On-chip ESR measurements of DPPH at mK temperatures

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Abstract
We study electron spin resonance (ESR) of DPPH at mK temperatures. Here we employ a superconducting coplanar microwave resonator that allows convenient implementation in a dilution refrigerator as well as operation at multiple ESR frequencies, in this case 1.5 GHz, 3.0 GHz, and 4.5 GHz. We find a strong temperature and magnetic field dependence of the ESR of DPPH below 1 K, which is consistent with an antiferromagnetic transition. Our study documents the potential of this on-chip ESR technique for mK experiments and elucidates the possibility to use DPPH as an ESR reference material in this regime.

Keywords: DPPH, ESR, EPR, mK temperatures, superconducting coplanar resonator

1 Introduction

Electron spin resonance (ESR) spectroscopy is a powerful tool to study magnetic properties of diverse materials in physics, chemistry, and biology. Commercial ESR spectrometers are widely established and most commonly work at X-band (∼10 GHz) or Q-band (∼34 GHz) frequencies, corresponding to resonance fields of 0.33 T and 1.2 T for a $g = 2$ spin system (free electrons). ESR studies at cryogenic temperatures can be performed down to $^4$He temperatures (i.e. lowest achievable temperature around 2 K) using commercial ESR cryostats, which cool the sample while the rest of the spectrometer, including the microwave resonator for the particular frequency, is kept at room temperature. Technological developments to push the limits of these relevant parameters of ESR spectrometers (i.e. ESR frequency, magnetic field range, sample temperature) mostly focused on higher frequencies and magnetic fields ('high-field EPR'), where higher sensitivity can be achieved [14, 8].

But for several material classes the opposite limit of ESR parameters, namely lower frequencies, magnetic fields, and temperature, is of particular interest. This is the case for materials that undergo magnetic phase transitions at very low temperatures and/or low magnetic fields. A prime example is the heavy-fermion metal YbRh$_2$Si$_2$, which orders antiferromagnetically at...
temperatures below 70 mK and magnetic fields below 60 mT. This field-suppressed magnetic order leads to pronounced quantum-critical behavior \([6, 4, 7]\). Since heavy-fermion behavior in general and this quantum phase transition in particular are related to the interplay of local moments and conduction electrons, ESR experiments can reveal important microscopic information about the magnetic response provided that the spins are ESR-active, as is the case for \(\text{YbRh}_2\text{Si}_2\) \([23, 13]\). Other materials that call for ESR experiments at temperatures well below the \(^4\text{He}\) range are doped semiconductors (also in the context of quantum information processing) \([15, 17]\) as well as certain low-dimensional and/or frustrated local-moment systems \([18]\).

Here we have the case of \(\text{YbRh}_2\text{Si}_2\) in mind, i.e. we want to work at multiple low-GHz frequencies, fields below 200 mT, and temperatures down to 30 mK. The low temperature directly calls for a \(^3\text{He}/^4\text{He}\) dilution refrigerator, and our approach to cover several ESR frequencies with good sensitivity is using several harmonics of a one-dimensional microwave resonator based on a superconducting coplanar transmission line \([21]\). This particular device is one example for several on-chip techniques that have been developed in recent years in different contexts and that can be easily incorporated in commercial dilution refrigerators \([16, 22, 2, 9, 26]\). Any ESR experiment requires that the static magnetic field at the sample position is known precisely, as this directly limits the precision of the experimental determination of the \(g\) factor of the sample. One way to ensure exact knowledge of this static field is including a small reference sample with known \(g\) factor, which is then measured simultaneously with the sample of interest with unknown \(g\) factor. A material that is widely established as such an ESR reference is DPPH \([27]\).

