to 0.35 K.

Fig. 1 displays the phase diagram of FeSi$_{1-x}$Ge$_x$ obtained from magnetic, transport and thermal measurements. The solid circles, solid diamonds, and open squares represent the gap in the susceptibility, the transport gap and the resistivity minimum for $x \leq 0.24$, respectively. The solid lines and shaded area are guides to the eyes for phase boundaries and energy gap, respectively. The dashed line is the decrease of the gap with $x$ according to a selfconsistent theory for KI with ligand defects.

In contrast, $\chi(T)$ qualitatively changes with further Ge doping. For $0.25 \leq x \leq 0.50$ the magnetization gradually increases with decreasing $T$ as seen in Fig. 2 (b), suggesting the appearance of a ferromagnetic component. In fact, for $x \geq 0.53$, the ferromagnetic transition is given by a step-like increase upon cooling (inset of Fig. 2 (b)). $T_C$ is determined by the kink in the magnetization and shown as the solid triangles in Fig. 1. $T_C$ monotonically increases with $x$ until it reaches the known value for FeGe.

The sharp jump of the magnetization of FeGe around 280 K appears to be consistent with a first order transition [10]. The distorted rocksalt structure lacks of inversion symmetry giving rise to a Dzyaloshinskii-Moriya (DM) interaction. A renormalization group study [17] of

$$\chi(T) = (C/T) \exp(-\Delta_s/k_B T),$$  

(1)

where $\Delta_s$ is the spin gap. The left inset of Fig. 2 (a) shows that $\ln(T\chi(T))$ vs. $T^{-1}$ for 150 K $< T < 350$ K follows a straight line, indicating that Eq. (1) represents $\chi(T)$ well. The most significant effects of the Ge substitution on $\chi(T)$ are: (i) a systematic increase with $x$, (ii) a maximum starts to show at about 300 K for $x \geq 0.2$, and (iii) the spin gap $\Delta_s$ monotonically decreases with $x$, as seen in Fig. 1. At low $T$, $\chi(T)$ displays a Curie tail, which is attributed to impurities or defects. Since this tail is approximately the same for all $x \leq 0.24$, we conclude that the impurity concentration is roughly constant with $x$.

![Fig. 1: Phase diagram of FeSi$_{1-x}$Ge$_x$. Solid circles and solid diamonds represent gaps from $\chi(T)$ and $\rho(T)$, respectively, open squares correspond to the minimum temperature of $\rho(T)$, and the solid triangles are the ferromagnetic $T_C$. The solid lines and shaded area are guides to the eyes for phase boundaries and energy gap, respectively. The dashed line is the decrease of the gap with $x$ according to a selfconsistent theory for KI with ligand defects.](image1)

![Fig. 2: (a) Susceptibility vs. temperature for $x = 0$, 0.1, and 0.24 measured in a field of 0.1 T. The slope in the left inset is the thermal activation energy for $\chi(T)$ for $x \leq 0.24$. The right inset represents the effective moment for $x > 0.25$. The solid lines are guides to the eye. (b) Magnetization as a function of $T$ in a field of 0.1 T for $x \geq 0.25$. For $x > 0.6$ the transition is discontinuous, while for $x < 0.6$ the ferromagnetism disappears continuously.](image2)
the ferromagnetic DM instability predicts that the magnetic structure is helical of long period and the transition into the paramagnet is of first order. Experimentally the transition remains discontinuous for \( x > 0.6 \). In the range \( 0.25 < x < 0.60 \), on the other hand, the magnetization tends to zero continuously at \( T_C \), probably as a consequence of disorder in the sample. The alloying of FeSi with FeGe necessarily leads to Ge-rich and Si-rich regions and hence to a distribution of transition temperatures, such that the total magnetization is continuous. The effective moment \( \langle p_{\text{eff}} \rangle \) of Fe is obtained by fitting a Curie-Weiss law for \( T \geq T_C \), and is shown in the right inset of Fig. 2(a). \( p_{\text{eff}} \) are almost independent of \( x \) and roughly correspond to \( S = 1 \).

