Investigation of role of antisite disorder in pristine cage compound $FeGa_3$

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Abstract

The role of controlled disorder in the strong correlated narrow gap semiconductor candidate $FeGa_3$ has been investigated. Polycrystalline samples were synthesized by the combination of arc-melting furnace and successive annealing processes. Deviations of the occupation number of Fe and Ga sites from those expected in the pristine compound were quantified with X-ray analysis. Besides that, electrical transport and magnetization measurements reveal that hierarchy in Fe and Ga site disorder tunes the ground state of $FeGa_3$ from paramagnetic semiconducting to a magnetic metal. These findings are discussed within the framework of Anderson metal-insulator transitions and spin fluctuations.

Contents

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1 Introduction

The disorder is ubiquitous to realistic quantum materials. The presence of random defects, like vacancies, dislocations and impurities, is unavoidable in the sample preparation and usually are seen as unfavorable for novel quantum states in matter [1]. Although the presence of random disorder can diminish some intrinsic properties of a quantum material a controlled modification of disorder can be used as a driving force to investigate other emergent quantum phenomena that go beyond the scope of decoherence and localization of fermions inducing Anderson-localized states [2]. This is the case, for instance of antisite disorder in double pervoskites and low-dimensional oxides compounds, where exotic magnetic and electronic states emerge [3, 4]. Thus, to investigate the influence of antisite disorder on the correlations between electron and spin degrees of freedom is timely to set alternative routes to uncover new quantum states of matter.

$FeGa_3$ is a strongly correlated narrow-gap semiconductor candidate and has been widely studied because of its unconventional magnetic and electronic properties and as promising thermoelectric material [5–9]. Electrical resistivity measurements show an intrinsic activation gap ≈ 0.4 eV and indicate the presence of in-gap donor states just below the conduction band [10, 11], even in single-crystals. Although $FeGa_3$ has been widely accepted as a semiconductor, the inclusion of subtle amount of disorder might drive $FeGa_3$ to p-type metal [12]. Magnetic susceptibility and Mössbauer spectroscopy confirms the absence of magnetic order in pristine $FeGa_3$ [11, 13], in agreement with predicted by Density-Functional Theory (DFT) calculation [14]. However, neutron scattering shows the presence of a magnetic ground state, interpreted as a complex antiferromagnetic structure [15]. The chemical doping substitution in the solid solution $FeGa_{3-x}Ge_x$ induces a transition from a diamagnetic semiconductor to a ferromagnetic metal, with a putative quantum critical point at $x_c \approx 0.14$. However, the coexistence between long-range and short-range magnetic order above x_c suggests that disorder induced by random Ge substitution plays a important role in the zero temperature phase transition [16]. It is noteworthy that deviations from the electronic and magnetic ground states expected in pristine semiconductor $FeGa_3$ can be tuned by controlled disorder which can induce the formation of a complex structure of metallic in-gap states responsible for forming magnetic moments in the ground state [17, 18].

To advance the understanding of the interplay between antisite Fe disorder and electronic correlation in $FeGa_3$, we present an investigation of the influence of disorder in $FeGa_3$ polycrystalline samples with a controlled disorder. In addition we use different annealing temperatures to tune the concentrations of defects in the samples. We succeeded to synthesize $Fe_{1+\delta}Ga_3$ polycrystalline samples where tiny excess of Fe and antisite Fe disorder is reveled by X-ray diffraction (XRD), electrical transport and magnetic measurements. We investigated the evolution of electronic and magnetic properties under the influence of disorder.

2 Experimental

We prepared a polycrystalline $Fe_{1+\delta}Ga_3$ sample with nominal $\delta = 0.04$ using an arc-melt furnace with successive heat treatments. We melted high purity Ga and Fe pallets in a cold water-cooled copper crucible under an argon atmosphere at ambient pressure, the as-cast sample were ground in an agate mortar, and the powder subsequently homogenized in size. For the heat treatment, the samples were encapsulated in a quartz tube under vacuum $\approx 10^{-5}$ mTorr and different heat treatment temperature T_a for 24h and cooled down until ambient temperature using a 0.4 °C/min rate.

