Correlation effects in the small gap semiconductor FeGa$_3$

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Abstract. We report investigations of the effect of electron doping in FeGa$_3$ via electric resistivity, specific heat and magnetic susceptibility measurements in single crystals. FeGa$_3$ is a non-magnetic small gap semiconductor ($\Delta \sim 0.3-0.4$ eV). Low concentration of Co in FeGa$_3$ induces a crossover to a metallic-like behavior, also creating weakly coupled local moments. Electronic specific heat and resistivity suggest a mass enhancement of charge carriers. Thus, the low carrier density metal formed by doping FeGa$_3$ presents some physical properties that resemble heavy fermion metals.

FeGa$_3$ crystallizes in the tetragonal $P4_2/mnm$ (No. 136) structure with 4 formula units per unit cell. Recently it was found to be a semiconductor [1], which puts it in the interesting class of Fe-based, non-magnetic, small gap semiconductors, such as FeSi [2] and FeSb$_2$ [3]. The semiconducting gap is due to the hybridization of the 3$d$ band with the $p$ states of group 13 and 14 elements. For FeGa$_3$, this hybridization, of Fe 3$d$ and Ga 4$p$ levels, was predicted, by band structure calculations, to produce a gap of 0.3-0.4 eV [1, 4]. Estimation of the energy gap via electric and Hall resistivity [5, 6], magnetic susceptibility and via valence-band x-ray photoemission [7] are consistent with the predicted range of values. Interestingly CoGa$_3$, which crystallizes in the same FeGa$_3$-type structure [8], is a good diamagnetic metal with residual resistivity ratio of the order of 100 [1]. Because it has one more electron, compared to FeGa$_3$, it shifts the Fermi level above the $d$-$p$ hybridization gap, allowing metallic conductivity [1].

Small band-gap semiconductors are regarded as potential thermoelectric materials. They are also good candidates for half-metallic ferromagnetism, relevant for spintronic applications. Pure FeSi has optical properties very similar to that of Ce-based semiconductors, also known as Kondo insulators [9, 10]. It has been shown that lightly doped FeSi is host to strong electron correlation effects, such as quantum interference in the magnetotransport [11] and undercompensated Kondo effect [12]. Maybe the most unexpected result is that Co doping in FeSi ultimately leads to a half-metallic ferromagnet [11], while none of the end compounds is magnetic. This motivated us to investigate the effect of Co doping in FeGa$_3$.

In this paper, we describe the effect of a few percent Co doping in the magnetic and physical properties of the non-magnetic narrow-gap semiconductor FeGa$_3$. Single crystals of Co-doped FeGa$_3$ are synthesized from the standard Ga-flux method [13], with molar ratios of (1-$x$):$x$:10(Fe:Co:Ga), for five nominal concentrations, 1, 5, 15 and 30%. Pure CoGa$_3$ is also grown for comparison. Powder x-ray diffraction confirms the FeGa$_3$-type structure, with
systematic changes in the crystal parameters due to the Co doping (see Table 1). The actual Co concentrations are determined via energy dispersive x-ray spectroscopy (EDS), in very good agreement with the nominal value. In this paper we mainly focus on the properties of the $x = 0.05$ sample. Magnetic susceptibility is measured in a commercial SQUID vibrating sample magnetometer. Specific heat, electric resistivity and Hall resistivity measurements are performed in a physical properties measurement system (PPMS). Electric resistivity $\rho(T)$ is measured in needle-like single crystals, with current applied along the needle axis.

Fig. 1(a) shows that 5% Co doping is sufficient to make the compound metallic. The residual resistivity ratio is small compared to pure CoGa$_3$, suggesting a bad metal. From the carrier density $n$ (see below) and residual resistivity values we estimate $k_F \ell \sim 0.9$, which is near to the metal-insulator crossover transition. We found that a metal-insulator crossover is induced in our sample by moderate magnetic field, as shown in Fig. 1(b). Surprisingly, there is also a maximum at 19 K at $H = 0$. This behavior is reminiscent of characteristic heavy fermion (HF) $\rho(T)$ dependence, where the maximum sets the coherence $T$ below which collective Kondo screening of the local moments takes place, leading to heavy quasi-particle band. Hall resistivity as a function of field $R_H(H)$ is measured for the Fe$_{0.95}$Co$_{0.05}$Ga$_3$ and CoGa$_3$ samples, at different $T$ from 300 K down to 50 K and the absence of any $T$ dependence suggest that the anomalous Hall effect contribution is negligible, and that there is only one type of carrier. From the $R_H(H)$ data we estimate $n = 1.5 \times 10^{27}$ m$^{-3}$ (Fig. 1(c)), which is $10^4$ times larger than what was found for the pure FeGa$_3$, at 300 K [6], and 3 times smaller than CoGa$_3$. By assuming that each Co contributes with one electron to the compound, the estimated carrier density is $n = 0.05Z/V_{u.c}$, where $Z$ is the number of formula units and $V_{u.c}$ the volume of the unit cell, and yields a value close to the experimental one. This suggests that each Co effectively gives one electron to the conduction band.

