Effect of Co substitution on the magnetic properties in Fe_{1-x}Co_xGa_3

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Abstract. We investigated the effect of Co substitution in Fe_{1-x}Co_xGa_3 by means of electric resistivity and magnetic measurements. Nearly ferromagnetic behaviors were observed in Fe_{1-x}Co_xGa_3 system by the chemical substitution of Co for Fe in diamagnetic mother compound FeGa_3, accompanying with a semiconducting to metallic transition. With the substitution of Co, the magnetization of Fe_{1-x}Co_xGa_3 increases first, and then decreases and finally it becomes diamagnetic. The magnetic properties of Fe_{1-x}Co_xGa_3 were analyzed in terms of self-consistent renormalization (SCR) theory and Takahashi’s theory. The spin-fluctuation parameters, fourth order expansion coefficients of magnetic free energy (\tilde{F}^4), the magnetic susceptibility in the ground state \chi(0), the spectral widths of the spin fluctuation spectrum T_0 and T_A in the frequency and wave-number spaces, respectively, were estimated from the parameters derived from magnetic measurements. The magnetic properties of Fe_{1-x}Co_xGa_3 can be understood almost quantitatively by the SCR theory and Takahashi’s theory of spin fluctuations.

1. Introduction
Various stoichiometric intermetallic compounds with unusual properties, such as magnetic, thermal, and strong correlated behaviors etc., have been discovered. Most of these compounds are found to be metallic. However there exist a few exceptions, such as semiconductors RuAl_2 [1], RuGa_3 [2], Fe_2VAl [3], and FeGa_3 [4], which draw great attention for prospective thermoelectric properties due to their complex band structures. The thermoelectric properties of these compounds are studied [5, 6, 7, 8] for such purpose, and high Seebeck coefficient values are achieved subsequently.

Among those intermetallic semiconductors, FeGa_3 has attracted much interest recently because of its intriguing magnetic behavior at finite temperature. FeGa_3 crystallizes into a tetragonal structure with space group of P4_2/mnm, and Fe atoms make pairs and form dimers within the ab plain in FeGa_3. The energy gap E_g of FeGa_3 was estimated to be around 0.3 to 0.5 eV by various methods, such as photoemission and inverse photoemission spectroscopic study [9], electronic resistivity measurements [4], magnetic measurement in the high-temperature region [10], which was confirmed by the band structure calculations based on the density functional theory [11, 12]. The energy gap is assumed to be formed by strong hybridization between
$d$ electrons of Fe and $p$ electrons of Ga. Yin et al. suggested the presence of the strong antiferromagnetic coupling between spins on Fe sites of Fe dimers leads to the formation of spin singlets [12]. Around 600 K, it shows the transition from semiconducting to a paramagnetic metal because of the thermally excited electrons above the energy gap [10]. Here we report paramagnetic properties of Co substituted Fe$_{1-x}$Co$_x$Ga$_3$ systems based on the SCR theory and Takahashi’s theory of spin fluctuations.

2. Experiment

Single crystals of Fe$_{1-x}$Co$_x$Ga$_3$ were grown with Ga-self flux method. A mixture of highly pure Fe, Co, and Ga elements in ratio of Fe : Co : Ga = 1-X : X : 9 (X ∈ [0, 1]) were placed and sealed in quartz ampoules. The mixture was melted and homogenized in a furnace at 1273 K and then cooled down to room temperature slowly. Excess Ga flux was removed by decanting and corrosion of HCl acid. The obtained single crystals were annealed at 700 K for weeks for homogeneity. The purity of obtained crystals were checked by Cu-Kα radiation, and lattice parameters were calculated using the Rietveld method. The chemical composition were measured by energy-dispersive x-ray spectroscopy (EDS). Magnetization curves were measured up to 7 T using a Quantum Design superconducting quantum interference device magnetometer. The electrical resistivity were measured by a home-built quadrupole electrical conductivity measuring apparatus from 5 to 300 K.

3. Results and Discussion

![Figure 1. Lattice parameters $a$ and $c$ as functions of $x$ for Fe$_{1-x}$Co$_x$Ga$_3$ represented by red squares and black squares, respectively.](image)

Structural characterizations at room temperature were carried out on powdered crystals of Fe$_{1-x}$Co$_x$Ga$_3$ using XRD, and no evidence of impurity phase was found in various Fe$_x$Co$_{1-x}$Ga$_3$. The lattice parameters were estimated by the refined diffraction patterns and shown in Fig. 1. The values of $a$ and $c$ are in good agreement with former reports [13, 14]. The Co substitution in FeGa$_3$ leads to monotonic decreases in both lattice parameters $a$ and $c$ with increasing $x$, following Vegard’s law.

