Spin dynamics of FeGa$_{3-x}$Ge$_x$ studied by electron spin resonance

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Abstract
The intermetallic semiconductor FeGa$_3$ acquires itinerant ferromagnetism upon electron doping by a partial replacement of Ga with Ge. We studied the electron spin resonance (ESR) of high-quality single crystals of FeGa$_{3-x}$Ge$_x$ for $x$ from 0 up to 0.162 where ferromagnetic order is observed. For $x=0$ we observed a well-defined ESR signal, indicating the presence of pre-formed magnetic moments in the semiconducting phase. Upon Ge doping the occurrence of itinerant magnetism clearly affects the ESR properties below $\approx 40$ K, whereas at higher temperatures an ESR signal as seen in FeGa$_3$ prevails independent on the Ge content. The present results show that the ESR of FeGa$_{3-x}$Ge$_x$ is an appropriate and direct tool to investigate the evolution of 3d-based itinerant magnetism.

Keywords: itinerant ferromagnetism, electron spin resonance, correlated semiconductor

(Some figures may appear in colour only in the online journal)
conduction electron spin resonance (CESR) in itinerant magnets shows a narrow and observable linewidth in the presence of ferromagnetic correlations. This holds, in particular, for Kondo lattice systems like YbRh$_2$Si$_2$ and CeRuPO [7] but also for 3d itinerant magnets such as ZrZn$_2$ [8, 9], Sc$_{1.12}$In [10], TiB$_2$ [11], or NbFe$_2$ [9, 12]. Recently, the interplay between a CESR and ferromagnetism was investigated for Cr$_2$B where a paramagnetic to ferromagnetic transition is induced by Fe-doping [13]. Without ferromagnetic correlations the CESR linewidth is mainly determined by spin-flip scattering which also determines the electrical resistivity.

In this paper we could interpret the spin resonance in FeGa$_{3-x}$Ge$_x$ in a dual way: at low temperatures and $x > 0.06$ in terms of a CESR with strong ferromagnetic correlations and at high temperatures in terms of a resonance of local spins.

2. Experimental

ESR probes the absorbed power $P$ of a transversal magnetic microwave field as a function of an external magnetic field $\mu_0 H = B$. To improve the signal-to-noise ratio, a lock-in technique is used by modulating the static field, which yields the derivative of the resonance signal $dP/dB$. The ESR experiments were performed at X- and Q-band frequencies ($\nu = 9.4 \text{ GHz}$ and $34 \text{ GHz}$) using a continuous-wave ESR spectrometer. The sample temperature was set with a helium-flow cryostat allowing for temperatures between 2.7 and 300 K and a nitrogen-gas flow cryostat for temperatures up to 500 K.

The obtained spectra were fitted by a Lorentzian line shape yielding the parameters linewidth $\Delta B$ which is a measure of the spin-probe relaxation rate, and resonance field $B_{\text{res}}$ which is determined by the effective $g$-factor ($g = \frac{\hbar \nu}{\mu_0 B_{\text{res}}}$) and internal fields. The fitting included also a dispersion-to-absorption ratio $D/A$ from metallic contributions, as was done for the ESR spectra in the ferromagnetic metal NbFe$_2$ [12]. $D/A$ parametrizes an asymmetry in the lineshape. $D/A = 1$ refers to ESR spins within the microwave skin depth which is smaller than the sample thickness due to the electrical conductivity. The ESR intensity $I_{\text{ESR}}$ corresponds to the integrated ESR absorption and was calculated using the line amplitude, line width and $D/A$ as reported in [14]. $I_{\text{ESR}}$ is determined by the static spin-probe susceptibility, i.e., it provides a direct microscopic probe of the magnetic system.

