

Synthesis and characterization of the semiconducting intermetallic compound FeGa_3

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Abstract. FeGa_3 polycrystalline samples were synthesised using the gallium self flux method. The stoichiometry was confirmed via energy dispersive spectroscopy and the tetragonal crystal structure was refined from X-ray diffraction data. Mössbauer effect spectroscopy was performed down to 120 K at ambient pressure, as well as at 3 K and 4 GPa in a diamond anvil pressure cell, and shows an absence of magnetic ordering at these temperatures and pressures. The isomer shift and quadrupole splitting are consistent with a $3+$ charge state for Fe with a $5/2$ spin state.

1. Introduction

Materials with complex band structure have very interesting electronic, magnetic and transport properties [1]. Recent phenomena such as the Kondo insulating state, heavy fermion behaviour and unconventional superconductivity have been reported for those materials [2]. Such phenomena are usually seen in the rare-earth compounds where the hybridization between different electrons in the atoms forms narrow electronic bands or pseudo-gaps at the Fermi level [3].

Ruthenium and iron compounds (such as RuAl_2 , RuGa_3 , FeSi , FeSb_2 , Fe_2Al_2 and FeGa_3) are semiconductor compounds in which the energy gap, of the order of 0.1 eV, is formed by the hybridization between the d states of the transition metal with the p states of the group 13 or 14 elements [2]. These compounds are of interest due to their unusual transport and magnetic behaviour [4]. Amongst the above compounds, FeSi and FeSb_2 show strong correlated electron properties similar to rare-earth based Kondo semiconductors. The distinguishing feature between a Kondo semiconductor and a band-gap semiconductor is that, in the Kondo semiconductor, the gap disappears upon heating already at temperatures and energies lower than the energy gap. This feature has been observed in both FeSi and FeSb_2 in the temperature dependence of the optical conductivity [5].

FeGa_3 is one of such intermetallic compounds which are composed of metallic elements, and yet their combination is a semiconductor. The band gap in FeGa_3 arises in particular from the hybridization between the Fe $3d$ and Ga $4p$ states [6]. FeGa_3 crystallizes in the tetragonal lattice with space group $P4_2/mnm$ (No. 136) [7]. In the tetragonal structure of FeGa_3 , Fe atoms occurs as dimers along the (110) and $(\bar{1}\bar{1}0)$ directions, as it shown in figure 2 (b). The band gap of this compound has been measured experimentally using photoemission spectroscopy and predicted using density functional theory calculations within the local density approximation, where it was found to be in the range 0.3 - 0.5 eV [6, 8]. This value is in good agreement with the observed

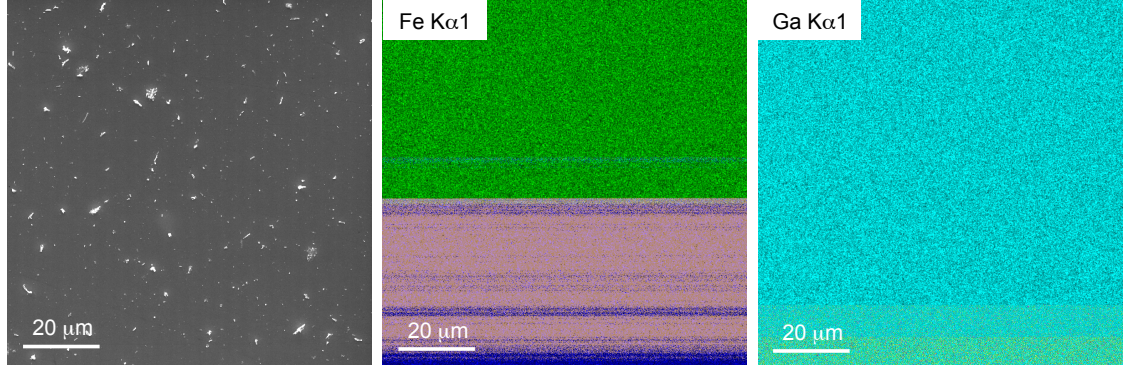


Figure 1. Representative SEM image and EDS compositional maps of a polished FeGa₃ sample. A uniform distribution of the elements Fe and Ga is observed.

gap of 0.25 - 0.47 eV previously reported for FeGa₃ [5, 7, 9, 10]. Lue *et al.* observed metallic conductivity above 10 K in their electrical resistivity measurements [8]. The resistivity exhibits a minimum at 160 K, below which it has negative temperature coefficient (semiconducting) and above 160 K there is a typical metallic-like trend (positive temperature coefficient) [6].