XRD diffraction were collected with a Diffractometer Rigaku Ultima III with angular step

of 0.02° and K_α-Cu wavelength. Magnetization is measured at ambient temperature using a vibrating-sample-magnetometer (VSM). For electrical transport measurements samples were compressed in circular pellets of 3 mm in diameter. Electrical resistivity (ρ) is measured in Van-der-Pauw configuration down to 16 K. Electrical contacts are prepared using 50 μm Cu wires and silver paint.

3 Results

Figure 1 shows the XRD patterns of the powdered samples at different annealing temperatures, T_a. The $P4_2/mnm$ space group symmetry of the $FeGa_3$ phase is confirmed by Rietveld refinement (RR) for all T_a. No spurious phase is observed in the resolution of our XRD instrumentation. The lattice parameters in the as-cast sample $a = 6.2645(4)$ Å and c=6.5568(7) Å are in agreement with those values reported in literature for single-crystals [18]. Under heat treatment we did not observed significant change in the lattice parameter.

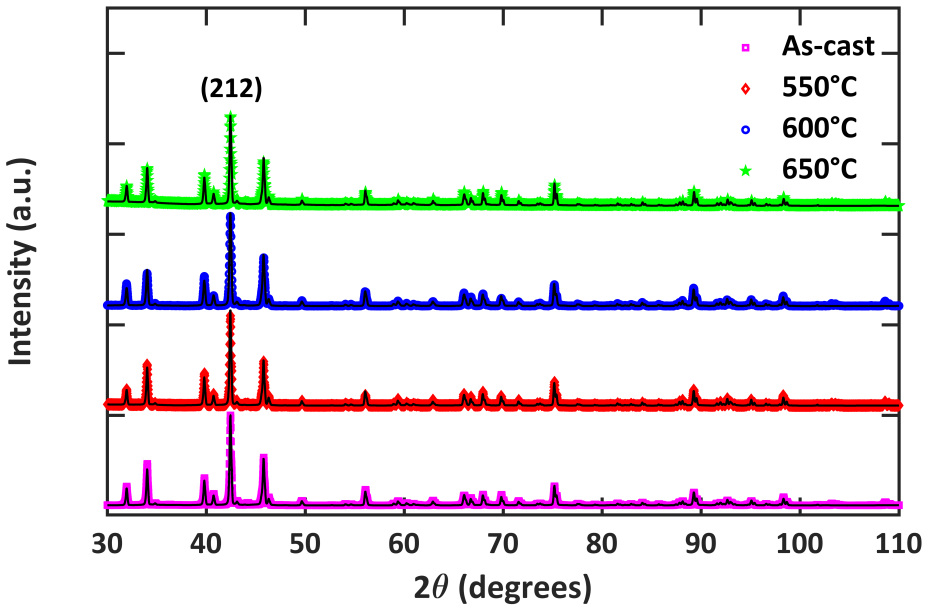

Figure 1: Experimental (open points) and calculated (black line) XRD patterns of annealed $FeGa_3$ samples .

The model used for the RR considers the possibility of antisite disorder between the atomic sites. It means Fe atoms partially occupy Ga sites and vice versa. We use this model because including antisite disorder in the RR has improved the intensity-based R-factors parameters for all the samples. In the not disordered case, the R_{Bragg} factor (weighted profile R-factor, based on the structure factors [19]) for the samples, as-cast and annealed at 550°C, 600°C, and 650°C, are respectively, 7.36%, 10.23%, 9.89%, and 13.37%. When antisite disorder is included in the model, the R_{Bragg} are reduced to 6.92%, 9.7%, 9.57%, and 13.27% in the same order.

From our XRD data we compute the structure factor as function of q-vector $S(q)$ for as-cast and annealing-temperature samples. Figure 2 depicts the difference between $S(q)$ respect to the structure factor expected for the pristine $FeGa_3$ polycrystal, $S_p(q)$. We can infer from Figure 2 that the most pronounced deviation of $S(q)$ from the $S_p(q)$ implies more random disorder, where the extreme case is associated with the as-cast sample.