High-quality, ultrapure single crystals of FeGa$_3$ and FeGa$_{3-x}$Ge$_x$ were grown by the Czochralski method from Ga-rich solutions at temperatures below the peritectic transformation. Whereas for FeGa$_3$ the crystal growth has already been described elsewhere [15] the problem with FeGa$_{3-x}$Ge$_x$ was the missing ternary Fe–Ga–Ge phase diagram. We assumed only a weak change of the liquidus by adding small amounts of Ge (bulk, 99.999%, ChemPur) and did a couple of normal freezing experiments in order to determine the solid-phase compositions being in equilibrium with various ternary Ga-rich solutions. From this, we found a pseudobinary segregation coefficient $< 1$ resulting in a slight axial increase of the Ge content along the growth direction. Starting in three Czochralski growth runs with ternary solutions in which 2.35, 5.0, and 5.75% of the Ga was substituted with Ge, we got FeGa$_{3-x}$Ge$_x$ single crystals in the range $0.054 \leq x \leq 0.165$. All Czochralski-grown crystals were pulled along the [001] direction using undoped FeGa$_3$ seeds and very low pulling rates of $0.05–0.1 \text{ mm h}^{-1}$. The ESR experiments on FeGa$_{3-x}$Ge$_x$ were performed on pieces cut from these crystals showing an axial Ge concentration gradient. This gradient was determined by electron probe microanalysis (WDX). We studied samples with $x = 0, 0.06, 0.127, 0.133,$ and $0.162$.

3. Results

The observed ESR in FeGa$_{3-x}$Ge$_x$ shows two different and independent types of spectra, one with and one without dispersive (i.e., metallic) contribution. The metallic type appears only for higher Ge concentrations ($x > 0.06$) and only for temperatures below $\approx 40 \text{ K}$. This appearance of metallic properties is remarkable as it has not been observed in results of NQR [3] and $\mu$SR [6]. The other type of signal is much weaker than the first type and is seen above $\approx 40 \text{ K}$ (for $x = 0$ above $5 \text{ K}$) up to the highest investigated temperature of $500 \text{ K}$. The presence of these two different spectra types indicates the complex way magnetism is created in FeGa$_{3-x}$Ge$_x$, which is a topic that recently came into focus [5]. In the following we present and discuss the ESR spectra for undoped FeGa$_3$ and the effect of Ge-doping on the spectra.

3.1. FeGa$_3$

Typical ESR spectra in the high- and low-temperature regimes are shown in the left frame of figure 1. The noise level indicates their small intensity which is in the order of the background intensity. Therefore, the shown spectra are obtained from subtracting a broad background signal. The lines were fitted by Lorentzians yielding temperature-dependent parameters as shown in the right frame of figure 1. The spectra consist of two well-defined resonance lines, a broad and a narrow one, denoted as line 1 and line 2. The narrow line appears at temperatures below $\approx 40 \text{ K}$ whereas the broad one is observable in the whole temperature range $5–300 \text{ K}$. Both lines appear at resonance fields corresponding to a $g$-value of 2.05. This indicates a configuration $3d^6$ (Fe$^{3+}$) rather than $3d^6$ (Fe$^{2+}$) for which, due to contributions from the orbital momentum, a much larger $g$-value is expected [16].

We interpret the narrow line 2 as a resonance of Fe impurity centers because its intensity is very small ($\approx 1000$ times weaker than line 1, note the intensity scale in figure 1) and line 2 is not reproducible in samples from different batches.

Regarding line 1, it is important to note that very similar lines are also observed in the Ge-containing FeGa$_3$ (see the following section). This particularly holds for the temperature dependencies of all ESR parameters as shown in the right frame of figure 1 where the dashed lines refer to the Ge concentration $x = 0.127$. For both $x = 0$ and $x = 0.127$ (and all the other Ge concentrations, see figure 2) a continuous increase of $\Delta B$ and decrease of $B_{\text{res}}$ is observed towards low temperatures (discussion in the following paragraph). The ESR intensity
shows a clear Curie law \( I_{ESR} \propto 1/T \) which indicates the local character of the ESR-active probes.

At high temperatures a remarkable kink in linewidth and intensity occurs. It originates from an additional line superimposed on line 1 as indicated by the blue arrow in figure 1. Near above \( \approx 400 \) K this line dominates the single-Lorentzian line fitting. With further heating this additional line gets narrower and less intense, which is characteristic for paramagnetic centers near magnetic order. Thus the appearance of this spectral feature suggests the onset of magnetic order near
below 400 K of some of the paramagnetic centers. This conclusion is consistent with neutron diffraction measurements which indicate antiferromagnetic order in FeGa₃ above 300 K [17]. The presence of the Fe-rich foreign phase Fe₃Ga₄ with its magnetic transition at 360 K [18] should also be taken into account to understand features at high temperatures. However, the influence of Fe₃Ga₄ on the low-temperature ESR properties should be negligible because, as indicated by the small and noisy ESR intensity, its concentration seems to be tiny.