![Figure 1](image1.png)

Figure 1. (a) $T$ dependence of $\rho(T)$ divided by the value at $T = 350$ K, for FeGa$_3$, Fe$_{0.95}$Co$_{0.05}$Ga$_3$ and CoGa$_3$. Inset: (b) Low-$T$ dependence of $\rho(T)$ for Fe$_{0.95}$Co$_{0.05}$Ga$_3$ at $H = 0$, 4 and 9 T. (c) Density of carriers as a function of $T$ for Fe$_{0.95}$Co$_{0.05}$Ga$_3$ and CoGa$_3$, from Hall resistivity measurement.

![Figure 2](image2.png)

Figure 2. Low-$T$ dependence of $\chi(T)$ at $H = 1$ T, for Fe$_{0.95}$Co$_{0.05}$Ga$_3$ and CoGa$_3$. The solid red line is the Curie-Weiss fit to the data. Inset: Magnetization as a function of field, at $T = 2$ K, for Fe$_{0.95}$Co$_{0.05}$Ga$_3$. The solid blue line is the Brillouin fit to the data.

Figure 2 shows the low-$T$ magnetic susceptibility $\chi(T)$, measured at $H = 1$ T, for the Fe$_{0.95}$Co$_{0.05}$Ga$_3$ and CoGa$_3$ single crystals. Magnetization data at $T = 2$ K, as function of $H$, $M(H)$, is also shown as an inset in Fig. 2. No appreciable change is observed performing
zero field versus field cooling (not shown). The upturn in $\chi(T)$ combined with the saturation behavior in $M(H)$ suggests that Co doping creates local magnetic moments. We were able to fit the 5% Co-doped data for $\chi(T)$ to the Curie-Weiss law, plus a $T$ independent term $\chi_0$, with the parameters given in Table 1. In contrast to pure FeGa$_3$ ($\chi \approx -0.3 \times 10^{-4}$ emu/mol, at room-$T$) [7, 6] and CoGa$_3$ that are diamagnetic, intermediate values of $x$ in Fe$_{1-x}$Co$_x$Ga$_3$ have positive $\chi_0$ values at low-$T$. The constant $\chi_0$, corrected for the core diamagnetism (taken as FeGa$_3$ susceptibility), is the $T$ independent Pauli paramagnetism $\chi_{\text{Pauli}}$ (see Table 1). Similarly, we fit the magnetization data to a linear plus Brillouin-type function for $g = 2$ and $J = 1/2$ (see solid line in the inset of Fig. 2): $M(H) = \chi_0 H + N g \mu_B B J(g \mu_B H/k_B T)$, where $N$ is the number of magnetic moments per mol formula unit and $B J(g \mu_B H/k_B T)$ the Brillouin function. The choice of $g$ and $J$ follows from preliminary estimate dividing the initial slope $M'(0)$ at low-$H$ by the saturation value $M_{\text{sat}}$ at 7 T. The fitting parameters for the $\chi(T)$ and $M(H)$ data are consistent with each other and indicate that the concentration of magnetic moments is less than the actual Co doping. In other words not all Co atoms create a local moment. For all other dopings, we found that the concentration of local moments increases with Co doping as $x^{-1/3}$ rather than linear in $x$ (not shown). In the FeGa$_3$-type structure the transition metal site has a coordination of 9 with only one of the nearest neighbors being another transition metal. We speculate that the formation of magnetic moments may require a special condition such as having a Co-Co dimer. Further investigation is needed.

### Table 1. Experimental parameters for Fe$_{1-x}$Co$_x$Ga$_3$. Data for $x = 0.00$ is from Ref. [6].

| $x$ | $a$ (Å) | $c$ (Å) | $\chi_{\text{Pauli}}$ (emu/mol) | $\mu_{\text{eff}}$ (µB) | $\theta$ (K) | $\gamma$ (mJ/mol K$^2$) | $n^{\dagger}$ (m$^{-3}$) | $\chi_{\text{dia}}$ (emu/mol) |
|-----|---------|---------|-------------------------------|-----------------|-------------|-----------------|-----------------|-----------------|
| 0.00 | 6.262   | 6.556   | 0.03                          | 1.00            | $1 \times 10^{23}$ | $\sim -0.33 \times 10^{-4}$ |
| 0.05 | 6.264   | 6.554   | 2.85 $\times 10^{-4}$         | 0.155           | 6.3         | $1.5 \times 10^{27}$ |
| 1.00 | 6.230*  | 6.431*  | 2.6                           | 4.5 $\times 10^{27}$ | $\sim -0.78 \times 10^{-4}$ |