Figures 2 and 3 show the temperature dependence of electric resistivity $\rho$ for mother compound FeGa$_3$ and Co-substituted Fe$_x$Co$_{1-x}$Ga$_3$, respectively. The resistivity of FeGa$_3$ shows a Kondo-insulator like behavior. In the range of temperatures $5 < T < 180$ K, electrons in donor levels are excited to conduction band by thermal energy and resistivity decreases with increasing temperature. FeGa$_3$ begins to show metallic behavior from 180 to 260 K, suggesting the electron donors are thermally activated and saturated in this range. The resistivity decreases again with further increasing temperature above 260 to 300 K, and is shown as the inset (a) on a logarithmic scale. As shown in the inset (a), the electric resistivity above 260 K is linear in logarithmic scale, and is well described by the Arrhenius law $\rho(T) = \rho_0 \exp[(E_g/(2k_BT))]$, which gives energy gap...
\( E_g \) of FeGa\(_3\) approximately equals to 0.4 eV, in agreement with former reports. The inset (b) resistivity follows \( \rho(T) \propto \exp\left[\frac{T_M}{T}\right] \) relation at low temperature, indicating the variable range hopping (VRH) among the Anderson localized states in 3D systems. Such dependence is also seen in few lightly doped semiconductors and Kondo-like insulators. Fig. 3 shows the effect of electron doping by Co substitution for Fe on normalized electric resistivity \( \rho(T)/\rho(300K) \) of Fe\(_{1-x}\)Co\(_x\)Ga\(_3\). The resistivity of Fe\(_{1-x}\)Co\(_x\)Ga\(_3\) increases with increasing temperature, and the residual resistivity ratio is relatively small, suggesting Fe\(_{1-x}\)Co\(_x\)Ga\(_3\) belongs to a bad metal.

The magnetic ordering was checked by the magnetization measurement as a function of applied magnetic field at 2 K in Fig. 4. Both end compounds, FeGa\(_3\) and CoGa\(_3\), are diamagnetic. The magnetization first increases with Co substitution and achieves maximum around \( x = 0.2 \), and then it decreases. The value of magnetization is significantly small, and no rapid increment nor saturation up to 7 T was observed in Fig. 4, indicating the paramagnetic nature of Fe\(_{1-x}\)Co\(_x\)Ga\(_3\) (0.1 \( \leq x \leq 0.7 \)). More clear evidence of no magnetic ordering can be gained from the Arrott plots of the magnetization curves of Fe\(_{1-x}\)Co\(_x\)Ga\(_3\) in Fig. 5 to Fig. 8 for various compositions. No intersection of the Arrott plot with the positive half of the \( M^2 \) axis at any temperature is regarded as a criterion of no spontaneous magnetic moment. The larger the intercept of Fe\(_{1-x}\)Co\(_x\)Ga\(_3\) obtained from Arrott plots at 2 K, the stronger magnetization is.
formed by the Co substitution.

Now we analyze the magnetic properties of Fe$_{1-x}$Co$_x$Ga$_3$ according to self-consistent renormalizaton (SCR) theory [15] and Takahashi’s theory [16, 17] of spin fluctuations based on the idea of crucial roles of spin fluctuations on various magnetic properties in itinerant electron magnets. According to SCR theory, the imaginary part of dynamical magnetic susceptibility $\chi''(q, \omega)$ is characterized by two important parameters, $T_0$ and $T_A$, the measures of distribution widths of the frequency $\omega$ and wave-vector $q$ spaces, respectively. In the SCR theory, another parameter, the mode-mode coupling constant $F_1$ is regarded as the independent theoretical parameter. For exchange enhanced paramagnets, according to Takahashi, new parameter $\sigma_p^2$ corresponding to spontaneous magnetic moment squared in units of $(2\mu_B)^2$ is defined by $\sigma_p^2 = N_0/\chi(0)F_1$. The temperature $T_p$ corresponding to the Curie temperature for ferromagnets is also defined by $T_p = t_pT_0$, with $t_p$ given by solving

$$A(0, t_p) = \frac{T_A}{15T_0}\sigma_p^2, \quad A(y, t) = \int_0^1 dz \left[ \log u - 1/2u - \psi(u) \right], \quad u = z(y + z^2)/t$$  \(1\)

where $y = N_0/[2TAX(T)]$ and $A(y, t)$ is the reduced thermal spin fluctuation amplitude as a function of the reduced inverse of magnetic susceptibility $y$ and reduced temperature $t = T/T_0$. 