The magnetism of FeGa₃ is subject to debate and has not yet been directly observed. Some measurements such as conductivity, magnetic susceptibility, Mössbauer spectroscopy and specific heat have not shown strong magnetic correlations. This justifies the absence of magnetism at room temperature [8, 11]. Recently, weakly coupled local moments have been suggested in Co-doped FeGa₃ by Bittar *et al.* [12]. In particular they postulate that the doping creates spin-1/2 local moments and drives the compound from semiconducting to the metallic state [12]. Work done by Umeo *et al.* [4] pointed out that electron-type doping in this compound using Ge introduces a crossover to a correlated metallic state at $y \approx 0.006$ in FeGa_{3-y}Ge_y.

Here, we report on the synthesis and the characterisation of FeGa₃ polycrystalline samples. Mössbauer effect spectroscopy measurements have been performed down to 120 K at ambient pressure, as well as at 3 K and at a pressure of 4 GPa. All the spectra show the characteristic line shape of a quadrupole split doublet consistent with an Fe³⁺ charged state and a 5/2 spin state. No evidence for a magnetic state has been detected, contrary to theoretical and experimental work which propose spin polarons [11] and Fe dimers [13], respectively.

2. Experimental Details

FeGa₃ polycrystalline samples were prepared via the self flux method described in Ref. [8]. High purity Ga (from Alfa Aesar, 99.99999%) and Fe (from Sigma Aldrich, 99.9%) were mixed according to the molar ratio Fe₁₅Ga₈₅. The mixture was pressed into a pellet and loaded into an alumina crucible which was vacuum sealed ($p \sim 10^{-5}$ Pa) inside a quartz ampoule under argon gas. The sample was heated to 1000 °C at a rate of 500 °C/hr, held at this temperature for 40 hrs, cooled down to 850 °C for 12 hrs, cooled down again to 700 °C for 75 hrs and finally allowed to cool to room temperature. Excess gallium was removed by heating the pellet and washing with dilute HCl and deionised water. A photograph of the FeGa₃ sample (showing large facets) is shown in figure 2 (c).

The crystalline structure was checked by means of x-ray diffraction (XRD) measured with monochromatic Cu K_α radiation on a powdered specimen using a Philips Analytical X-Pert PRO system. The XRD pattern was refined using the Jana 2006 program [14]. The stoichiometry and the compositional homogeneity were checked with energy dispersive spectroscopy (EDS) using a Tescan Vega3 electron microscope equipped with an Oxford EDS spectrometer. From the EDS multi-spot analysis it was consistently found to be at the nominal value, within the detection