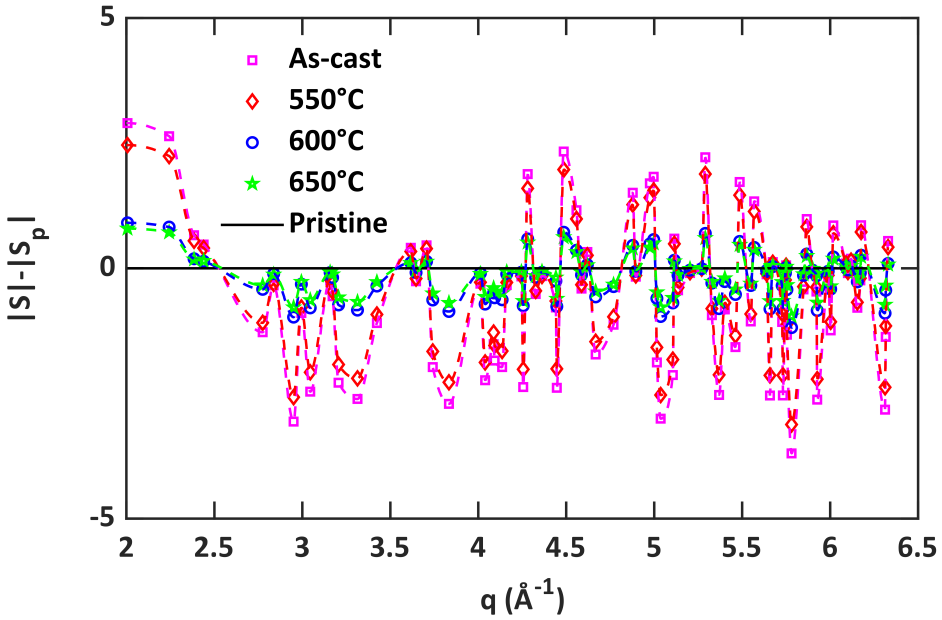

Figure 2: Difference between the structural factor $S(q)$ for $FeGa_3$ polycrystalline samples annealed with different temperatures with respect to the structure factor expected for the pristine $FeGa_3$ polycrystal, $S_p(q)$.

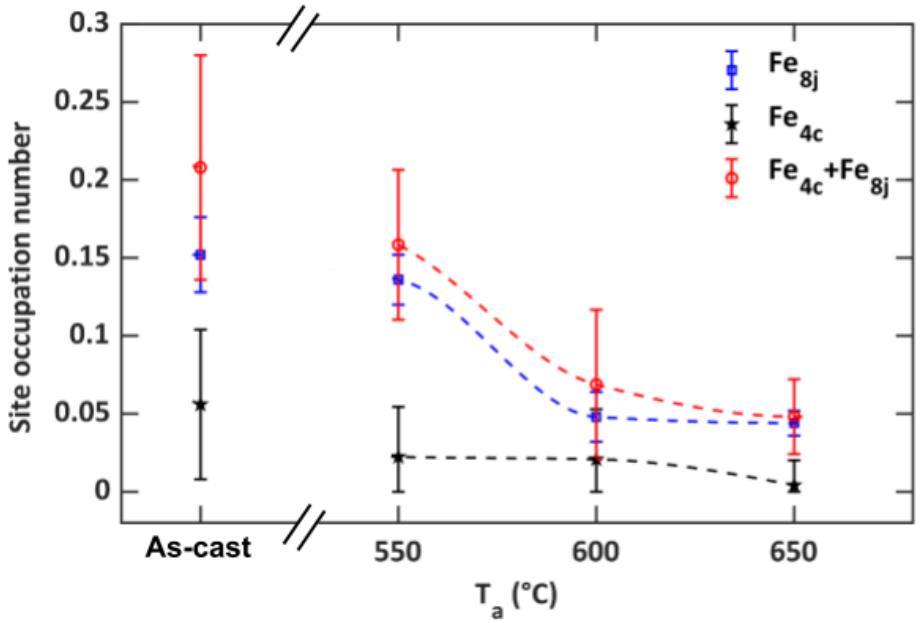

Figure 3: Site occupation number (SON) of antisite Fe as function of annealing temperature and compared with SON for as-cast sample. Where Fe can occupy different non-equivalent crystallographic sites. The dashed lines are guide for the eyes.