$\dagger T = 300$ K $\ddagger T = 2$ K *Ref. [8]

The specific heat $C(T)$ of the Fe$_{0.95}$Co$_{0.05}$Ga$_3$ sample is measured from 5 K down to 0.5 K for different $H$. Figure 3 shows the low-$T$ electronic specific heat data, $C_{el}/T = (C - C_{\text{lattice}})/T$, in log$T$ scale. The lattice contribution $C_{\text{lattice}}$ is obtained from a linear fit to $C/T$ vs $T^2$ at $H = 9$ T. The dependence of $(C - C_{\text{lattice}})$ does not follow a typical spin glass ($\sim 1/T$) nor Schottky type behavior ($\sim 1/T^2$). At $H = 0$, the extrapolated Sommerfeld coefficient, $\gamma$, is approximately 200 and 3 times greater than the $\gamma$ values for pure FeGa$_3$ and CoGa$_3$, respectively. At finite $H$, $C_{el}/T$ saturates below a characteristic $T$, 0.7 K at 2 T and larger for higher fields, while the $\gamma$ value decreases. The inset of Fig. 3 shows the decreasing $\gamma$ for increasing $H$. $C_{el}$ is essentially $T$-independent for 9 T, with an upturn at the lowest $T$ that is likely due to nuclear Schottky contribution of Co and/or Ga. The $H$-dependence of the $C(T)$ is reminiscent of HF systems like CeCu$_{3.2}$Ag$_{0.8}$ [14] and CeCoIn$_5$ [15] where the saturation $T$ sets the crossover from non-Fermi liquid (NFL) to Fermi liquid (FL) regime. This interpretation is valid as long as $n(H)$ is constant and the $\gamma$ value is inversely proportional to the saturation $T$. The latter is realized in Fe$_{0.95}$Co$_{0.05}$Ga$_3$ for $2 \leq H \leq 6$ T, suggesting a $H$ suppression of the effective mass as in HF systems. Alternatively there might be a gap opening with $H$: the decrease in $n(H)$ would suppress $\gamma$ and would give non-metallic $\rho(T)$ (Fig. 1(b)).

Using the experimental value of $n$ (Table 1) we calculate the free electron density of states at the Fermi level, given by $g(\varepsilon_F) = m/\hbar^2 \pi^2 (3\pi^2 n)^{1/3}$, where $m$ is the free electron mass. The value we get, $g(\varepsilon_F) = 1.14 \times 10^{42}$ states/J mol, corresponds to a Pauli susceptibility...
of $\chi_{\text{Pauli}} = 9.78 \times 10^{-6} \text{emu/mol}$ ($\chi_{\text{Pauli}} = \mu_B^2 g(\varepsilon_F)$), and to a Sommerfeld coefficient of $\gamma_0 = 0.71 \text{ mJ/mol K}^2$ ($\gamma_0 = (\pi^2/3)k_B g(\varepsilon_F)$). Comparing with the experimental values, we find a mass enhancement of approximately 9 from the ratio $\gamma_{\text{exp.}}/\gamma_0$, which is too large to be attributed to a band mass. Consistently with $\rho(T)$, $C(T)$ thus suggests HF behavior. Also, the calculated $\chi_{\text{Pauli}}$ is approximately 29 times smaller than the experimental value. The enhancement of $\chi_{\text{Pauli}}$ is unexpectedly large, and points to a Stoner type mechanism, characteristic of itinerant systems close to a ferromagnetic instability. Further studies should elucidate whether Co-doped FeGa$_3$ is on the verge of half-metallic ferromagnetism.

In summary, we have synthesized Co-doped FeGa$_3$ single crystals and found that the doping creates spin 1/2 local moments in the diamagnetic host and also drives it from semiconductor to metal. The magnetic moment concentration is less than what is expected from the actual Co doping, suggesting that it takes more than one Co to create each spin 1/2. Mass enhancement of the carriers is observed in $C(T)$ at $H = 0$, in agreement with $\rho(T)$, which shows characteristics of HF metals. These results suggest that a similar mechanism, namely the Kondo screening of local moments, might be at work in this purely $d$-electron system. Doped semiconductors thus offer new routes towards the formation of strongly correlated metallic states [12].

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