Strain-Induced Extrinsic High-Temperature Ferromagnetism in the Fe-Doped Hexagonal Barium Titanate

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Diluted magnetic semiconductors possessing intrinsic static magnetism at high temperatures represent a promising class of multifunctional materials with high application potential in spintronics and magneto-optics. In the hexagonal Fe-doped diluted magnetic oxide, 6H-BaTiO3-d, room-temperature ferromagnetism has been previously reported. Ferromagnetism is broadly accepted as an intrinsic property of this material, despite its unusual dependence on doping concentration and processing conditions. However, the here reported combination of bulk magnetization and complementary in-depth local-probe electron spin resonance and muon spin relaxation measurements, challenges this conjecture. While a ferromagnetic transition occurs around 700 K, it does so only in additionally annealed samples and is accompanied by an extremely small average value of the ordered magnetic moment. Furthermore, several additional magnetic instabilities are detected at lower temperatures. These coincide with electronic instabilities of the Fe-doped 3C-BaTiO3-pseudocubic polymorph. Moreover, the distribution of iron dopants with frozen magnetic moments is found to be non-uniform. Our results demonstrate that the intricate static magnetism of the hexagonal phase is not intrinsic, but rather stems from sparse strain-induced pseudocubic regions. We point out the vital role of internal strain in establishing defect ferromagnetism in systems with competing structural phases.

The search for dilute magnetic oxides (DMOs) is at the forefront of spintronics and magneto-optics research and application1–6. The great interest has been triggered by the possibility of combining diverse functionalities of semiconductor electronics and magnetism in a single material, which would boost its application potential. Existence of magnetoelectric coupling in wide-band-gap semiconducting oxides at room temperature would be of great technological importance, given that the magnetic ordering is indisputably intrinsic. Indeed, a number of studies have claimed such intrinsic ordering has been observed in non-magnetic oxide semiconductors lightly doped with paramagnetic transition-metal ions. These findings are, however, a subject of controversy7–9. Very often the corresponding studies are focused only on routine characterization and modelling of the material’s properties rather than critical analysis of the origin of the observed static magnetism. Recently, more detailed experiments have proven wrong a significant part of the claims about intrinsic magnetism in DMOs10–14. Moreover, aggregation of magnetic ions that leads to chemical phase separation on a nano-scale, also known as spinodal decomposition into regions with high/low concentration of dopants and a crystal structure imposed by the semiconducting host, has been lately witnessed in various cases2,3,15–17. Thus, the need for careful analysis of the magnetic properties of these systems at the microscopic level and their critical assessment are of paramount importance.

Since the discovery18 of room-temperature ferromagnetism in the bulk Fe-doped hexagonal19 6H-BaTiO3,δ (Figure 1) that can be stabilized from the pseudocubic (3C) perovskite structure (Figure 1) by transition-metal doping20, this system has been in the focus of investigations. Although simultaneous magnetic and polar orders (multiferroicity), highly desired for device applications, cannot be achieved in this material (1% Fe doping destroys ferroelectric order18), the magnetoelectric coupling has recently been demonstrated21. Moreover, arguments speaking in favour of its intrinsic ferromagnetism would make Fe-doped 6H-BaTiO3,δ rather special in the
identifying any spurious effects. Therefore, we performed a comprehensive magnetic investigation, combining both bulk magnetic measurements as well as the complementary local-probe measurements of electron spin resonance (ESR) and muon spin relaxation (μSR), in the broad temperature range between 2 and 850 K. Here, we report a plethora of magnetic anomalies that appear in the Fe-doped 6H-BaTiO$_3$-a below ~700 K. These coincide with the electronic instabilities of the Fe-doped pseudocubic 3C-BaTiO$_3$ polymorph. We provide firm experimental evidence that the previously reported static magnetism is not an intrinsic property of the doped 6H-BaTiO$_3$ hexagonal phase, but is instead related to sparse regions of strain-induced pseudocubic phase, which arise as a consequence of locally competing structural phases.

Results

In order to provide clear evidence for either intrinsic or extrinsic origin ofagnetism in the Fe-doped 6H-BaTiO$_3$-a, an in-depth experimental study, which combines bulk and local-probe magnetic characterization techniques, is necessary. All our measurements were performed on high-quality polycrystalline samples (see Methods); some of which were additionally annealed. This annealing proves crucial for the existence of FM behaviour. In what follows, we label the non-annealed and annealed samples with FeBTO and FcBTOa, respectively. Here $c$ denotes the doping percentage of Fe$^{3+}$ ions at the Ti sites.