### 3.2. FeGa₃₋ₓGeₓ

A partial substitution of Ga by Ge leads to a strong change in the magnetic properties of FeGa₃ (see the phase diagrams in [3, 6]). Also, as illustrated in figure 2, the ESR properties change dramatically, namely for the higher concentrations x ≥ 0.127 a striking change appears in linewidth and resonance field at temperatures of ≈40 K. When cooling below this temperature we observed a remarkable crossover to a strong and narrow line developing out of the noisy and relatively weak high-temperature line. This crossover is most obviously seen in the linewidth but also, as shown in the lower insets of figure 2, in the resonance field and the dispersion-to-absorption ratio (D/A). The change in resonance field is strongest for x = 0.162 which is the composition with the strongest ferromagnetic correlations [3, 6]. The change from a symmetric signal (D/A = 0) to an asymmetric signal (D/A = 1) demonstrates that the influence of the electrical conduction in the environment of the spin probe becomes important. Again it is the sample with the strongest ferromagnetic correlations, x = 0.162, where a pronounced line asymmetry reaches up to the highest temperatures.

Above ≈40 K the ESR lines and their properties seem to remain unchanged by Ge doping (compare figures 1 and 2 and note the common plot of parameters for x = 0 (solid square) and x = 0.127 (dashed line) in figure 1). With increasing temperature the linewidth continuously decreases in way agreeing well with a Tᵢ⁻¹/₂ law (dashed line in figure 2). This behavior points towards a relaxation by spin fluctuations if it is the sample with the strongest ferromagnetic correlations, x = 0.162, where a pronounced line asymmetry reaches up to the highest temperatures.

Above ≈40 K the ESR linewidth Bₑ₀, above ≈40 K could originate from the temperature evolution of effective internal magnetic fields. The presence of such internal fields sounds most plausible for FeGa₃ (x = 0) for which AFM order is suggested by our high-temperature ESR results (see section below).

For the compositions with x ≥ 0.127 the low-temperature ESR results are influenced by strong FM correlations and FM ordering. This is illustrated in greater detail in figure 3 where the linewidth and ESR intensity is compared with the DC magnetic susceptibility χ measured at the same samples. Broad linewidth maxima indicate a crossover to a low-temperature region with an intense, narrow and asymmetric ESR. As shown in the lower frame the temperature dependencies of both ESR intensity and susceptibility coincide roughly below temperatures where the linewidth displays a broad maximum. This demonstrates that in the low-temperature region the ESR probes the same bulk magnetic properties that determine the DC magnetic susceptibility.

Comparing the linewidth with the reciprocal susceptibility as shown in the upper frame of figure 3 suggests a direct relation between these quantities. Plotting ΔB versus χ⁻¹ as shown in figure 4 further establishes such a relation which in turn is consistent with the properties of a CESR in spin systems with magnetic correlations. As was observed, for instance, in the itinerant ferromagnet ZrZn₂ [8], a ‘ferromagnetic slowing down’ of the relaxation rate (or ‘exchange enhancement’ of the spin lifetime) [8, 20] strongly reduces the spin-orbit relaxation and thus leads to a narrow CESR linewidth with ΔB ∝ χ⁻¹. This relation allows to check whether a power law behavior in χ ∝ T⁻σ/3 for three-dimensional ferromagnetic quantum critical fluctuations [21] can be found in the ESR linewidth. Indeed, as shown in the inset of figure 3, taking into account a reasonable residual, temperature independent contribution ∆B₀, the linewidth temperature dependence for x = 0.133 is consistent with T³/3. This power law is also reported for the NQR-probed dynamical susceptibility of the critical composition x = 0.15 [3].

The inset of figure 4 illustrates for x = 0.127 a characteristic hallmark of a CESR, namely a linear relation between the temperature dependencies of linewidth and electrical resistivity (ρ − ρ₀ ∝ T³/3). This behavior is similarly observed for the itinerant ferromagnets ZrZn₂ and NbFe₂ above magnetic ordering [9, 12].

