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Chapter 7

Magnetic resonance force microscopy of trivalent iron defects in STO-(100)

7.1 Introduction
In this chapter, we describe the first measurements with the full-featured SQUID-based Magnetic Resonance Force Microscope (MRFM). We show that we are able to approach the cantilever magnet in three dimensions towards an optimal position, at which the coupling to the detection coil is large enough to detect the thermal motion of the cantilever at 56 mK, and which is only at a few microns distance from the superconducting Radio-Frequency (RF) microwire. We used the setup to study Fe$^{3+}$ bulk defects in strontium titanate (STO). In Section 7.2 we first confirm the presence of these defects in an independent Electron Paramagnetic Resonance (EPR) experiment. We show that, using MRFM at milliKelvin temperatures, we are able to estimate the density of the defects. Furthermore, we show that by measuring the cantilever response to spin excitations at a broad frequency range, we can obtain a spectrum that contains information about the crystal field parameters of STO.

7.2 Conventional EPR characterization of paramagnetic defects in Strontium Titanate
Strontium titanate (SrTiO$_3$, or STO) is a perovskite-type crystal that exhibits a variety of interesting physical phenomena, such as low-temperature incipient ferroelectricity [91], room-temperature ferroelectricity in vacancy-rich thin films [92], a quantum paraelectric$^1$ phase below 4 K [93], and superconductivity at

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$^1$Paraelectricity is the ability of a material to become electrically polarized under an applied electric field. Unlike ferroelectrics, the polarization returns to zero upon removal of
temperatures up to 0.3 K when it is doped with charge carriers [94,95]. At room temperature, STO has a pseudocubic structure, in which each Ti atom, located at the unit cell corners, is in the center of an oxygen octahedron (See Fig. 7.1a). The Sr atom is located at the center of the cubic unit cell. Around 105 K, a second-order phase transition occurs to a tetragonal structure [91, 96–99], in which the oxygen octahedra are rotated around a fourfold axis by an angle $\phi$ which was measured to be 2.1 $^\circ$ at 4.2 K [98] (See Fig. 7.1b).

Most of the naturally occurring impurities in STO result from oxides containing cations with a lower valence than Ti$^{4+}$, such as Fe$^{3+}$ and Cu$^{2+}$ [100]. The iron oxide contamination results in Fe$'_{T_i}$ and V$^{**}_O$ defects\(^2\) in the STO crystal in a ratio 2 : 1. For single-crystalline STO, grown in the Verneuil process, naturally occurring defect concentrations are reported to be in the order of $10^{23}$ m$^{-3}$ for Fe$'_{T_i}$, $10^{21}$ m$^{-3}$ for Cr$'_{T_i}$, and $10^{20}$ m$^{-3}$ for Mn$^\times_{T_i}$ [97,101]. When an iron ion and a vacancy occupy nearest neighbor sites, they form a highly anisotropic defect center (Fe$'_{T_i}$–V$^{**}_O$)* [100, 102, 103]. In non-doped STO, the density of these iron-vacancy complexes was measured to be 0.2 % of the Fe$'_{T_i}$ defect density [104].

The Fe$'_{T_i}$ center has been extensively studied as a probe of the STO crystal structure, either as a naturally occurring contamination or, in higher concentrations, as a purposefully implemented dopant. The electronic configuration of trivalent iron is (3$d)^5$ and the ground state of the ion is $^6S_{5/2}$. The spin

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\(^2\)We use the Kröger-Vink notation [100] to describe the defects: Fe$'_{T_i}$ means that a Fe$^{3+}$ ion sits at a Ti$^{4+}$ site. The charge mismatch of $-1$ electron charge is designated by the single bar, '. V$^{**}_O$ means that a vacancy, V, sits at an O$^{2-}$ site. The charge mismatch is now +2 electron charges and is indicated by the two dots, **. A charge-neutral defect is indicated by a cross, ×.
Hamiltonian describing the iron defect is [97, 105]:

\[
H = - g \mu_B \vec{B}_0 \cdot \hat{S} + \frac{a}{6} \left[ \hat{S}_x^4 + \hat{S}_y^4 + \hat{S}_z^4 - \frac{1}{5} S(S + 1)(3S^2 + 3S - 1) \right] + D \left[ \hat{S}_z^2 - \frac{1}{3}(S^2 + S) \right]
\]  

(7.1)

Here, the g-tensor is taken as isotropic with \( g = 2.0023 \), the free electron g-value. The absolute value of the crystal field splitting parameter is \( \left| a \right| = 0.0198 \text{ cm}^{-1} \) at room temperature and increases to \( \left| a \right| = 0.023 \text{ cm}^{-1} \) at 1.9 K. The sign of \( a \) is reported to be positive [97, 98] as well as negative [96]. The zero-field splitting parameter is \( D = 0 \) at room temperature, but becomes \( D = (6.3-7.7) \cdot 10^{-4} \text{ cm}^{-1} \) at 77 K, and rises to \( D = (11.2-16.1) \cdot 10^{-4} \text{ cm}^{-1} \) at 4.2 K [96–98].

