Journal of Physics: Conference Series **200** (2010) 012014 doi:10.1088/1742-6596/200/1/012014

Correlation effects in the small gap semiconductor $FeGa_3$

E M Bittar[1,2], C Capan[1], G Seyfarth[1,3], P G Pagliuso[2] and Z Fisk[1]

[1] Department of Physics and Astronomy, University of California Irvine, CA 92697, USA
[2] Instituto de Física "Gleb Wataghin", UNICAMP, C. P. 6165, 13083-970, Campinas, SP, Brazil
[3] Département de Physique, Université de Montréal, Montréal, Quebec H3C 3J7, Canada

E-mail: bittar@ifi.unicamp.br

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 unitcell. 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 $3d$ band with the p states of group 13 and 14 elements. For $FeGa_3$ this hybridization, of Fe $3d$ and Ga $4p$ levels, was predicted, by band structure calculations, to produce a gap of 0.3-0.5 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 proprieties 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 $k_F l \sim 0.9$, 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 $n = 1.5\times10^{27}$ 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.

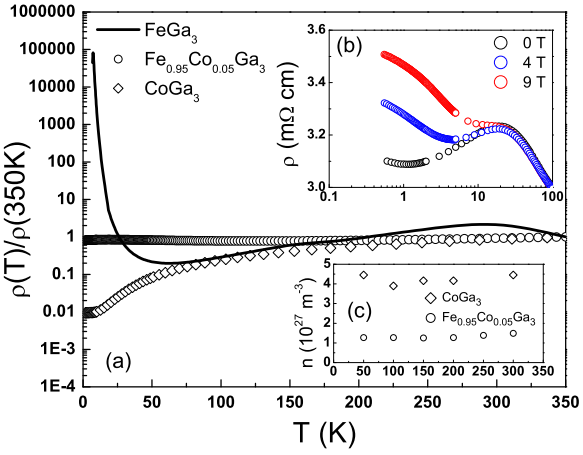

Figure 1. (a) T dependence of $\rho(T)$ divided by the value at $T = 350$ K, for $FeGa_3$, $Fe_{0.95}Co_{0.05}Ga_3$ and $CoGa_3$. Inset: (b) Low-T dependence of $\rho(T)$ for $Fe_{0.95}Co_{0.05}Ga_3$ at $H = 0$, 4 and 9 T. (c) Density of carriers as a function of T for $Fe_{0.95}Co_{0.05}Ga_3$ and $CoGa_3$, from Hall resistivity measurement.

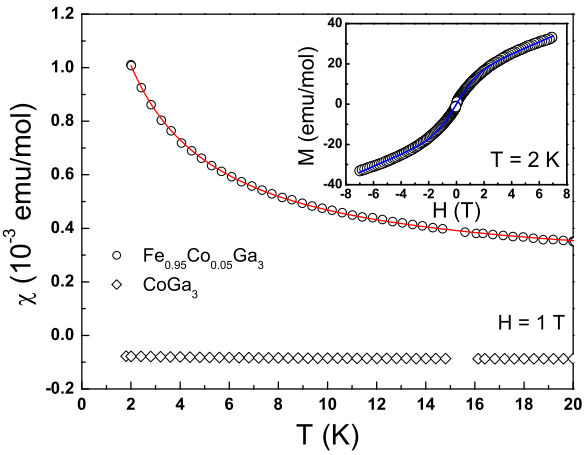

Figure 2. Low-T dependence of $\chi(T)$ at $H = 1$ T, for $Fe_{0.95}Co_{0.05}Ga_3$ and $CoGa_3$. The solid red line is the Curie-Weiss fit to the data. Inset: Magnetization as a function of field, at $T = 2$ K, for $Fe_{0.95}Co_{0.05}Ga_3$. The solid blue line is the Brillouin fit to the data.

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 χ_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 $Fe_{1-x}Co_xGa_3$ have positive χ_0 values at low-T. The constant χ_0, corrected for the core diamagnetism (taken as $FeGa_3$ susceptibility), is the T independent Pauli paramagnetism χ_{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): $M(H) = \chi_0 H + Ng\mu_B JB_J(g\mu_B JH/k_BT)$, where N is the number of magnetic moments per mol formula unit and $B_J(g\mu_B JH/k_BT)$ 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_{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 $Fe_{1-x}Co_xGa_3$. Data for $x = 0.00$ is from Ref. [6].

x	a (Å)	c (Å)	χ_{Pauli} (emu/mol)	μ_{eff} (μ_B)	θ (K)	γ (mJ/mol K^2)	$n^\dagger$ (m^{-3})	$\chi^\ddagger_{dia}$ (emu/mol)
0.00	6.262	6.556				0.03	1×10^{23}	$\sim$ -0.33$\times10^{-4}$
0.05	6.264	6.554	2.85×10^{-4}	0.155	-1.5	6.3	1.5×10^{27}	
1.00	6.230*	6.431*				2.6	4.5×10^{27}	$\sim$ -0.78$\times10^{-4}$