The above discussed presence of an ‘exchange enhancement’ implies that the influence of ferromagnetic correlations on the ESR linewidth should depend on the applied
magnetic field. The ESR data presented so far were taken at $\nu = 9.4$ GHz (X-band) that corresponds to a resonance at a field of $\approx 0.31$ T (figure 2). Using $\nu = 34$ GHz (Q-band) with $B_{\text{res}} \approx 1.17$ T one can expect a strengthened effect of the ferromagnetic correlations to the ESR parameters. This, indeed, could be observed as shown in figure 5. The low-temperature linewidth depends on both the Ge content and the resonance field (at X-, or Q-band). The stronger the ferromagnetic correlations, i.e. the larger the Ge content, the more clear are the effects on the linewidth.

The linewidth is quite obviously related to the Ge content (see figure 3) which determines the formation of ferromagnetism in a delicate way. Muon spin rotation results indicate short range ferromagnetic order for a Ge content larger than $x = 0.11$ [6]. The weak increase of the linewidth for $x = 0.162$ at low temperatures evidences long-range ferromagnetic order which leads to pronounced anisotropies in the ESR parameters as shown in figure 6. The crystal was rotated around the crystallographic $c$-axis and a clear anisotropy with a 90 degree periodicity was found only for temperatures below the ferromagnetic ordering temperature $T_C = 6$ K and, moreover, not found for samples with a composition showing no magnetic order. Mössbauer spectroscopy results [6] have demonstrated that the ordered moments are aligned in the plane perpendicular to the crystallographic $c$-axis. Thus, the observed anisotropies shown in figure 6 are indeed a consequence of FM magnetic ordering and point out that the observed line actually is a ferromagnetic resonance mode.

3.3. High temperature properties

Neutron scattering measurements on FeGa$_3$ suggested antiferromagnetic order at temperatures above 300 K [17]. We therefore investigated the ESR properties of FeGa$_{3-x}$Ge$_x$ for temperatures between 300 K up to 500 K. It is also in this temperature region where upon heating the electrical resistivity starts to decrease (activated behavior with gap $\approx 0.4$ eV, [15, 17]) and the susceptibility shows a continuous increase [17, 22].

By heating the FeGa$_{3-x}$Ge$_x$ samples up to 500 K and cooling them back to 300 K we observe a remarkable ‘heat effect’ on the ESR spectra. As shown in figure 7 this heating-cooling cycle reversibly changes the ESR of Ge-containing FeGa$_{3-x}$Ge$_x$ whereas the ESR properties of pure FeGa$_3$ can be fully recovered. The ESR properties of Ge-containing FeGa$_{3-x}$Ge$_x$ seem to change upon heating towards properties which are very similar to those of pure FeGa$_3$; the intensity as well as the linewidth approach values of FeGa$_3$. This observation allows the conclusion that Ge doping strengthens the high-temperature ESR signal in FeGa$_3$. However, the ESR

Figure 4. Relation of the X-band linewidth $\Delta B$ (at $T < 40$ K) to the inverse magnetic susceptibility $\chi^{-1}$ and the electrical resistivity $\rho - \rho_0$ with temperature as implicit parameter ($\rho_0 = 0.7159$ m$\Omega$cm denotes the temperature independent part of $\rho(T)$). Dashed lines indicate linear behavior.

Figure 5. Comparison of the temperature dependence of the ESR linewidth $\Delta B$ measured for 9.4 GHz (X-band) and 34 GHz (Q-band). Inset shows selected Q-band spectra (open circles) together with a Lorentzian fit (solid line) of their lineshapes.

Figure 6. In-plane angle dependence of X-band linewidth $\Delta B$ and resonance field $B_{\text{res}}$ on the sample rotation around the crystallographic $c$-axis with the applied field $B \perp c$. At low temperatures a weak anisotropy indicates magnetic order. The field orientation of the base of the cuboid shaped sample is shown for two angles by the grey squares.
properties of FeGa\textsubscript{3-}\textsubscript{x}Ge\textsubscript{x} below 40 K (i.e. the CESR) are not influenced at all from such a heating-cooling cycle. This in turn means, that the Ge ions have two possibilities to influence the ESR-probed magnetism. They contribute to a stable, heat-insensitive CESR and also to the ESR with properties as seen in the undoped FeGa\textsubscript{3}. A thorough investigation on how the Ge ions are distributed on the Ga-sites as a function of temperature will be the subject of future NQR measurements.