In order to characterize our substrate, we investigated a clean fragment of the STO-(100) chip that was used in our cryogenic MRFM experiments with an EPR spectrometer. In this EPR setup, the sample is placed inside a microwave cavity, which is resonant with an excitation frequency of 9.77 GHz. Using a network analyzer, the frequency of the absorbed microwave radiation is measured as a function of the polarizing magnetic field strength, \( B_0 \). The sample can be rotated manually with respect to the direction of \( B_0 \), enabling the measurement of angle-dependent absorption spectra at room temperature.

In Fig. 7.2 we show the derivative of the microwave absorption spectrum for an angle \( \theta = (74 \pm 10)^\circ \) between \( B_0 \) and the \( \langle 001 \rangle \) crystal axis of the STO sample. Referring to X-band EPR measurements that are reported in the literature [96–98, 101, 104], we identify 5 absorption lines that we attribute to transitions between the 6 spin-5/2 energy levels of the Fe\(_{\text{Ti}}\) defect. In addition, we observe a sharp spin-1/2 transition, which has been attributed to a Cr\(_{\text{Ti}}\) defect, as well as a relatively small absorption peak that we believe to be due to the (Fe\(_{\text{Ti}}\)–V\(_{\text{O}}\))\(^*\) defect, since its resonant field is dependent on the crystal orientation (see Fig. 7.3). Comparison of the area of the Cr\(_{\text{Ti}}\) absorption peak with the total area of the five Fe\(_{\text{Ti}}\) absorption peaks indicates that the concentration of chromium is 1.2 \% of the iron concentration. The (Fe\(_{\text{Ti}}\)–V\(_{\text{O}}\))\(^*\) peak area is about 5 \% of that of the Fe\(_{\text{Ti}}\) peaks combined, however we cannot infer the relative concentration of these defects from this, due to the strong dependence of the signal intensity on the orientation of \( B_0 \) [101].

In Fig. 7.3, we show the measured locations of the absorption peaks in the EPR spectra as a function of the angle, \( \theta \), between \( B_0 \) and the STO \( \langle 100 \rangle \) crystal axis. The solid lines in the graph are the theoretical resonant fields, calculated from an approximate solution of the Hamiltonian (7.1) [97]. Since the measurement was performed at room temperature, we set the zero-field splitting parameter at \( D = 0 \) and the cubic crystal-field splitting parameter at \( a = 0.01977 \text{ cm}^{-1} \). The measured absorption peak positions of the Fe\(_{\text{Ti}}\) fit well

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\(^3\)In the conventional EPR literature, wavenumbers are used as a unit of energy. Multiplying the wavenumber in reciprocal meters, \( 1/\lambda \), by the speed of light, \( c \), and Planck’s constant, \( h \), yields the energy of the wave, \( E = hc/\lambda \).
Figure 7.2: X-band EPR spectrum of STO-(100) at 293 K, revealing the presence of 3 types of paramagnetic defects: Fe$^{+}_T$, Cr$^{+}_T$, and (Fe$^{+}_T$–V$^{_{••}}_O$). The angle between the magnetic field, $B_0$, and the $\langle 001 \rangle$ crystal axis was manually aligned at $\theta = (74 \pm 10) ^\circ$.

Figure 7.3: EPR absorption spectrum peak positions versus the angle between the (001) crystal axis of the STO-(100) sample and the magnetic field, $B_0$. 
to the theoretical curve, thus confirming that this is indeed the paramagnetic defect that is dominant in our STO substrate.

The absorption peak that is attributed to chromium defects does not depend on the sample orientation, as is expected for a spin-1/2. The \((\text{Fe}^{\prime}_\text{Ti} - \text{V}^{\text{••}})\) peak, which we observed for two orientations only in the measured range of \(B_0\), has a resonant field that depends on the sample orientation due to its anisotropic \(g\)-tensor [102].

7.3 MRFM experimental methods

Figure 7.4: Cantilever fabrication and alignment. a) A scanning electron microscopy image of the free end of the cantilever, to which we have glued a 3.5 \(\mu\)m diameter, spherical, NdFeB-based magnet, using Pt electron beam induced deposition. b) Approximate alignment of the cantilever with respect to the Nb detection coil and RF microwire on the STO-(100) substrate. We estimate that the magnet was located at about 3 \(\mu\)m from both the center of the RF microwire and the center of the detection coil line that is drawn here. The magnet is polarized along the \(z\)-axis. The contours of the field of the magnet are drawn on the chip, calculated for a distance of 3.6 \(\mu\)m between the magnet center and the surface. The fundamental mode of the cantilever is a vibration along the \(x\)-axis, causing a magnetic flux change in the detection coil that is detected with a dc SQUID.