In our particular case, use of an EPR reference material is particularly advisable as we apply a static external field with a commercial superconducting solenoid (controlled with a power supply that allows nominal field steps not smaller than 0.1 mT) and as we use a superconducting planar resonator that can distort the external magnetic field \([2]\). Furthermore, both of these superconducting devices can in principle exhibit hysteresis during field sweeps \([1]\), which again calls for an independent field determination at the sample position. At the present stage, there is no generally established reference material for ESR studies at mK temperatures. While DPPH is commonly used at temperatures above 1 K, application at mK temperature might be impeded by magnetic ordering \([25]\). Therefore, we investigate the ESR properties of DPPH at temperatures between 30 mK and 800 mK and at ESR frequencies between 1.5 GHz and 4.5 GHz, corresponding to static magnetic fields between 52 mT and 156 mT.

2 Experiment

The core of our experiment is a superconducting coplanar microwave resonator \([21]\). A coplanar resonator is conceptually similar to a coaxial cable. There is a signal-carrying inner center conductor and a grounded outer conductor. We fabricate this planar structure with photolithography, starting with a thin film of niobium which is sputter-deposited on a sapphire substrate. The center conductor line has two gaps of 80 to 90 \(\mu\text{m}\) (Fig. 1a). The resonator cavity is formed through these gaps and the length of the inner conductor between the two gaps determines the allowed frequencies \(f_{0,n}\) of the resonator.

\[
f_{0,n} = \frac{nc}{2\sqrt{\varepsilon L}}
\]

with \(n\) the number of the mode, the length of the resonator \(L\), the vacuum speed of light \(c\), and the effective dielectric constant \(\varepsilon\). The data shown below belong to the modes \(n = 1, 2,\) and 3
with corresponding frequencies of $f_0 = 1.5 \text{ GHz}$, $3.0 \text{ GHz}$ and $4.5 \text{ GHz}$.

Using a resonator not only enhances the interaction between microwave signal and sample, thus leading to improved sensitivity, but also helps to overcome some challenges of cryogenic microwave spectroscopy [21]: if the resonance line in the measured microwave spectrum is sufficiently narrow, then the damping and phase shift of the coaxial cables do not have to be taken into account, which otherwise is increasingly difficult for lower temperatures [20, 24].

The DPPH sample was a powder which was attached to the superconducting resonator chip using vacuum grease. The total volume of DPPH was around $1.6 \cdot 10^5 \mu m^3$ compared to an approximated volume of the resonator cavity of $1.8 \cdot 10^{11} \mu m^3$. The placement of the DPPH sample can be seen in Fig. 1b.

The superconducting resonator was mounted inside a sample holder box made of brass. This box, which was fitted with 1.85 mm coaxial connectors by Anritsu, was mounted to the cold finger of a commercial He$^3$/He$^4$ dilution refrigerator. The microwave measurement is performed with an Agilent vector network analyzer (VNA), measuring the transmission coefficient $S_{21}$ of the microwave signal passing through the resonator. The VNA and the sample box are connected by a sequence of coaxial cables inside the cryostat, namely (starting from the room temperature side) semi-rigid stainless steel coaxial cables, superconducting coaxial cables (for effective thermal decoupling), semi-rigid stainless steel, and flexible copper coaxial cables. A room-temperature amplifier was included on the detection side before the VNA input. We measured the transmission through the resonator as a function of frequency (around each resonance mode), magnetic field, and temperature.

3 Results

The key experimental quantity in this work is the quality factor $Q$ of the resonator [12]. The quality factor is defined as the energy stored in the system divided by the energy loss per cycle; thus the losses in the system are directly related to the quality factor. The experimental access
to the quality factor is via the resonance frequency $f_0$ and the width of the resonance $\Delta f$ in the measured transmission spectra. To determine the quality factor, a Lorentzian curve was fitted to these data. The fit parameters of this curve identify the resonator $Q$ by

$$Q = \frac{f_0}{\Delta f}. \tag{2}$$

This $Q$ was determined for each magnetic field $B$ of a field sweep (at a fixed temperature). For further analysis a Dysonian shaped function was fitted to the data $Q(B)$. This Dysonian model [10] is given in Eq. 3, where $P(B)$ is the absorbed power depending on the external magnetic field $B$.