4. Discussion

The ESR results in FeGa\textsubscript{3-}\textsubscript{x}Ge\textsubscript{x} show a remarkable temperature behavior which strongly depends on the Ge content. The picture that evolves is characterized by a conduction spin resonance (CESR) developing at low temperatures and a local spin resonance at elevated temperatures.

Below temperatures of \(\approx 40\) K and for \(x > 0.06\) we observed a well-defined and strong resonance in a conductive environment with typical asymmetric lineshapes. The resonant spin system may be interpreted as a CESR with the properties of a strongly coupled 3d—conduction electron system. The spin dynamics of this coupled system can be related to the resistivity and magnetization yielding information on the nature of interactions as was done for various other itinerant 3d ferromagnetic materials [10].

Two relaxation mechanisms for CESR in itinerant magnets are important namely the spin-lattice relaxation by spin-orbit coupling to transport collisions (characterized by the momentum scattering time \(\tau\) which also determines the electrical resistivity) [23] and a reduction of the relaxation rate by exchange enhancement (characterized by the magnetization) [24]. Whether or not the temperature dependence of \(\tau\) dominates the relaxation depends on how strongly the exchange effect depends on temperature: the corrections introduced from the resistivity may be small compared to line width variations due to changes in magnetization, as observed in ZrZn\textsubscript{2} [8, 9] or in Sc\textsubscript{1.12}In [25]. In TiBe\textsubscript{2} the linewidth broadening can be interpreted as a variation in \(\tau\) because there the exchange effect is constant also at high temperatures (only d-electron pockets in the Fermi surface contribute and the interaction strength to other electrons is small). In our case of FeGa\textsubscript{3-}\textsubscript{x}Ge\textsubscript{x} the low-temperature relaxation is clearly related to the inverse magnetization, see figure 4. Its relation to the electrical resistivity, shown in the inset of figure 4, points to a typical CESR property although the temperature independent part of the resistivity is considerable.

Above temperatures of \(\approx 40\) K the resonance properties point to a local spin probe although pure FeGa\textsubscript{3} is expected to be non-magnetic [26]. Preformed magnetic moments may arise from the presence of Fe dimers in the structure [15] because their magnetic properties are very sensitive to the electronic environment [27] (being in turn affected by structural defects). Substituting some Ga by Ge stabilizes this magnetism and the high-temperature ESR spectra gain intensity without strongly changing their other parameters (see figure 2). Approaching the highest temperatures (500 K) the local spin resonance for FeGa\textsubscript{3-}\textsubscript{x}Ge\textsubscript{x} with \(x > 0\) irreversibly changes its properties in such a way that the ESR properties of pure FeGa\textsubscript{3} are ‘recovered’. This observation implies that heating up to 500 K changes the way Ge-doped electrons are distributed in the lattice. As there are two different Ge-substitutable Ga sites [3, 6] it might be possible that heat shifts the Ge to a preferred site.
and this site would then have less influence on the Fe dimers magnetism. The insensitivity of the low-temperature CESR to a heating-cooling cycle may indicate that the presence of itinerant spin probes does not depend on which of the two Ga sites are substituted by Ge.

5. Conclusion

The presented ESR studies confirm the rather complex microscopic formation of magnetism in FeGa$_{3-x}$Ge$_x$. Structural defects easily lead to residual Fe moments which are the origin of the local-type ESR observed for temperatures above $\approx$40 K. The ESR properties strongly depend on the substitution of Ga sites by Ge which leads to electron doping. This supports an itinerant type of resonance below $\approx$40 K but it also leads to a stabilization of the local Fe dimers magnetism, increasing the intensity of the local type of resonance.

The itinerant-type resonance can be interpreted as a conduction spin resonance (CESR) of a system with a strong coupling between 3d- and conduction electrons. Strong ferromagnetic correlations allow an exchange enhancement of the spin lifetime, thus leading to a narrow and well-observable CESR. This resonance should be an appropriate tool to investigate the evolution of ferromagnetic correlations close to the suggested ferromagnetic quantum critical point [3] in FeGa$_{3-x}$Ge$_x$.

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