In Fig. 7.4a we show an electron microscope image of the free end of the cantilever-magnet assembly. We used an IBM-type cantilever [31] with a length, width, and thickness of 148 \(\mu\)m, 5 \(\mu\)m, and 0.1 \(\mu\)m, respectively. Using the added-mass method [36], the stiffness of the cantilever was determined to be \(k = 8.1 \cdot 10^{-5} \text{ N/m}\). A spherical NdFeB-based alloy particle with a diameter of 3.5 \(\mu\)m (the magnet) was glued close to the free end of the cantilever. The magnet was thereafter polarized along the direction of the cantilever in a 5 T field, at room temperature. The remanent field of the NdFeB alloy is reported to be \(\mu_0 M_r = (1.3 \pm 0.1) \text{ T} [22, 23]\), from which we infer a magnetic moment of \(\mu_m = 2.3 \cdot 10^{-11} \text{ Am}^2\).
Using 3D coarse approach motors and a fine-scanning stage (see Sect. 3.4), the cantilever tip is approached to the STO-(100) chip, on which a Nb detection coil and RF microwire are fabricated. Both structures have a linewidth of 1 µm and a thickness of 147 nm. The square detection coil has sides of 30 µm and is part of a superconducting circuit that, via a transformer on a separate chip, is coupled to the input coil of a dc SQUID (see Sect. 3.2 for more details). In Fig. 7.4b, we show the approximate alignment of the cantilever during the experiments. The magnet is positioned as close as possible to the RF microwire, so that the sample spins to which it is coupled can be efficiently excited by microwave pulses. The cantilever is in such a position that its motion causes a relatively large magnetic flux change through the detection coil.

The experiment is mounted in a cryogen-free dilution refrigerator with a base temperature of 10 mK. In typical experimental conditions, the resonant frequency of the cantilever-magnet assembly is \( f_r = 3.15 \text{ kHz} \) with a quality factor of \( Q = 3 \cdot 10^4 \) when it is far away from the chip surface. Close to the surface, the resonant frequency shifts to \( f_r \approx 4 \text{ kHz} \), depending strongly on the position with respect to the coil and the RF microwire lines, and the quality factor drops to \( Q \approx 4 \cdot 10^3 \).

An STO single crystal was purchased from SurfaceNet GmbH, Germany. According to the information provided by the company, the crystal was grown with the Flame Fusion method (also called the Verneuil process) and diced to a 10mm×10mm×0.5mm chip, which was then polished on both sides. The chip top surface has the (100)-orientation and the edges have the (010)-orientation. We patterned 3 sets of Nb coils and microwires on the chip, after which we diced it into 3mm×3mm chips using a tungsten wire cutter, so that each fragment contained at most one detection coil and one microwire. We used one empty fragment for sample characterization with EPR. Before the dicing process, we spin coated a layer of PMMA onto the chip surface in order to protect the Nb structures and to prevent surface contamination. The PMMA layer was removed with acetone just before assembling the experiment.

### 7.4 Cantilever thermal noise and force sensitivity

We have demonstrated before that the SQUID-based cantilever detection enables us to observe the cantilever thermal noise down to 25 mK, corresponding to a force noise as low as 0.5 aN/√Hz in a 1.1 Hz bandwidth [48]. Those preliminary measurements were performed with the cantilever chip clamped above a multiturn detection coil, without the possibility of tip alignment and microwave excitation of a sample. Here, we show that a similar noise figure can be achieved with the cantilever mounted on a 3D coarse approach motor and a much smaller, single loop detection coil in the vicinity of an on-chip RF microwire. This is an improvement over a previous experiment [106] in which we could apply microwaves but could not detect the thermal motion of the cantilever due to a poor lateral alignment.
Figure 7.5: Thermal noise of the cantilever, with the center of the magnet at \( d = 3.7 \) \( \mu m \) from the chip surface. \( \textbf{a)} \) Power spectral density of the cantilever displacement noise at two different bath temperatures, 16 mK (blue line) and 73 mK (red line), around the fundamental mode resonant frequency. The noise curves can be well fitted by Lorentzian lineshapes (black lines) added to the SQUID white noise. \( \textbf{b)} \) Noise temperature of the cantilever, obtained by calculating the area of the Lorentzian peaks, plotted versus the cryostat bath temperature. The continuous blue line represents a fit to the data with a saturation curve (see text), yielding a saturation temperature of \( T_0 = (56 \pm 1) \) mK.

In Fig. 7.5a, the power spectral density of the cantilever displacement noise is shown for two bath temperatures, 16 mK and 73 mK. The cantilever is aligned in-situ, such that the center of the magnet is at a distance \( d = 3.7 \) \( \mu m \) from the chip surface. Around the cantilever resonant frequency, the noise can be fitted well with a Lorentzian lineshape. We observe that the resonant frequency as well as the cantilever damping factor change upon increasing the temperature. This dependence will be discussed in more detail in Sect. 7.5.

By calibrating the energy coupling \( \beta^2 \) between the cantilever magnet and the detection coil as well as the responsivity of the total detection circuit (see Sect. 3.2.1), we can infer the detector gain in \( V/m \). At this particular cantilever position, we measured a coupling of \( \beta^2 = 4.9 \times 10^{-5} \). At the lowest temperatures, the displacement sensitivity of the detector is then 13 pm/\( \sqrt{\text{Hz}} \). The bandwidth in which the amplitude of the thermal motion of the cantilever exceeds the noise floor by more than a factor of \( \sqrt{2} \) is 3.8 Hz.