Fluctuations on the site occupation number (SON), defined as chemical occupancy times site multiplicity normalized to the multiplicity of the general position of the group, reveal the presence of Fe atoms at the inequivalent crystallographic positions $4c$ and $8j$, which are occupied only by Ga atoms in the pristine compound.

Figure 3 shows that the number of antisite Fe decrease as T_a increases, indicating the annealing induces a more ordered crystallographic structure, in the temperature range investigated in this work. This also agrees with $S(q)$ plotted in Figure 2, where the structure factor approaches to that expected for the pristine compound $FeGa_3$ as annealing temperature increases.

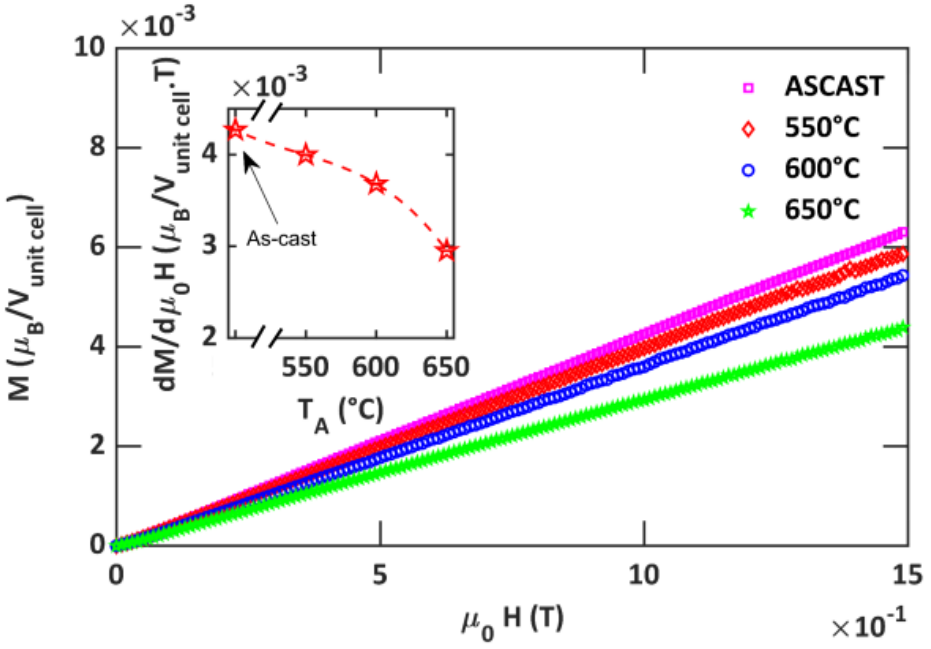

Figure 4: Field dependence of the magnetization at room temperature for different annealing temperatures. The inset shows the annealing temperature dependence of the magnetic susceptibility at ambient temperature.

The field dependence of the magnetization (M), figure 4, shows that the inclusion of antisite Fe induces a magnetic state on the samples. The linear dependence of M with the field indicates a paramagnetic behavior at ambient temperature. The increase of T_a lowers the magnetic susceptibility $\frac{dM}{d\mu_0 H}$ in the samples, caused likely by lower presence of antisite Fe and thus the magnetic moments.

The electrical resistivity (see figure 5) shows that the annealing induces significant changes in the electronic states. Starting from the as-cast specimen, $\rho(T)$ shows a metallic behavior. Subsequent annealing induces an upturn on $\rho(T)$ at $T \approx 200K$ attributed to a semiconducting extrinsic response due to in-gap donors states. This metal-semiconductor transition oppositely to that is reported in $FeGa_{3-x}Ge_x$, where a system undergoes to a putative QPC at the diamagnetic/semiconducting-ferromagnetic/metallic phase transition [20]. The metal-semiconductor transition is possibly related to the fact that the annealing decreases the concentration of antisite Fe.