({\text{Figure 5}}). Arrott plots of Fe$_{1-x}$Co$_x$Ga$_3$ with $x = 0.45$. 

({\text{Figure 6}}). Arrott plots of Fe$_{1-x}$Co$_x$Ga$_3$ with $x = 0.7$. 

({\text{Figure 7}}). Arrott plots of Fe$_{1-x}$Co$_x$Ga$_3$ with $x = 0.45$. 

({\text{Figure 8}}). Arrott plots of Fe$_{1-x}$Co$_x$Ga$_3$ with $x = 0.7$. 


The digamma function is denoted by ψ(u). With these parameters, $σ_p$ and $T_p$, magnetic properties of paramagnets can be treated in the same way as ferromagnets.

![Graphs showing temperature dependence of magnetic properties for different values of x.](image)

**Figure 9.** Estimation of $\bar{F}_1$ of Fe$_{1-x}$Co$_x$Ga$_3$ with $x = 0.1, 0.2, 0.45,$ and 0.7.

The parameter $\bar{F}_1$ represents the fourth expansion coefficient of the free energy in magnetization $M$ in the ground state, the value of which can be estimated from the inverse slope of the Arrott plot of magnetization curve. In Fig. 9, values of $\bar{F}_1(T)$ estimated at several temperatures corresponding to those in Figures from 5 to 8 for Fe$_x$Co$_{1-x}$Ga$_3$ are plotted. The values of $\bar{F}_1$ in the ground state are estimated by extrapolating the linear fitting of those at finite temperatures to zero temperature. They are given by 3.04, 0.75, 1.28, and 7.88 (×10$^7$ K) for $x = 0.1, 0.2, 0.45,$ and 0.7, respectively. According to the theory of spin fluctuations [15, 16, 17], the following relation is satisfied among $T_0$, $T_A$, $T_p$ and $σ_p^2$:

$$σ_p^2 = \frac{5T_0}{T_A} C_{4/3} \left( \frac{T_p}{T_0} \right)^{4/3}, \quad C_{4/3} = 1.00608 \cdots.$$  \hspace{1cm} (2)

By assuming the total spin-fluctuation amplitude is conserved (TAC) independently with temperature in Takahashi’s theory, $\bar{F}_1$, $T_A$, and $T_p$ follow:

$$\bar{F}_1 = 2T_A^2/15cT_0.$$ \hspace{1cm} (3)

where $c$ is defined as the $y$ linear coefficient of the zero-point fluctuation amplitude, given by 1/2 for Lorentzian distribution function [17]. In addition, we can estimate the value of $T_A$ from the $T^2$-linear coefficient of $1/χ(T)$ at low temperature by using:

$$T_A = \frac{1}{σ_p^2} \left( \frac{75c}{8α} \right)^{1/2}.$$ \hspace{1cm} (4)
where $\alpha$ is defined by the relation: $\chi(0)/\chi(T) = 1 + \alpha T^2$. Then, the inverse magnetic susceptibility can be calculated using above parameters with the expression:

$$y = \frac{1}{c}[A(y, t) + A(0, t_p)].$$

(5)

We calculated an inverse magnetic susceptibility for a typical composition $x = 0.45$. A comparison of the theoretical estimation versus experimental result for Fe$_{0.55}$Co$_{0.45}$Ga$_3$ is shown in Fig. 10. As shown in the figure, a tolerable agreement between experimental and calculated results are obtained, suggesting the importance of spin fluctuations in Fe$_{1-x}$Co$_x$Ga$_3$.

4. Summary

In summary, single crystals of Fe$_{1-x}$Co$_x$Ga$_3$ with various compositions were successfully synthesized. Co substitution for Fe site drives drastic changes in Fe$_{1-x}$Co$_x$Ga$_3$ on the electrical resistivity and the magnetic ground state. Transition from a diamagnetic mother host FeGa$_3$ to paramagnetic metals was observed. Magnetic properties of Fe$_{1-x}$Co$_x$Ga$_3$ system are discussed in terms of the SCR theory and Takahashi’s theory of spin fluctuations. The experimental and theoretical results achieved relatively good agreements with each other, suggesting the importance of spin fluctuations in Fe$_{1-x}$Co$_x$Ga$_3$ system.

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