By calculating the area of the Lorentzian lineshapes, we obtain the mean squared displacement \( \langle x^2 \rangle = \frac{k_BT_{\text{cant}}}{k_{\text{eff}}} \), where \( T_{\text{cant}} \) is the cantilever noise temperature and \( k_{\text{eff}} \) is the effective spring constant. The effective spring constant is the sum of four terms: 1) the cantilever stiffness, 2) the interaction stiffness between the cantilever magnet and the induced detection coil field, 3) the spatial derivative of the superconducting repulsion force of the coil lines and RF wire, and 4) the interaction stiffness between the magnet and magnetic features of the substrate. In Fig. 7.5b, we have plotted \( T_{\text{cant}} \) versus the temperature of the cryostat as measured with a resistance thermometer. There is a good agreement between the cantilever temperature and the bath temperature down to 60 mK, below which temperature the cantilever noise energy levels off to a constant value. We can fit the data reasonably well with a standard saturation curve \( T_{\text{cant}} = (T_0^n + T_{\text{bath}}^n)^{1/n} \), which yields \( n = 6 \pm 3 \) and \( T_0 = (56 \pm 1) \)
mK. The value of the exponent is consistent with either a thermal boundary effect or a phonon-mediated bulk thermal transport [43, 62]. Assuming that the thermalization is limited by phonon-mediated thermal transport through the silicon cantilever beam, the saturation temperature can be explained by a power dissipation in the cantilever of the order of 1 femtowatt.

At the lowest bath temperature of 16 mK, the quality factor of the resonance is $Q_{16\text{mK}} = (3.8 \pm 0.3) \cdot 10^3$, which corresponds to a damping factor of $c = (1.4 \pm 0.1) \cdot 10^{-12}$ Ns/m. Using the fluctuation-dissipation theorem [64], we can calculate the equivalent force noise amplitude spectral density $\sqrt{S_F}_{16\text{mK}} = \sqrt{4k_B T_0 c} = (2.1 \pm 0.2) \text{aN}/\sqrt{\text{Hz}}$. We observe that upon increasing the bath temperature to 40 mK, the quality factor increases to $Q_{40\text{mK}} = (5.8 \pm 0.8) \cdot 10^3$, while the cantilever noise temperature stays constant at $T_0 = 56$ mK. We can thus obtain a force noise of $\sqrt{S_F}_{40\text{mK}} = (1.6 \pm 0.2) \text{aN}/\sqrt{\text{Hz}}$. At an alignment distance of $d = 3.65 \mu m$, we calculate by numerical simulation that the maximum force that a spin-$-\frac{5}{2}$ electronic defect can exert on the cantilever is 1.2 aN. In a measurement bandwidth of 3.8 Hz, we should then in principle be able to detect an ensemble of 3 fully polarized Fe$^{+}_{\text{Ti}}$ defects in the STO substrate. If we would be able to decrease the distance to $d = 1.8 \mu m$, the force of a single spin-$-\frac{5}{2}$ defect could be more than 20 aN. However, the damping factor, and hence the force noise, is expected to also increase further upon approaching the surface [72].

7.5 Temperature-dependent cantilever-sample interaction measurements

![Graph](image)

Figure 7.6: a) The cantilever resonant frequency shift $\Delta f_r = f_r - f_{r,0}$, determined by fitting Lorentzian lineshapes to the thermal noise peaks, as a function of the cryostat temperature $T$. At high temperatures the resonant frequency approaches $f_{r,0} = 3974.4$ Hz. The blue lines represent the modeled frequency shift for a cantilever that is coupled to a 3D distribution of spin-$-\frac{5}{2}$ electrons. b) Detail of the data in a) which shows that the increase of $\Delta f_r$ with increasing $T$ at temperatures below 35 mK is consistent. The dataset was obtained after stepping up the power in the experiment heater, causing the experimental mass to warm up to 22.2 mK in the course of 1.5 hours.
When the cantilever is scanned across the superconducting detection coil, we observe frequency shifts up to a few kilohertz due to the magnetic and superconducting interaction stiffness (see Sect. 4.3). Here, we have aimed to align the cantilever such that this interaction is minimal, while maintaining a sufficiently high coupling to be able to detect the cantilever thermal noise. At a small separation distance from the surface, we then increase the bath temperature in order to distinguish between any substrate effect and the interaction with the coil. In Fig. 7.6a, we show the resonant frequency shift $\Delta f_r$ of the cantilever at constant height, obtained by fitting Lorentzian lineshapes to the thermal peak, versus the bath temperature $T$. We observe that the resonant frequency increases slightly when warming up from 15 mK to 35 mK, and then decreases as the temperature increases further. A $1/T$ curve fit to the high temperature values of the resonant frequency yields an asymptote of $f_{r,0} = (3974.60 \pm 0.08)$ Hz, which is 824 Hz higher than the cantilever resonant frequency at large magnet-surface separations. We infer that this is the frequency shift due to the interaction with the detection coil, from which we can calculate the effective cantilever stiffness $k_{\text{eff}} = 1.29 \cdot 10^{-4}$ N/m, 1.6 times higher than the mechanical stiffness of the cantilever beam. The additional frequency shift up to 7 Hz at low temperatures, shown here, should be solely due to interaction with the STO substrate\(^4\).

Above 0.1 K, $\Delta f_r$ scales like $1/T$. In previous work on a Si-SiO$_2$ substrate, we observed a similar behavior, which we showed to be consistent with the presence of a homogeneous layer of paramagnetic defects [106]. However, on Si-SiO$_2$ we did not observe a decrease of $\Delta f_r$ when cooling below 100 mK. To stress that this trend is really significant in our current data, we show a detail of the graph in Fig. 7.6b, which contains 7 consecutive datapoints that were obtained after stepping up the power of our experiment heater. As the experimental chamber tends to its new, higher, equilibrium temperature in the course of $\sim 1.5$ hours, the resonant frequency unambiguously increases by about 0.2 Hz. We stress that this trend was not observed on Si-SiO$_2$ because the resonant frequency was then determined by driving the cantilever with a piezo actuator, as in contrast to measuring the thermal noise, thus effectively dissipating a sufficient amount of power in the electron spin bath to prevent the spins to cool to the lowest temperatures.