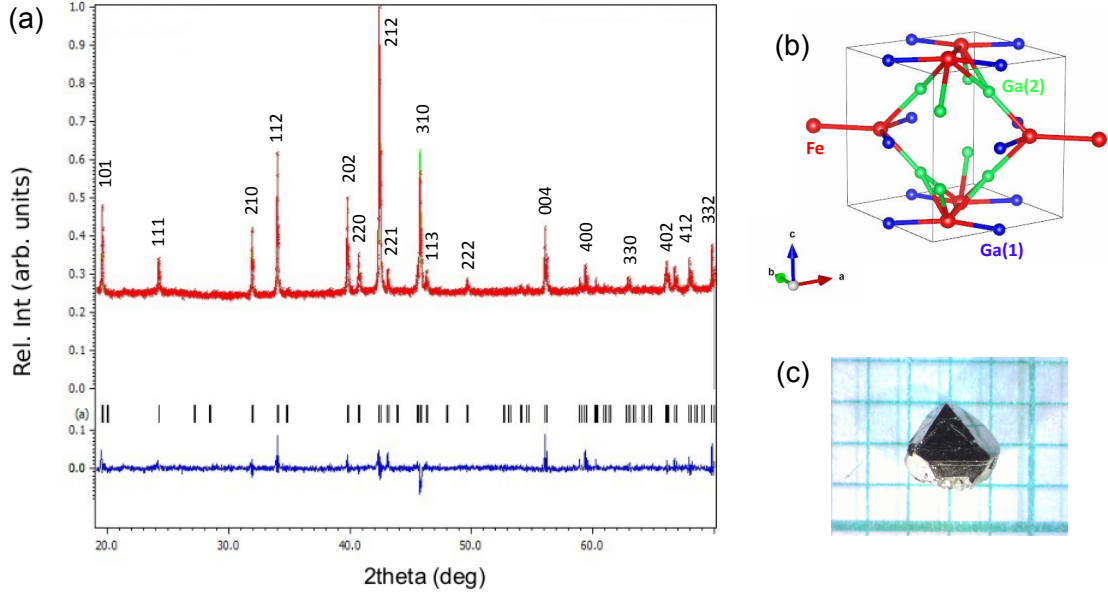


Figure 2. (a) Experimental indexed XRD pattern for FeGa_3 (red) along with the Rietveld refinement (green). The peak positions are represented by vertical bars (black), while the residual is in blue. (b) Schematics of the tetragonal unit cell of FeGa_3 , where Fe atoms are represented by bigger red circles, and Ga(1) and Ga(2) atoms are represented by smaller blue and green circles respectively. The Fe-Fe dimers are shown connected via red bars. (c) One block in the photograph represents a scale of 1 mm.

Table 1. Structural parameters obtained from the Rietveld refinement of the crystal structure based on the x-ray powder diffraction pattern measured at room temperature.

Lattice parameters	values	atom	Wyckoff site	x	y	z
$a(\text{\AA})$	6.2636	Fe	4f	0.3426(11)	0.3444(11)	0
$b(\text{\AA})$	6.2636	Ga(1)	4c	0	0.5	0
$c(\text{\AA})$	6.5550	Ga(2)	8j	0.1565(5)	0.1565(5)	0.2633(7)

limits of the technique ($\text{FeGa}_{2.97 \pm 0.03}$). EDS elemental maps confirmed the homogeneity of the samples, as reported in figure 1.

The sample was crushed into powder to a thickness of $\sim 11 \text{ mg/cm}^2$ to perform Mössbauer spectroscopy measurements. A constant acceleration spectrometer with a conventional $^{57}\text{Co}(\text{Rh})$ source was used for Mössbauer measurements at ambient pressure. Measurements to low temperature were performed in a top-loading cryostat, with both source and sample kept at the same temperature. The Mössbauer spectrum at 3 K and $p = 4 \text{ GPa}$ was measured at the beamline ID18 at the European synchrotron radiation facility [15] using the synchrotron Mössbauer source (SMS). The sample was loaded into a Merrill-Basset diamond anvil cell (DAC). Sample was pressurized in $200 \text{ }\mu\text{m}$ cavity of a Re gasket pre-indented to a thickness of $20 \text{ }\mu\text{m}$. Pressure was determined from the ruby fluorescence of tiny balls inserted in the cavity [16]. All spectra were calibrated with respect to $\alpha\text{-Fe}$.