The \( T \)-dependence of the resistivity, \( \rho(T) \), normalized to its value at 300 K is shown in Fig. 3. Two distinct regimes have to be distinguished: For \( x < 0.24 \) the resistivity decreases with \( T \), characteristic of a semiconductor, while for \( x > 0.25 \) \( \rho(T) \) is an increasing function and the behavior is metallic. Starting from the nonmagnetic semiconductor FeSi, the Ge substitution dramatically reduces \( \rho(T) \). We assume a thermal activation law describes the insulating behavior in the Si rich region,

\[
\rho(T) = \rho_0 \exp(\Delta_t/2k_BT) ,
\]

where \( \Delta_t \) is the transport gap. For \( x \leq 0.21 \) the resistivity for \( 25 \text{ K} < T < 210 \text{ K} \) is well represented by the activation law (see inset of Fig. 3). The dependence of \( \Delta_t \) on \( x \) is displayed in Fig. 4. For FeSi \( \Delta_c \) and \( \Delta_t \) have the same value, but with increasing \( x \) the transport gap becomes much smaller than the magnetic spin gap. This difference is due to the randomness in the sample, consequence of the alloying. While in a transport measurement the electrons travel along the path of least resistance, i.e. the one with the smallest effective gap, a thermodynamic measurement averages over the entire sample. Necessarily, \( \rho(T) \) should have the smaller gap. Below 20 K the resistivity saturates, which is attributed to impurity states in the gap.

The resistivity of FeGe is clearly metallic. Substituting Si for Ge gradually increases \( \rho(T = 0) \) because of disorder scattering, but the system remains a poor metal up to the metal-insulator transition at \( x_c \approx 0.25 \). For \( x \geq 0.53 \) a small kink in \( \rho(T) \) can be observed at the onset of ferromagnetic long-range order at \( T_C \). The qualitative change in \( \chi(T) \) and \( \rho(T) \) at \( x_c = 0.25 \) is consistent with a first order transition. For \( x < x_c \) they follow activation laws with their gaps decreasing with \( x \), while for \( x > x_c \) the system is FM at low \( T \).

The specific heat divided by temperature, \( C_p(T)/T \), vs. \( T^2 \) is shown in Fig. 4. For \( T < 2K \), \( C_p/T \) displays an upturn, believed to originate from 1-2\% of impurities. The estimated low-\( T \) entropy up to 2 K is consistent with the Curie constant obtained from the tail of the impurity states of \( \chi(T) \) for \( x \leq 0.24 \). The specific heat of the compound (electrons and phonons) is obtained by fitting the data for \( 5 \text{ K} < T < 40 \text{ K} \) to the expression

\[
C_p(T) = \gamma T + \beta T^3 + \delta T^5 ,
\]

where \( \gamma T \) is the electronic contribution, shown in the inset of Fig. 4. In the insulating regime, i.e. \( x < x_c \), \( \gamma \) is almost zero, suggesting a very small or no density of states at the Fermi energy. However, for \( x > x_c \), i.e. in the FM regime, \( \gamma \) is nonzero, has its largest value at \( x \approx 0.4 \) after a steep increase, and then it decreases to a constant value (for \( x \geq 0.6 \)) of about 11 mJ/mole-K².

The Debye temperature can be obtained from \( \beta \). \( \theta_D \) decreases with \( x \) from 600 K for FeSi to 280 K for FeGe.
As seen in Fig. 1, FeSi$_{1-x}$Ge$_x$ has a first order transition from KI to FM at \( x_c \approx 0.25 \). Recent LDA+\( U \) band structure calculations \[12\] have shown that FeSi is a semiconductor that is close to a ferromagnetic instability. With increasing \( U \), it is found that at a critical \( U_c = 3.2 \) eV, a first order transition from paramagnetic semiconductor to FM takes place. The calculation \[20\] has been extended to the alloy FeSi$_{1-x}$Ge$_x$ using experimental lattice constants and averages of Si and Ge for the potential parameters. A first order insulator-metal transition is predicted at \( x_c = 0.4 \) for \( U = 3.7 \) eV, in agreement with the experimental findings.