Interestingly, the absence of a saturation in our data indicates that the spin bath cools to temperatures below 20 mK, while the cantilever noise temperature was shown to stay constant at 56 mK. In order to check whether such a temperature gradient between cantilever and sample is stable, we estimate the power that is transferred from the cantilever to the spin bath by:

$$\bar{P}(f) = 2\pi^2 c_s f^2 |\hat{x}(f)|^2$$

(7.2)

Here, $c_s = 2\pi f_r m (1/Q - 1/Q_0)$ is the damping factor due to the interaction

\(^4\)Since the temperature is well below the critical temperature of niobium, and the magnetic field of the magnet at the location of the superconducting structures is always lower than the lower critical field of niobium, we expect no significant change in the superconducting repulsion of the magnet upon varying the temperature.
between the cantilever and the spins. The root-mean-squared displacement of the cantilever at 56 mK is 77 pm, from which we calculate that the power dissipation into the spin bath is 2.2 yW, 9 orders of magnitude lower than the minimal heat transport through the cantilever beam at $\Delta T = 50$ mK. Thus, it is plausible that, while the cantilever magnet is heated to 56 mK by microwave thermal radiation from room temperature wiring, the sample temperature remains below 20 mK.

Since no external fields are applied in our experiment, we expect that spin-carrying particles in the substrate align their magnetic moments $\mu$ along the field lines of the cantilever magnet, as long as $B_m \gg B_{loc}$, where $B_m$ is the magnet field and $B_{loc}$ is the average dipolar field that sample spins feel from their neighbors. To each spin, $i$, we assign a potential energy $U_i = -\mu_i \cdot B_m(\vec{r}_i)$. The force that the cantilever experiences due to a single spin, in its soft direction along $x$, is $F_{x,i} = -\frac{\partial}{\partial x} U_i$. We can associate a stiffness with the interaction between the spin and the magnet by taking the derivative of the force:

$$k_{x,i} = \frac{\partial^2}{\partial x_i^2} U_i = -\frac{\partial^2}{\partial x_i^2} (\mu_i \cdot B_{m,i})$$  (7.3)

By weighing the expression for the Boltzmann polarization $P(B_m, T)$ and integrating over the sample volume, we find an expression for the total interaction stiffness:

$$k_{spin} = \sum_i P(B_{m,i}, T) k_{x,i} \approx \rho \int_V P(B_m(\vec{r}), T) k_x(\vec{r}) d^3r$$  (7.4)

In the volume in which the Boltzmann polarization is higher than 5 percent at the lowest temperatures, the magnet field $B_m$ ranges from one to a few hundred millitesla. Even for proton spins, the Larmor frequency $f_L = \gamma B_m$, where $\gamma$ is the spin gyromagnetic ratio, is then always much higher than the resonant frequency of the cantilever. Thus, when the cantilever moves, $B_m$ changes adiabatically for the spins, in which case the sample magnetization always lies along the direction of the magnetic field [11]. Equation (7.3) then simplifies to

$$k_{x,i} = -\mu_i \frac{\partial^2}{\partial x_i^2} B_{m,i}$$  (7.5)

We have shown in Sect. 7.2 that the dominant paramagnetic bulk defect in our STO substrate is the spin-$\frac{5}{2}$ Fe$^{5+}$ center. The magnitude of the magnetic moment of this spin is $\mu_{Fe} = \frac{5}{2} \gamma \hbar = 5 \mu_B$, where $\mu_B = 9.27 \cdot 10^{-24}$ Am$^2$ is the Bohr magneton. At high fields, when the Zeeman term of the hamiltonian in Eq. (7.1) is dominant, we can express the polarization of a spin ensemble as:

$$P(B_m, T) = \frac{\sinh \left( \frac{\mu_{Fe} B_m}{k_B T} \right) + \frac{3}{5} \sinh \left( \frac{3\mu_{Fe} B_m}{5k_B T} \right) + \frac{1}{5} \sinh \left( \frac{\mu_{Fe} B_m}{5k_B T} \right)}{\cosh \left( \frac{\mu_{Fe} B_m}{k_B T} \right) + \cosh \left( \frac{3\mu_{Fe} B_m}{5k_B T} \right) + \cosh \left( \frac{\mu_{Fe} B_m}{5k_B T} \right)}$$  (7.6)

In Fig. 7.6a, we have plotted the calculated frequency shift of the cantilever interacting with a bulk distribution of Fe$^{5+}_{Ti}$ defects (blue lines), using Eqs.
Varying only the magnet-sample distance, \( d \), and the spin density, \( \rho \), we obtain reasonably good fits for \( d = (3.65 \pm 0.10) \mu m \) and \( \rho = (0.65 \pm 0.05) \cdot 10^{23} m^{-3} \). The distance is in accordance with what we have estimated using capacitive sensors on our coarse approach motor. The density of \( Fe'_Ti \) defects that we find corresponds well to values reported in the literature [97], in particular to the concentration of \( 0.7 \cdot 10^{23} m^{-3} \) that is reported in Ref. [101].