Detection of magnetic instabilities by bulk magnetic measurements. Bulk magnetization ($M$) measurements display a clear difference between the non-annealed and annealed samples (Figure 2a). While the latter exhibit complicated zero-field cooled (ZFC)/field-cooled (FC) split $M(T)$ curves, a paramagnetic (PM) phase is found in the former. The PM phase is characterized by a monotonic temperature dependence and absence of the ZFC/FC bifurcation. The corresponding molar susceptibility (per mole Fe) for the non-annealed samples, $\chi_{mol} = M/H$ ($H$ denotes the applied magnetic field), agrees well with the Curie-Weiss model $\chi_{mol} = N_\chi \mu_0^2/3k_B(T - \theta_{CW})$. Here $N_\chi$ and $k_B$ denote the Avogadro and the Boltzmann constant, respectively, $\theta_{CW}$ is the Weiss temperature and $\mu_0 = 4.611(1) \mu_B$ is the average magnetic moment per Fe dopant. The derived magnetic moment is common to both F10BTO and F20BTO samples and is somewhat reduced from the value of $g\mu_B \sqrt{3(S+1)} = 5.92 \mu_B$ expected for Fe$^{3+}$ ($S = 5/2$) moments. However, the Fe$^{3+}$ valence was clearly revealed by X-ray absorption near-edge structure (XANES) spectroscopy$^{29,30}$ as being by far dominant in 6H-BaTiO$_3$-a. For F10BTO and F20BTO samples we find antiferromagnetic (AFM) Weiss temperature of -3(1) K and -7(2) K, respectively. This parameter scales linearly with the doping concentration and provides the energy scale of the average exchange coupling $J$ between the iron dopants. We find $J$ to be rather small compared to room temperature, where the FM state has been reported. Secondly, it is AFM and thus questions the intrinsic origin of the FM order.

At high temperatures ($T > T_{c1} \sim 700$ K) the $M(T)$ curves of the annealed samples match those of the non-annealed ones, proving the same PM state. This behaviour, however, drastically changes below $T_{c1}$, especially in the low applied field of 10 mT (Figure 2a). On decreasing temperature a ZFC/FC splitting is observed in F20BTOa at $T_{c1}$, with the FM component being enhanced below $T_c2 \sim 570$ K, and the ZFC/FC difference increased below $T_{c3} \sim 450$ K. Finally, an additional magnetic anomaly, reflected in a local-probe magnetic spectroscopy, which arises as a consequence of locally competing structural phases.
Producing an effective temperature $T_e$ the doping concentration $c_2$ can then be accounted for by a renormalization factor that has been found to decrease steadily with temperature. Such a renormalization factor is significant even at low temperatures. Such a renormalization factor was limited to doping concentrations below 5%. The disappearance of the fine structure in our non-annealed samples suggests enhanced magnetic interactions (dipolar and/or exchange) between iron dopants.

In order to support the claim of sizable magnetic interactions we analyse the line width of the PM ESR spectra in the non-annealed samples. The peak-to-peak line width $\Delta B$ (Figure 3b) scales proportionally with the doping level ($\Delta B^{c2}$ = 45(2) mT, $\Delta B^{c3}$ = 91(2) mT). Such a linear increase is in accordance with the linearly increasing magnetic anisotropy and exchange interactions (see Methods), as deduced from the Weiss temperatures of both non-annealed samples. On the contrary, the dipolar interactions in the absence of isotropic exchange coupling would yield much smaller line widths (see Methods). ESR thus verifies that the average exchange interaction $J$ among dopants is not negligible. Furthermore, the line width, being proportional to $c_2$, is a fingerprint of a uniform PM phase. Aggregation of magnetic ions into nano-scale clusters, on the other hand, would result in an inverse dependence of the ESR line width on $c_2$, as was recently observed$^{17}$ in Mn-doped SrTiO$_3$.