The Arrhenius law can well describe the electrical resistivity of the annealed samples, $\rho \propto e^{E_g/2k_bT}$, in the range of 100 K-160 K, where E_g is the energy separation from in-gap donor states to the conduction band (figure 5 (b)). The E_g decreases with T_a, indicating that the donor states are near the conduction band. The linear dependence of ρ with T^2, figure 5 (c), shows a Fermi-Liquid behavior for the as-cast sample, with quadratic coefficient A_f of 0.38(2) $\mu\Omega cm/K^2$. The large A_f indicates a strong renormalization on the effective electronic mass, possibly induced by the presence of strong electronic correlations, or spin fluctuations, as well as by the enlargement of the phase space available for momentum relaxation resulting from the softening of the kinematic constraints due to disorder [21]. The metallic sample

shows a $\rho \propto T^{5/3}$ dependence from 90 K-230 K, (5 (d)), followed by a slow saturation at higher temperatures. This behavior is consistent with the self-consistent renormalized (SCR) spin fluctuation theory, showing the presence of paramagnetic or ferromagnetic spin fluctuations [22, 23].

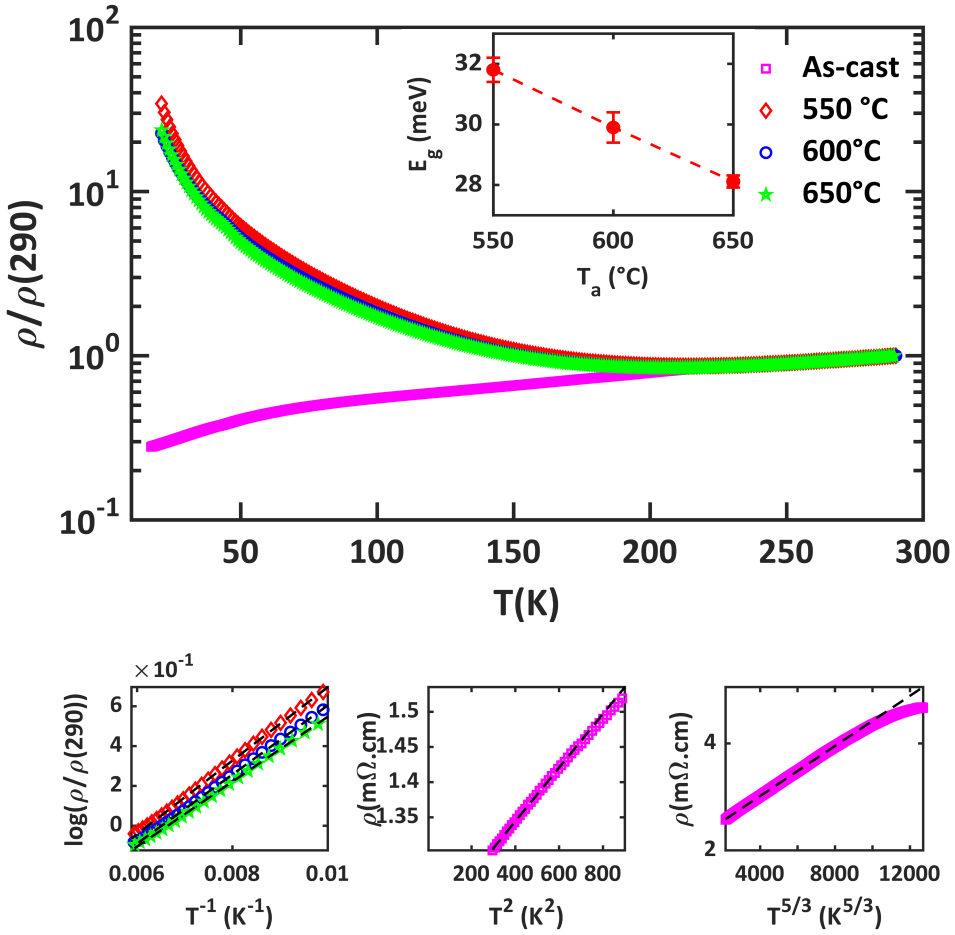

Figure 5: Figure (a): Temperature dependence of normalized electrical resistivity of $FeGa_3$ annealed at different T_a. The inset shows the temperature dependence of the energy gap from the in-gap donor state to the conduction band, lines are guide for the eyes. Figure (b): Arrhenius plot at 100 K to 160 K temperature range for the annealed samples. Figure (c): Low temperature T^2 dependence of electrical resistivity of not annealed sample. Figure (d): $T^{5/3}$ dependence of electrical resistivity of not annealed sample .

4 Discussion

Recent Density Functional Theory (DFT) calculations have predict that the presence of intrinsic disorder in $FeGa_3$ can induce the formation of in-gap states responsible for forming magnetic moments in the system's ground state [17]. Low-temperature magnetization measurements have shown the development of ferromagnetic ordering for non-stoichiometric Fe-rich $FeGa_3$ single crystals and the formation of this magnetic state was addressed to disorder-induced magnetic metallic in-gap states [18]. Electrical transport and spin-lattice relaxation experi-

ments have indicated the presence of magnetic in-gap states intrinsic to $FeGa_3$ [24]. These previous results corroborate the scenario where the presence of Fe disorder is responsible for the emergence of in-gap states, near the conduction band, which turns out also in the paramagnetic behavior observed in this work.