### 7.6 MRFM spectroscopy of \( Fe'_Ti \) centers in STO

Now that we have inferred from the temperature-dependent cantilever frequency shift that the magnet is coupled to spin-\( \frac{5}{2} \) \( Fe'_Ti \) centers, we study the cantilever response to the selective excitation of spin subsets by applying microwave pulses via the RF microwire. While we monitor the cantilever resonant frequency, by continuously driving it at a peak-to-peak amplitude of 25 nm in a phase-locked-loop with a bandwidth of 300 Hz, we (partly) saturate resonant spins with short, high-intensity RF pulses. From the resulting change in the resonant frequency, \( \Delta f_r = f_r - f_{r,0} \), we then calculate the change in interaction stiffness:

\[
\Delta k_{\text{spin}} = k_{\text{eff}} \left( \frac{f_r}{f_{r,0}} \right)^2 - 1
\]

#### 7.6.1 Results

![Figure 7.7: Change in interaction stiffness, \( \Delta k_{\text{spin}} \), between sample spins and cantilever magnet as a function of time for two different excitation frequencies at 4 GHz and 6 GHz. The grey areas indicate the 50 ms time window when the microwave power was switched on. The power of the pulses was 2.5 \( \mu W \). The time between consecutive pulses was 10 s. The center of the cantilever magnet was aligned at an estimated distance of \( d = 3.6 \mu m \) from the surface. The red curves were obtained by averaging over 100 measurements. The black curves are obtained by smoothing the data over 1000 datapoints. The blue curves represent double exponential fits to the experimental data.](image)

In Fig. 7.7 we show two representative \( \Delta k_{\text{spin}} \) measurements as a function
of time for the microwave excitation of the sample at 4 GHz and 6 GHz. We applied 50 ms pulses (grey areas) with a power of 2.5 \( \mu \)W at the experiment, corresponding to an estimated r.m.s. RF field of \( B_1 \approx 15 \mu \)T at the location below the magnet. During the pulses, we observe a fast decrease of the interaction stiffness. When the pulses are switched off, the polarization recovers to its equilibrium value within a few seconds. The post-pulse part of the curves can be fit reasonably well to a double exponential decay function, indicating that different timescales are involved in the recovery of the polarization.

Curve fitting of several saturation-recovery curves for excitation frequencies between 3.5 GHz and 6.0 GHz yields a clear distinction between a slow decay, \( \tau_1 = (1.0–1.7) \) s, and a relaxation which is one order of magnitude faster, \( \tau_2 = (0.16\pm0.05) \) s. Since our signal strength depends on the net magnetization of the sample, we attribute the slowest process, with time constant \( \tau_1 \), to spin-lattice relaxation. The faster process could be due to a redistribution of magnetization via spin-spin interactions. Since the average spacing between the iron ions, which we calculate from the density, is 25 nm, it is unlikely that a magnetization current will flow through interactions with neighboring electron spins, e.g. diffusion through flip-flop interactions would already be quenched at field gradients as low as 2 T/m. Since STO contains several species of nuclear spins, namely \(^{87}\)Sr, \(^{47}\)Ti, \(^{49}\)Ti, and \(^{17}\)O, hyperfine coupling could play a role. An alternative explanation for the presence of multiple timescales in the magnetization recovery is that spins at various magnetic field strengths are excited simultaneously with a single pulse (see Fig. 7.11). Spins that experience a less strong polarizing field, will in theory exhibit a shorter \( T_1 \) relaxation time [11].

A \( \Delta k_{\text{spin}} \) spectrum for a wide range of microwave frequencies is shown in Fig. 7.8. In order to minimize the power dissipation in the sample, we reduced the pulse length to 20 ms, while keeping the pulse power at 2.5 \( \mu \)W. The dataset that is represented by the red circles was measured with the center of the cantilever magnet at a distance of \( d = (3.55 \pm 0.05) \) \( \mu \)m from the chip surface. At frequencies below 1 GHz, we observe three zero crossings of the \( \Delta k_{\text{spin}} \) curve. Crossing III, between 800 MHz and 850 MHz, can be explained by the transition from exciting high-field spins, close to the magnet, with predominantly positive \( k_{\text{spin}} \) contributions, to exciting low-field spins with mainly negative \( k_{\text{spin}} \) (see Fig. 7.9b and c). We have observed such a zero-crossing before on spin-\( \frac{1}{2} \) \( P_\beta \) centers in Si-SiO\(_2\) [106]. The origin of the double zero-crossing at \( f_{RF} = 500 \) MHz (feature II) cannot be so easily explained. In the next section we will show that it is characteristic of the paramagnetic Fe\( ^{3+} \) defect in STO-(100) and that it depends on the crystal field parameters in the spin Hamiltonian (7.1).