In sharp contrast to the simple ESR line shape of the PM non-annealed samples, the ESR spectra of the annealed samples are much more complex below $T_{c3}$. Here, they exhibit several well-displaced lines (Figure 3c) that shift significantly with temperature (Figure 3d). The field shift of the side bands from the $g = 2$ position is the same at 9.4 GHz and at 24.3 GHz (Figure 3c), which is indicative of static internal magnetic fields characteristic of the PM phase. Very importantly, above $T_{c3}$ a single-line spectrum is observed at $g \approx 2$ (Figure 3a) in all the annealed samples despite the fact that the PM state persists to much higher temperature, $T_{c3} \sim 700$ K. With its peak-to-peak line width $\Delta B = 91(1)$ mT, this spectrum is markedly narrower than the PM spectrum of the non-annealed samples. Moreover, its intensity strongly decreases between $T_{c3}$ and $T_{c2}$ (Figure 3e). The latter behaviour is in disagreement with the Curie-like decrease, characteristic of the PM non-annealed samples (Figure 3e), and is rather reminiscent of the PM magnetization decrease in the same temperature range (Figure 2a). Therefore, this $g \approx 2$ mode is still a FM mode. We stress that its single-component line shape reveals that the local magnetic anisotropy, which dictates the shape of the ESR spectrum in the PM state$^{27}$ and depends on local symmetry, drastically changes at $T_{c3}$.

Clustering of FM moments as evidenced by $\mu$SR. The ESR measurements provide convincing evidence of FM moments in the
PM/FM character of a particular sample (Figure 4a and 4b). It can be seen that the ESR relaxation is temperature dependent in the experimental time window, independent of the nature of the local symmetries of the Fe-doped BaTiO$_3$-$\delta$ samples. In addition, they reveal a novel and important (vide infra) magnetic ratio), however, in this static case the 1 mT longitudinal field would almost completely remove the relaxation of $P(t)$, which clearly contradicts the experiment (Figure 4c). The muon relaxation due to local fields fluctuating with the exchange frequency $\nu_\text{e}$ at 1 THz on the other hand, is not affected by such a small LF field, because $\gamma_\mu^2 1 \text{mT} = 85 \text{MHz} < \ll \nu_\text{e}$. A closer look at the ZF and LF data of the F20BTOa sample at room temperature, however, reveals a somewhat decreased muon relaxation in the LF experiment (Figure 4c). This can be attributed to the presence of some weaker static relaxation in addition to the dominant dynamical one. A simultaneous fit of both datasets to the corresponding model $P(t) = P_{\text{SE}}(t) \cdot P_{\text{KT}}(t)$ yields the static-field distribution width of $\Delta_\mu = 6.1(3) \times 10^{-2}$ mT. This value represents the upper bound of the frozen-FM-moments’ contribution in the annealed samples, since the static-field distribution may also partially arise from nuclear magnetic moments. However, for homogeneously distributed FM moments the calculated field-distribution widths at both oxygen sites, in the vicinity of which the muons are highly likely to reside in oxides, are almost an order of magnitude larger, $\Delta_\mu = 3.4(2) \times 10^{-1}$ mT (see Methods), even for the very small average value of the FM moments in F20BTOa (1.5$\times 10^{-2}$μB at 300 K). As the interaction strength between the muon and the FM moments decreases with the cube of their distance, the much smaller experimental value of $\Delta_\mu$ can be reconciled by considering clustering of the FM moments. This thus provides microscopic evidence that, in contrast to the homogeneous distribution of PM moments evidenced in the ZF data and the data obtained in the weak longitudinal field (LF) experiments, well suited for dynamical local fields in diluted spin systems. Here $\lambda$ denotes the muon relaxation rate and $\beta$ the stretch exponent. For each sample the relaxation rate is found to increase notably with increasing temperature ($P(t)$ curves in Figure 4a and 4b decrease faster at higher temperature). This increase of the relaxation rate is very similar in the annealed and non-annealed samples for a given concentration of dopants. Therefore, the muon relaxation in the Fe-doped BaTiO$_3$-$\delta$ system is attributed to the fluctuating paramagnetic moments.

Direct confirmation of this statement is provided by comparing the ZF data and the data obtained in the weak longitudinal field (LF) of 1 mT. Such field comparison shows a very similar relaxation response (Figure 4c). We note that in addition to the dynamical model of equation (1), the Lorentzian Kubo-Toyabe (KT) model also provides a satisfactory fit to the ZF data. The KT model is applicable to disordered static local fields with the distribution width $\Delta_\mu = 7.0 \times 10^{-2}$ mT ($\gamma_\mu = 2\pi \times 135.5$ MHz/T is the muon gyromagnetic ratio). However, in this static case the 1 mT longitudinal field would almost completely remove the relaxation of $P(t)$, which clearly contradicts the experiment (Figure 4c). The muon relaxation due to local fields fluctuating with the exchange frequency $\nu_\text{e} = k_B T / h \sim 1$ THz on the other hand, is not affected by such a small LF field, because $\gamma_\mu^2 1 \text{mT} = 85 \text{MHz} < \ll \nu_\text{e}$.