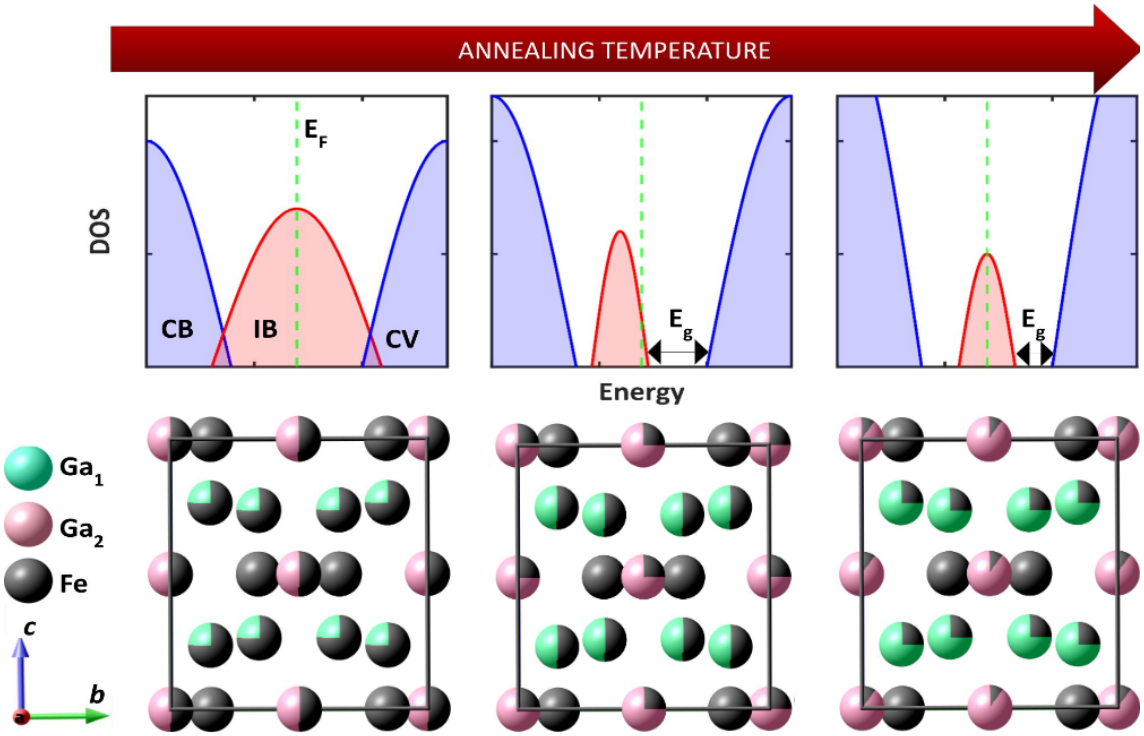

Figure 6: Schematic representation of the primitive unit cell and electronic band of $Fe_{1+\delta}Ga_3$ in function of annealing temperature. CB = conduction band, VB = valence band, IB = intermediate in-gap band and E_g is the extrinsic gap, that deceases with pressure. The semi-filled spheres represents the amount of antisite Fe at the Ga positions.

XRD indicates that as the temperature of annealing increases, the density of antisite Fe defects decreases, and it can induce a reduction of in-gap states near the Fermi energy, which explain the decrease of the magnetic susceptibility at ambient temperature with T_a.

The scenario of in-gap states can also be used to explain the metal-insulator transition observed in our investigation. A metal-insulator Anderson transition occurred when the number of defects on the sample increased to a critical concentration called the percolation threshold. Below the critical concentration of defects, the in-gap states are localized due to the Anderson-localization effect [2]. On the other hand, as discussed by Mott, as the number of impurities approaches the critical concentration, the mobility edges (energies that separate localized states in the band tails from delocalized extended states in the center of the impurity band) shift towards the band edges and above a critical point, all the impurity states become delocalized, inducing a metallic behavior in the system [25]. Therefore as the annealing temperature increases and the number of Fe-based defects are reduced, the band-edges of the impurity band (IB) shrink, separating the localized in-gap states from the delocalized extended states placing IB within the semiconductor intrinsic gap (see figure 6). It is possible to estimate the impurity activation gap (E_g) (plotted in the inset of figure 5 (a)). The decrease of E_g with the annealing temperature before $Fe_{1+\delta}Ga_3$ amorphyzes suggests that the localized impurity states approaches the conduction band and an associated reduction of the disorder bandwidth, even that the localized impurity concentration continues to decrease.