The black triangles represent the spectrum that we measured after retracting the cantilever by 3 \( \mu \)m. At this distance, we expect to see no resonant spins above \( f_{RF} \approx 2 \) GHz. Indeed, the signal has decreased by a factor of 5 overall, and the zero-crossings have disappeared, but we still observe a finite response over the entire excitation range. This indicates that a non-linear crosstalk exists between the RF microwire and the cantilever. Such a microwave-induced change in cantilever frequency has been reported also in
other magnet-on-cantilever MRFM measurements [19]. In cantilevers that are not magnetically tipped, non-linear driving has been proven possible through electrostatic coupling to trapped charges on a Si cantilever [107]. Although crosstalk is an issue that must be addressed in order to push MRFM to single-spin resolution, in our current experiment, in which we are coupled to many spins, it is small enough to clearly distinguish the spin signal.

7.6.2 Discussion

Whereas in the conventional EPR experiment, described in Sect. 7.2, the sample was subjected to a magnetic field with a single magnitude and direction per measurement, in our MRFM experiment almost all directions and magnitudes up to $\sim 100$ mT of the magnet field, $B_m$, are present in the sample. Figure 7.9a shows the energy level diagram of Fe\textsuperscript{T1} in STO when the magnetic field is along the $\langle 100 \rangle$ crystal axis. The grey area indicates the field magnitudes that are present inside the sample when our cantilever magnet is at a distance $d = 3.5 \, \mu m$ from the sample surface. For a fixed microwave excitation frequency, multiple level transitions (indicated by the red vertical lines) are possible simultaneously. As is shown in Fig. 7.3, the resonant field values depend on the polar angle, $\theta$, as well as on the azimuthal angle, $\phi$.

In order to understand the features in the measured $\Delta k_{\text{spin}}$ spectrum in Fig. 7.8, we built a model that simulates the change in spin-sample interaction stiffness for a given microwave excitation frequency. First, we calculate the
Figure 7.9: Calculations involved in modeling the $\Delta k_{\text{spin}}$ spectrum in Fig. 7.10. a) Energy level diagram for Fe$^{+}_{\text{Ti}}$ in STO as a function of magnetic field, calculated for angles $\theta = \phi = 0$ between the field and the crystal axis. The vertical lines indicate the possible level transitions for $f_{RF} = 6$ GHz: the red lines correspond to the most intense EPR signal. The grey area indicates the fields that are present due to the cantilever magnet. b) Contour plot at $y = 0$ of the magnetic field $B_m$ of the cantilever magnet inside the sample. The distance between magnet center and the surface is $d = 3.5 \, \mu\text{m}$. The red dots correspond to the transitions in Fig. a. c) Contour plot of the interaction stiffness per spin. The blue areas in the center correspond to regions where $k_{\text{spin}}$ is positive, while the red areas on the sides indicate where $k_{\text{spin}}$ is negative.
resonant fields $B_{\text{res}}$ corresponding to $f_{RF}$ for a range of values of $\theta$ and $\phi$, using the “EasySpin” EPR spectrum simulation software [108], as shown in Fig. 7.9a. Next, using an adaptive Marching Cubes (MC) algorithm [109] written in C++, we calculate the shape of the resonant slices by looking up for each voxel what the field direction is and what the corresponding resonant fields are. The red dots in Fig. 7.9b indicate resonant voxels for $f_{RF} = 6$ GHz and $\theta = \phi = 0$. Then, using Eq. (7.5), we calculate the interaction stiffness for each resonant voxel (see Fig. 7.9c). The interaction stiffness is weighed by the Boltzmann polarization (Eq. (7.6)) and by the local thickness of the resonant slice. Finally, by summing the interaction stiffness of all resonant voxels, we arrive at a net value for $\Delta k_{\text{spin}}$.

Figure 7.10: Modeled $\Delta k_{\text{spin}}$ spectrum. The roman numbers identify the features in the experimental spectrum in Fig. 7.8.

In Fig. 7.10 we show the modeled $\Delta k_{\text{spin}}$ spectrum for a magnet-sample distance of $d = 3.5 \, \mu \text{m}$ and a temperature $T = 60$ mK. The qualitative agreement with the experimental spectrum in Fig. 7.8 is remarkable. The resonant slices that correspond to the features in the spectrum that are indicated with roman numbers, are plotted in Fig. 7.11. At the lowest excitation frequencies, of which feature I at $f_{RF} = 0.25$ GHz is typical, the resonant slices extend far into the bulk, leading to a dominance of negative $k_{\text{spin}}$ spins, which results in a positive $\Delta k_{\text{spin}}$ signal upon excitation of these slices.

The sharp feature II at 500 MHz emerges in the model at a slightly higher frequency of 570 MHz. It is characterized by a relatively small amount of resonant slices (in fact, only one slice and four resonant “pockets”) which explains why at this particular excitation the positive $k_{\text{spin}}$ spins dominate. The feature in the model is less deep than in the experiment, which we believe is due to a too coarse binning of $\theta$ and $\phi$ in the $B_{\text{res}}$ lookup table. Indeed, the MC algorithm fails to plot the entire area of the positive $k_{\text{spin}}$ “dome” in the center of the slice.
Figure 7.11: Calculated resonant slices for the excitation frequencies corresponding to the features in Figs. 7.8 and 7.10. The circles indicate the size (3.5\(\mu\)m diameter) and position \((d = 3.5\ \mu\text{m})\) of the cantilever magnet. Blue areas correspond to \(k_{\text{spin}} > 0\) and red areas to \(k_{\text{spin}} < 0\). The intensity of the color indicates the signal strength.
At the zero-crossing (III) the positive and negative slices cancel. Its position depends on the magnet distance, $d$, and the sample temperature, $T$. We found the best qualitative agreement for the settings mentioned above, but the zero-crossing can also be reproduced by setting $T = 20$ mK and $d = 3.6 \, \mu m$, for example.