$^\dagger T = 300$ 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, $\frac{C_{el}}{T} = \frac{(C-C_{lattice})}{T}$, in log$T$ scale. The lattice contribution $C_{lattice}/T$ is obtained from a linear fit to C/T vs T^2 at $H = 9$ T. The dependence of $(C - C_{lattice})$ 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, γ, is approximately 200 and 3 times greater than the γ values for pure $FeGa_3$ and $CoGa_3$, respectively. At finite H, $\frac{C_{el}}{T}$ saturates below a characteristic T, 0.7 K at 2 T and larger for higher fields, while the γ value decreases. The inset of Fig. 3 shows the decreasing γ for increasing H. $\frac{C_{el}}{T}$ 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 $CeCu_{5.2}Ag_{0.8}$ [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 γ value is inversely proportional to the saturation T. The latter is realized in $Fe_{0.95}Co_{0.05}Ga_3$ for 2 T $\leq H \leq$ 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 γ 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, $g(\varepsilon_F) = 1.14\times10^{42}$ states/J mol, corresponds to a Pauli susceptibility

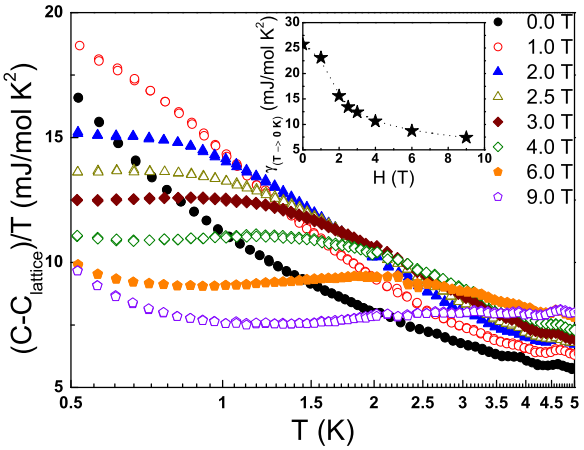

Figure 3. $(C - C_{lattice})/T$ vs log$T$ scale for $Fe_{0.95}Co_{0.05}Ga_3$ at $0 \leq H \leq 9$ T. Inset: γ at $T \to 0$ K, for the different H. The dotted line is guides to the eye.

of $\chi_{Pauli} = 9.78{\times}10^{-6}$ emu/mol ($\chi_{Pauli} = \mu_B^2 g(\varepsilon_F)$), and to a Sommerfeld coefficient of $\gamma_0 = 0.71$ 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 $\gamma_{exp.}/\gamma_0$, which is too large to be attributed to a band mass. Consistently with $\rho(T)$, $C(T)$ thus suggests HF behavior. Also, the calculated χ_{Pauli} is approximately 29 times smaller than the experimental value. The enhancement of χ_{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].

This work was supported by CNPq and FAPESP (Brazil) and NSF (USA).

References

[1] Häussermann U, Boström M, Viklund P, Rapp Ö and Björnängen 2002 *J. Solid Sate Chem.* **165** 94
[2] Jacarino V, Wertheim G K, Wernick J H, Walker L R and Arajs S 1967 *Phys. Rev.* **160** 476
[3] Petrovic C. Kim J W, Bud'ko S L *et al.* 2003 *Phys. Rev.* B **67** 155205
[4] Imai Y and Watanabe A 2006 *Intermetallics* **14** 722
[5] Amagai Y, Yamamoto A, Iida T and Takanashi Y 2004 *J. Appl. Phys.* **96** 5644
[6] Hadano Y, Narazu S, Avila M A, Onimaru T and Takanatake T 2009 *J. Phys. Soc. Jpn.* **78** 013702
[7] Tsujii N, Yamaoka H, Matsunami M *et al.* 2008 *J. Phys. Soc. Jpn.* **77** 024705
[8] Viklund P, Lindin S, Berastegui P and Häussermann U 2002 *J. Solid Sate Chem.* **164** 100
[9] Aeppli G, Fisk Z 1992 *Comm. Condens. Matter Phys.* **16** 155
[10] Fisk Z, Sarrao J L, Thompson J D, et al. 1995 *Physica B* **206-207** 798
[11] Manyala N, Sidis Y, DiTusa J F, Aeppli G, Young D P , Fisk Z 2000 *Nature* **404**, 581
[12] Manyala N, DiTusa J F, Aeppli G, Ramirez A 2008 *Nature* **454**, 976
[13] Canfield P C and Fisk Z 1992 *Philos. Mag.* B **65** 1117
[14] Heuser K, Scheidt E -W, Schreiner T and Stewart G R 1998 *Phys. Rev.* B **58** R15959
[15] Bianchi A, Movshovich R, Vekhter I, Pagliuso P G and Sarrao J L 2003 *Phys. Rev. Lett.* **91** 257001