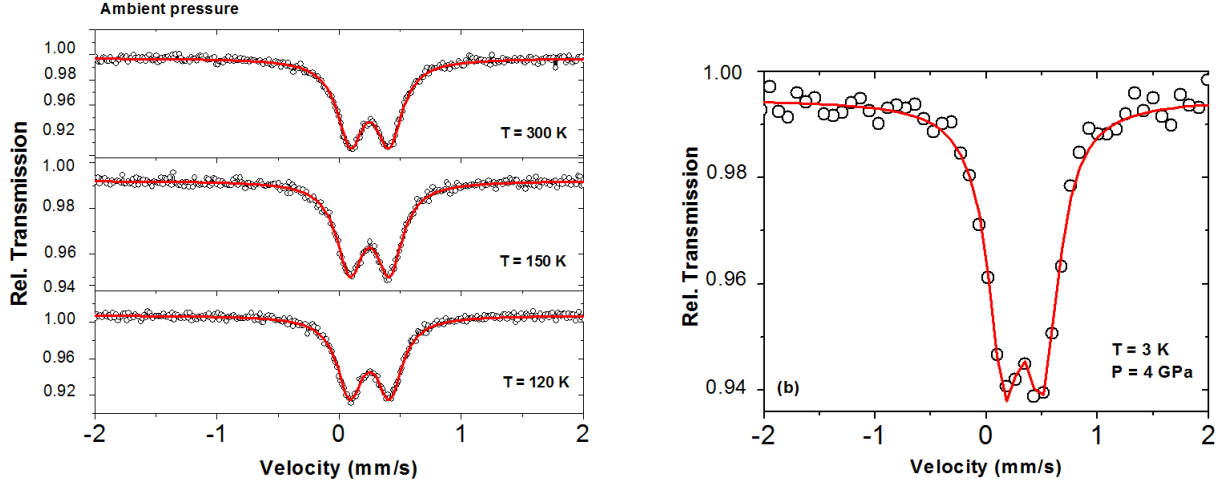


Figure 3. (a) Mössbauer spectra of the powdered sample recorded at 300 K, 150 K and 120 K at ambient pressure. (b) Mössbauer spectrum measured at ID18 at 3 K and 4 GPa. The solid red lines indicate the fit to the experimental data (open black circles).

3. Results and discussion

Figure 2 (a) shows the XRD pattern for FeGa₃. The Rietveld refinement of the diffraction pattern confirmed the tetragonal space group $P4_2/mnm$ and $Z = 4$. The lattice parameters and atomic positions obtained from the refinement are presented in table 1. These are in good agreement with values reported by Häussermann [6] and Lue [2].

The Mössbauer spectra of FeGa₃ recorded at 300 K, 150 K and 120 K are shown in figure 3. They have been fitted with a single quadrupole doublet, and the parameter values derived from fits to these spectra are presented in table 2. Our results at 300 K are similar to what has been previously reported by Tsujii *et al.* for FeGa₃ single crystals at room temperature [8]. The data presented in table 2 show that: (i) no deviation occurs in the isomer shift (δ) and the quadrupole splitting (ΔE_Q) at these temperatures; (ii) the value of the isomer shift (δ) and the quadrupole splitting ΔE_Q indicate that iron (III) is present in the 5/2 spin state.

A particular feature of the Mössbauer spectra is the quadrupole split doublet. The similar profile at all measured temperature indicates good phase purity and there is no indication of Fe-based amorphous/ disordered phases which would be difficult to detect by XRD. The sample under pressure shows broadened peaks, which are due to the SMS source. There is no indication of magnetic ordering down to temperatures of 120 K at ambient pressure and down to 3 K at 4 GPa (these would manifest as resonance dips in the wings of the spectrum).

Table 2. Parameters derived from fitting the Mössbauer spectra of FeGa₃.

	ΔE_Q (mm/s)	δ/Fe	Γ (mm/s)
T = 300 K, amb. p	0.32	0.28	0.26
T = 150 K, amb. p	0.33	0.38	0.26
T = 120 K, amb. p	0.33	0.38	0.25
T = 3 K, p = 4 GPa	0.33	0.33	0.35

4. Conclusion

In conclusion, we have synthesised and characterized FeGa₃. Single phase, homogeneous, polycrystalline FeGa₃ was obtained. This forms the basis for future studies of the electrical-transport behaviour under pressure, where a semiconductor-metal transition (correlation gap closure) is predicted to occur [1]. Importantly, Mössbauer-effect spectroscopy shows the absence of the magnetic ordering down to 120 K at ambient pressure and down to 3 K at 4 GPa. This sets the energy scale for magnetic coupling, which is either absence or is likely below ~ 3 K at pressure up to ~ 4 GPa. It is of interest to consider this in conjunction with recent electronic structure calculations which predict an Fe magnetic moment of $\sim 0.6\mu_B$ and antiferromagnetic coupling between the atoms in the Fe₂ pairs of the structure [13].

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