$$P_{\text{KT}}(T) = \frac{1}{3} + \frac{2}{3} (1 - \gamma_\mu \Delta_\mu t) e^{-\gamma_\mu \Delta_\mu t},$$

Figure 3 | ESR characterization of 6H-BaTiO$_3$-$\delta$ (a) The temperature dependence of the ESR spectra in 20% Fe-doped 6H-BaTiO$_3$-$\delta$ displaying a single line in the non-annealed sample and a multi-feature line in the annealed sample. Spectra are displaced vertically for clarity. The $g = 2$ position is marked with the vertical line. (b) The increase of the ESR line width with doping concentration in the non-annealed samples at 300 K. The peak-to-peak line width $\Delta B$ of both spectra is indicated by the horizontal arrows. (c) Comparison of the 300-K spectra of F20BTO at 9.4 GHz and at 24.3 GHz. Side-band shifts that are frequency independent are marked with vertical lines. (d) Resonance field of various resonance modes observed in the annealed Fe-doped 6H-BaTiO$_3$-$\delta$ samples below $T_c$. The temperature independent position (horizontal mode) corresponds to the $g = 2$ mode. (e) Comparison of the ESR line width decrease of the single-line FM mode observed above $T_c$ in F20BTOa and the PM signal of the F20BTO sample with Curie-like dependence. Both ESR intensities are normalized at 450 K.
Figure 4 | μSR characterization of $6H$-BaTiO$_3$. The temperature dependence of muon polarization in (a) 10% and (b) 20% Fe-doped $6H$-BaTiO$_3$ samples in zero applied field showing increased relaxation rates with increasing temperature. The upper panels correspond to non-annealed samples and the lower panels to annealed samples. The solid lines are fits to the stretched exponential (SE) model of equation (1). (c) The room-temperature muon polarization of the F20BTOa sample in ZF and in a weak longitudinal applied field. The dashed lines correspond to the static Kubo-Toyabe (KT) model of equation (2), while the solid lines are fits to the model encompassing both static KT and dynamical SE relaxation (see text for details). The error bars of muon polarization data are defined as a square root of the total number of detected positrons.

by ESR, the FM moments are not uniformly distributed throughout the sample.

**Discussion**

The small size of the average FM moments and their non-uniform distribution in the annealed Fe-doped $6H$-BaTiO$_3$ samples cast doubt on the intrinsic origin of these moments. It is therefore crucial to critically assess the origin of ferromagnetism in this system. It could well be that the FM behaviour either corresponds to some kind of “impurity” phase or that the spinodal decomposition occurs and very small dispersed lattice-matched FM clusters of Fe$^{3+}$ ions form during the annealing process. The latter scenario has been recently demonstrated in Mn-doped SrTiO$_3$. In order to check for the presence of such small clusters that would minimally deform the local crystal structure and would be practically undetectable even by high-resolution imaging techniques, we performed a magnetization relaxation experiment on the FM F20BTOa sample. After being exposed to the magnetic field of 1 T for 20 minutes, the subsequent remnant relaxation in zero field was measured. No magnetization relaxation towards zero has been detected on the time scale of several minutes (Figure 2c). This implies an unexpectedly slow relaxation process within the Stoner-Wohlfarth model of single-domain FM (nano)particles and thus excludes the presence of small FM clusters of Fe$^{3+}$ ions.