Detailed LDA band calculations by Mattheiss and Hamann \[21\] show that FeSi is a small (indirect) gap semiconductor. The bands closest to the Fermi level under consideration. It should be then meaningful to discuss FeSi$_{1-x}$Ge$_x$ within the framework of the Anderson lattice Hamiltonian without orbital degeneracy (one band). The magnetic instabilities of a KI (two electrons per site) have been studied within a mean-field slave-boson approach \[10\]. The key parameter driving the magnetic phases is the Hubbard/Anderson \( U \) over the hybridization between the localized and conduction states \( V \). (In the LDA+\( U \) approach \[13, 20\] the correlation strength is \( U \) over the bandwidth \( W \).) Two magnetic phases, an antiferromagnetic and a ferromagnetic one, are predicted. With increasing \( U/V \), the paramagnetic KI first undergoes a second order transition into an antiferromagnetic insulating phase. This, however, requires a bipartite lattice (two interpenetrating sublattices) symmetry, which is absent for the rocksalt structure. Consequently, antiferromagnetism is suppressed and the system has a discontinuous transition to the FM phase \[10\].

For FeSi$_{1-x}$Ge$_x$, we consider \( U \) a property of the Fe 3d shell and a constant for the alloy series. The hybridization of the 3d states with the ligand atoms, however, depends on \( x \) and the simplest assumption is an average hybridization, i.e. \( V_{eff} = (1-x)V_{Si} + xV_{Ge} \). According to XPS and band calculations for FeSi and FeGe \[17\], \( V_{Si} \) is larger than \( V_{Ge} \). Hence, the effective hybridization, \( V_{eff} \), decreases and \( U/V_{eff} \) increases with \( x \), thus leading to a discontinuous transition at \( (U/V)_{cr} \). The parameters \( U \) and \( V_{eff} \) are such that the compound is actually in the mixed valence and not quite in the Kondo regime \[13\]. Within the mean-field approach the critical parameter is \( (U/V)_{cr} = 1.54 \).

The \( \gamma \) coefficient, shown in the inset of Fig. 1, is a measure of the density of states at the Fermi level. Based on the KI picture, in the gapped region we have \( \gamma = 0 \), while in the metallic region \( \gamma \neq 0 \). The magnetization (and also \( T_C \)) increases with \( x \) (or \( U/V_{eff} \)), so that the number of electrons (holes) in the majority (minority) conduction (valence) bands increase with \( x \). Hence, \( \gamma \) as a function of \( x \) probes the density of states of the KI, which has a peak above (below) the band edges and then reaches a constant value for larger energy \( (x) \), in agreement with Fig. 1. A large magnetic field is expected to favor a magnetic state close to the insulator-metal transition \[14, 20\]. However, we found that the required fields are larger than the 45 T available at the NHMFL.

Finally, we address the rate of decrease of the gap with \( x \), which is by far too large to be explained by the \( x \)-dependence of \( V_{eff} \). It is then necessary to invoke the disorder introduced by the Ge substitution. An impurity in a KI gives rise to a bound state in the gap. Two situations have to be distinguished: (i) Substitution of magnetically active ions (Fe, Kondo holes) yields an impurity band close to the center of the band, while (ii) if ligand atoms are replaced, tails of impurity states develop close to the band edges reducing the spin gap \[11\].

Assuming that Ge enters the lattice randomly on ligand sites a selfconsistent calculation \[11\] yields a much faster decrease of the gap with \( x \) as shown in Fig. 1 (normalized to the gap for FeSi for \( V_{Ge} = 0.67V_{Si} \) and \( U/V_{Si} = 1.5 \)).

In summary, we studied the magnetic, transport, and thermal properties of single crystalline FeSi$_{1-x}$Ge$_x$ and found a first order transition from the correlated insulator phase to a ferromagnetic metal phase at \( x \approx 0.25 \). The systematic change of the spin and transport gaps in the insulating phase, and the evolution of the magnetization and the \( \gamma \)-coefficient of the specific heat in the metallic phase are consistent with the Kondo insulator picture.

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