The high concentration of defects in the as-cast sample induces delocalization of the interband in-gap states, generating a metallic behavior. The $T^{5/3}$ dependence of the ρ in a wide range of temperatures, followed by slow saturation, indicates the presence of spin fluctuations, which causes the renormalization of the quadratic coefficient at low temperatures. Spin-fluctuations are also observed in the metallic-ferromagnetic phase of $FeGa_{3-x}Ge_x$ to high dopant concentration and mediate marginal Fermi-liquid state on the border of ferromagnetism near the critical point [16]. The presence of spin-fluctuations induced by strong antisite disorder in our as-cast samples recalls the scenario that spin-dynamics might play a relevant role in the quantum critical behavior and non-canonical quantum critical material phase of $FeGa_{3-x}Ge_x$ system, which is tuned to a putative FM-QPC by random substitution of Ge [16]. These findings motivate the low-temperature investigation of the magnetic properties of $Fe_{1+\delta}Ga_3$ to identify the magnetic ground state's nature and the spin-fluctuations role in the sample in the disordered metallic phase.

5 Conclusion

The effect of controlled antisite disorder in $FeGa_3$ on the electronic, magnetic and crystallographic structure has been studied in polycrystalline $Fe_{1+\delta}Ga_3$ samples with a slight excess of Fe.

The Fe-defects induce paramagnetic and metallic states at ambient temperature. Subtle decrease of impurities in the samples induced by annealing reduces the magnetic susceptibility and drives the samples from a disordered correlated metal with spin fluctuations to a magnetic narrow-gap semiconductor. The later is possibly due to the transition of a delocalized impurity band to localized in-gap states as the number of defects approaches the percolation threshold. These findings contributes to a better understanding of the role of disorder in $FeGa_3$ and motivates further studies of the nature of the disordered-driven semiconductor-metal transition in $FeGa_3$ and the role of spin-fluctuation and strong correlations.

Acknowledgements

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