Therefore, the alternative scenario of “impurity” ferromagnetism is much more plausible and should be carefully considered. The Curie temperatures of the most common iron oxides that may develop as a by-product during the synthesis are much higher than $T_c$ (i.e., $T_c \approx 700 \text{ K}$, $T_c \approx 950 \text{ K}$ (Fe$_3$O$_4$) and $T_c \approx 850 \text{ K}$ (Fe$_2$O$_3$). On the other hand, the Curie temperature of $\approx 680 \text{ K}$ has been recently reported for the 3C bulk BaTiO$_{0.95}$Fe$_{0.05}$O$_{3.4}$ sample, where a much larger magnetic moment of $0.75 \text{ \mu B}$ per Fe has been found. Therefore, the high-temperature ferromagnetism has regularly been encountered in this pseudocubic polymorph, even at much higher Fe-doping concentrations (up to 75%), where the 3C phase is stabilized only by the confined geometry of thin films and nanoparticles. We note though that the Curie temperature of an impurity phase is usually size dependent for nano-particles, as well as it may depend on the level of doping. Therefore, the fair agreement of $T_{3c}$ with the Curie temperature of the 3C bulk BaTiO$_{0.95}$Fe$_{0.05}$O$_{3.4}$ sample cannot be taken as a solid proof that the FM character of the Fe-doped $6H$-BaTiO$_3$ is due to the impurity 3C phase. However, an unambiguous evidence that this is indeed the case comes from the slightly doping dependent $T_{3c}$ transition temperature ($T_{3c}^{10\%} = 430\text{ K}$, $T_{3c}^{20\%} = 450\text{ K}$; see Figure 3d), which exactly coincides with the doping dependent cubic-to-tetragonal structural transition of the 3C phase. Moreover, this structural transition is clearly reflected in the FM ESR line-shape change from the high-temperature single line to a multi-feature spectrum below $T_{3c}$, which corroborates the change of the local symmetry from highly symmetric above $T_{3c}$ to being less symmetric below $T_{3c}$. It is also worth noting that in epitaxially grown thin films, the 3C phase grows at the initial stages, while later on a disordered phase composed of 3C and 6H intergrowths forms. Since increasing thickness decreases the FM response of thin-film samples, their ferromagnetism is most naturally attributed to the 3C phase, for which it is also theoretically predicted as the ground state.

All the above-presented arguments give clear evidence that the FM behaviour of the annealed Fe-doped BaTiO$_3$ samples is related to internal strains that locally destabilize the 6H phase in favour of the 3C phase, much as it happens globally in the confined geometries of thin films and nanoparticles. The μSR results yielding only minor differences between the FM annealed and PM non-annealed samples, as well as the non-uniform distribution of FM moments, corroborate this scenario. Furthermore, ferromagnetism arising from the sparse strain-stabilized defect regions with the 3C crystal structure explains both the extremely small magnitude of the average ordered Fe moment and its unusual decrease with increasing doping concentration; the increasing doping level being known to destabilize the 3C phase. Finally, in the non-annealed samples that were heat-treated at lower temperature (see Methods for details) the crystallites are under significantly less strain than in the densely sintered annealed samples after additional annealing at higher temperature. Therefore, in the latter samples strong strain fields along crystallographically mismatched grain boundaries, or around plane defects, are likely regions for nucleation of stable pseudocubic domains with their own intrinsic ferromagnetism. These are not single-domain nano-sized FM defects, as magnetization relaxation is absent.

Our comprehensive magnetic investigation of various Fe-doped $6H$-BaTiO$_3$ samples has thus revealed that the FM response observed in the annealed samples is not intrinsic to the hexagonal crystallographic phase, as broadly speculated before. This conclusion is based on our complementary bulk and local-probe magnetic investigations, providing new microscopic insight and extending the experimental temperature range far beyond all previous reports. Bulk magnetization measurements have demonstrated that extremely small average static magnetic moments develop in the annealed
samples below $T_c \sim 700$ K and several additional magnetic instabil-
ities occur as the temperature is lowered further. Below the $T_c$ transition
(at around 430 K and 450 K in 10%- and 20%-doped samples, respectively)
a significant symmetry reduction of the local structure is
detected by ESR. The $T_1$ and $T_2$ transitions coincide with the ferromagnetic and ferroelectric transitions of the Fe-doped 3C-
BaTiO$_3$ polymorph, respectively, while the microscopic characteristics
determined by µSR imply non-uniformly distributed FM regions in the samples. This demonstrates that the FM response of the Fe-
doped 6H-BaTiO$_3$ system originates from sparse regions where the pseudocubic structural polymorph is stabilized by strain fields. The
strain-induced local competition between the two structural (and
magnetic) phases is inherent only to densely sintered annealed sam-
ples. Such scenario of ferromagnetism may turn to be important for
other DMO materials, where the competition between different structural phases is intrinsically present, in particular in confined geometries where strain effects are enhanced.