The features IV and V can be explained by observing that the slices at $f_{RF} = 1.5$ GHz (IV) do not extend far into the sample, leading to positive $k_{\text{spin}}$ dominance, whereas at $f_{RF} = 2.5$ GHz lower $B_{\text{res}}$ slices emerge due to the crystal-field splitting (the cubic term $a$ splits the zero-field energy levels in a doublet and a quartet that are separated by $3a \approx 2$ GHz).

At the highest excitation frequencies (VI), the slices become less complex (we approach the Zeeman-dominated regime) and smaller, leading to predominantly negative $\Delta k_{\text{spin}}$ signals. The calculated volume of the 6 GHz resonant slices is $0.62 \, \mu m^3$, which is the smallest accessible volume for this experiment. We derived from the temperature-dependent frequency shift data that the density of iron defects is $0.65 \, m^{-3}$. This means that we are coupled to at least 40000 electron spins. When we compare the magnitude of the modeled signal with the experimental signal, we observe that the experimental value is two times larger. If this is due to an underestimation of the slice thickness, the number of spins that we measure would actually be 80000.

A striking property of the $\Delta k_{\text{spin}}$ spectrum is that the positions of the sharp features II and V depend strongly on the crystal-field terms $a$ and $D$ in the Fe$^{\prime}_T$ Hamiltonian (7.1) and only weakly on the experimental details such as cantilever magnet alignment and sample temperature. In a way, the spectrum is a finger print of the specific spin system under study. This means that MRFM, employed in the way that is described here, allows for the determination of crystal structures at dilution refrigerator temperatures. The lowest temperature that we found to be reported in crystallographic EPR studies on STO is 1.9 K [96]. By measuring at effective temperatures less than 60 mK, we lowered this limit by a factor of at least 30.

Our model corresponds best to the data when we set the zero-field splitting term to $D = 0$. Finite values of $D$ lead to satellite peaks of feature II at 350 MHz and 750 MHz, which we do not observe in the data. This could either be due to a too low resolution of our measured spectrum, or, more likely, due to the fact that the STO crystal has three equivalent $\langle 100 \rangle$ axes that act as rotation axes for the oxygen octahedra. Whereas we chose the $z$-axis as the rotation axis, in reality the crystal will consist of domains in which either the $x$-, $y$-, or $z$-axis play this role.

The spectrum in Fig. 7.9 was calculated for $a = 0.023 \, cm^{-1}$, the highest value reported in the literature at a sample temperature of 1.9 K [96]. The model predicts the resonant frequency of feature II 70 MHz too high, when compared to the experimental frequency of $f_{RF} = 500$ MHz. By increasing the crystal field splitting term to $a = 0.0238 \, cm^{-1}$, feature III of the model shifts down to $f_{RF} = 540$ MHz, closer to the experimentally observed value. We conjecture that the crystal field splitting term of Fe$^{\prime}_T$ in STO-(100) is larger than $a = 0.0238 \, cm^{-1}$ at $T = 60$ mK. By increasing the resolution of the
measurement as well as of the model, this statement might be put to test in future experiments.

7.7 Conclusion and outlook

In our first full-featured experimental run with a SQUID-based MRFM, we have measured spin-$\frac{5}{2}$ Fe$^{'}$Ti defects in an STO-(100) crystal. The presence of these paramagnetic defects was confirmed in an independent EPR experiment. Micro-fabrication of a superconducting detection coil and RF microwire on top of the STO substrate allowed for cantilever detection and spin excitation, respectively. Using a 3D coarse approach motor, we were able to align the cantilever magnet close to the detection coil, such that its thermal motion could be detected.

By studying the temperature-dependent frequency shift of the thermal resonance peak, we were able to estimate the density of Fe$^{'}$Ti defects at $\rho = (0.65 \pm 0.05) \cdot 10^{23}$ m$^{-3}$. The experimental data suggest that the spin bath cools to temperatures below 20 mK, while the cantilever has a saturation temperature of 56 mK.

By driving the cantilever and measuring its frequency shift while applying microwave pulses to the sample, we measured a $\Delta k_{\text{spin}}$ spectrum that contains features that seem to be specific to the crystal field parameters in the Fe$^{'}$Ti spin Hamiltonian. By modeling the spectrum, we were able to reproduce the measured spectrum and to understand its specific features. Our data suggest that the crystal field splitting term, $a$, of Fe$^{'}$Ti in STO-(100) is larger than $a = 0.0238$ cm$^{-1}$ at $T = 60$ mK.

We have found that, in contrast to well-established techniques such as EPR and X-Ray Diffraction, MRFM spectroscopy of high-spin paramagnetic defects enables crystallography at dilution refrigerator temperatures. By measuring at a temperature lower than 60 mK, we have reduced the lowest reported temperature for the study of STO by more than a factor of 30. We believe that SQUID-based MRFM can be a very useful tool to the fields of EPR and, in general, crystallography, as it opens up the possibility to perform experiments at the sub-Kelvin temperature range as well as to probe micrometer scale variations in crystal parameters.