**Methods**

**Samples**. High quality 6H-BaTiO$_3$ polycrystalline samples with $c = 10$, 20% Fe$^{2+}$ions substituted for Ti$^{4+}$ were synthesized according to the procedure thoroughly
explained in Ref. 28. For each composition, after heat treatment at 1250°C, a part of
the sample was additionally annealed in oxygen atmosphere at 1500°C, typically for
5–10 hours. We label the non-annealed and annealed samples with FEBTO and FeBTOa, respectively. The variations of the annealing time showed no significant
influence on the magnetic properties. X-ray powder diffraction (XRD) was used to verify the single-phase hexagonal structure of all of our samples. The elemental analysis was performed by Energy Dispersion X-Ray Spectroscopy (EDX) on polished ceramic surfaces with SiM–7100 F (Jedl) field-emission scanning electron microscope equipped with an x-ray detector (X-Max 80, Oxford Instrument). Ten EDX characterizations were performed on each sample and were statistically treated to
obtain average values and standard deviations. The iron concentration in the nominally 10%-doped samples was found at 10.3 $\pm$ 0.5%, while in 20%-doped samples it amounted to 19.9 $\pm$ 0.6%. For all our samples the analytically determined compositions thus correspond to the nominal compositions within the small error
bars.

**Bulk magnetization**. Bulk magnetization measurements were performed on a couple of Quantum Design SQUID magnetometers and a vibrating sample magnetometer (VSM) as a function of temperature (between 2 and 850 K) in various magnetic fields and at various fixed temperatures as a function of varying magnetic field. Zero-field-cooled (ZFC) and field-cooled (FC) field temperature-dependent data were collected. A high-temperature insert was used for measurements above 400 K. The SQUID measurements were performed on samples sealed in quartz capillaries, while boronitride sample holders were used with VSM. The signal from the sample holders was carefully evaluated. The size of the ordered magnetic moment was estimated from the saturation value of the FM component in the hysteresis, by subtracting the linearly increasing PM part.

**ESR**. Electron spin resonance was measured with home-built resonator–cavity based X-band (9.4 GHz) and K-band (24.3 GHz) spectrometers. In the X band, a continuous-flow cryostat was used in the temperature range 5–300 K, while a
continuous-flow cryostat was used in the temperature range 5–300 K, while a
preheated-nitrogen-flow heating system was used above room temperature up to
620 K. The samples were sealed in ESR silent quartz tubes. The ESR intensity was calibrated at room temperature with a reference sample (CuS$_2$S–5H$_2$O). The ESR susceptibility of the non-annealed PM samples $\chi_{\text{mag}} = 0.06(3)$ Am$^2$/T per mole Fe was found compatible with the bulk molar susceptibility $\chi_m = 0.08$ Am$^2$/T, proving that ESR was detecting the intrinsic signal of Fe dopants in BaTiO$_3$.

The second moment of the ESR line $M_2$ arising from dipolar interactions is given by

$$M_2 = \frac{4}{3}\left(\frac{h}{e}\right)^2 8(S+1)(g_B) \sum_{\delta^b} \left\{ \cos^2 \delta^b - 1 \right\}^2 \frac{g_B}{\mu_B},$$

where $\mu_B$ is the magnetic permeability. The sum runs over all neighbours $k$ of a given site $j$, connected by the vector $r_{jk}$. $\delta^b$ is the angle between $r_{jk}$ and the applied field $H_A$. $M_2$ was calculated by polynomial averaging equation (3) for a lattice fully occupied with Fe$^{2+}$ ions on either the Ti(1) or Ti(2) site. In the limit of negligible exchange interactions $M_2$ yields the ESR peak-to-peak line width $\Delta B \approx M_2 / \sqrt{3} g_B$. For the fully occupied lattice and the line width $\Delta B \approx M_2 / \sqrt{3} g_B$.

In the dilute limit, we find $M_2(\text{dil}) = 2.25$ mT and $\Delta B(\text{dil}) = 3$ mT, which is far below the experimental values. In the exchange narrowing limit ($J_{\text{ex}} \gg g_B \Delta B$), on the other hand, the ESR line width is given by $\Delta B \approx M_2 / g_B k_J$. The second moment $M_2$ is quadratic in the anisotropic interaction (i.e., in the doping level $c$), therefore $\Delta B$ also scales linearly with $c$ for a linearly dependent $J$.
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Author contributions

A.Z. and M.V. designed and supervised the project. I.A., I.M. and M.V. synthesized and structurally characterized the samples. Z.I. and D.P. performed bulk magnetization measurements. M.P. and M.G. conducted ESR measurements. A.Z., M.G. and M.T. carried out the μSR study. All the experimental data were analysed by A.Z., who also wrote the paper. All authors discussed the results and reviewed the manuscript.

Additional information

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