$$P(B) = \frac{\Delta B + \alpha(B - B_0)}{4(B - B_0)^2 + \Delta B^2} + \frac{\Delta B + \alpha(B + B_0)}{4(B + B_0)^2 + \Delta B^2} \tag{3}$$

with the magnetic resonance field $B_0$, the full width at half maximum $\Delta B$ of the magnetic resonance and the dispersion-to-absorption ratio $\alpha$. This absorbed power depending on the external magnetic field $P(B)$ is inversely proportional to the field-dependent resonator quality factor $Q(B)$ plus an offset.

From the Zeeman effect for a spin 1/2-system one can derive the resonance condition for ESR,

$$hf_0 = g\mu_BB_0 \tag{4}$$

with the Planck constant $h$ and the Bohr magneton $\mu_B$. Eq. 4 is used to calculate the $g$ factor from experimentally determined data $f_0$ and $B_0$

In Fig. 2 the experimentally determined $g$ factors of our DPPH measurements are shown for temperatures from 4.7 K down to 30 mK. The shown data belong to a resonator frequency of approximately 1.5 GHz. Each line belongs to one temperature sweep and was measured from lowest to highest temperature. Each data point is obtained from a magnetic field sweep. The magnetic field sweeps had a maximum of either 80 mT if only the first resonator mode was measured or 170 mT if the first three modes were measured. Between some of the temperature sweeps, the geometry inside the sample box was changed. In later experiments we intend to study metallic samples as for example YbRh$_2$Si$_2$ which was mentioned in the beginning with respect to the DPPH reference. ESR experiments with coplanar resonators can be optimized through varying the distance between the resonator chip and the sample [3]. Another possible experiment would be angle dependent ESR measurements, where the sample is mounted to a metallic block, which is then rotated with respect to the external magnetic field and the superconducting resonator. This was done in this work.

Similar to previous mK studies with frequencies ranging from 42 MHz to 300 MHz on DPPH [5, 11, 19, 25], we observe a pronounced change of the ESR line between 100 mK and 500 mK. At these temperatures a transition from a paramagnetic state to an antiferromagnetic state occurs [5]. It is surprising that the experimentally determined $g$ in our experiment varies for different angles of a metallic block, the designated sample holder, inside the box. This difference of the $g$ factors at 41 mK is 0.7%. We believe that this difference does not reflect an intrinsic property of the DPPH, but instead is caused by a discrepancy between the externally programmed static field and the actual magnetic field at the DPPH site. Thus, this experiment underlines the need for an independent determination of the magnetic field for ESR experiments of this kind using superconducting resonators, at least if precise values for $g$ are desired (in this case better than 1%).
Figure 2: Experimentally determined $g$ factor for different geometries of the resonator box depending on the rotation angle of a metallic block inside the resonator sample box. This metallic block is the designated sample holder for samples with unknown magnetic properties. The inset shows the experimental resonance fields $B_0$ from which the $g$ factor was calculated.

Figure 3: Temperature-dependent ESR linewidth for different geometries of the resonator box.
Figure 4: (a) Experimentally determined $g$ factor of DPPH for three different output powers of the VNA: -23 dBm (blue squares), -30 dBm (red circles), and -40 dBm (green triangles). Within the error bars no power dependence is visible. (b) The $g$ factor in color code as a function of temperature and magnetic resonance field. These experimentally measured magnetic resonance fields belong to the first, second, and third mode of the resonator. For all magnetic resonance fields we find a tendency to higher $g$ factors as the temperature decreases. Furthermore for lower magnetic resonance fields the $g$ factor is higher. White circles indicate the measured points in this phase diagram.

In Fig. 3 we plot the ESR linewidth against the temperatures. With decreasing temperatures we observe a broadening of the ESR line. According to [5] this can be interpreted as follows: for higher temperatures the exchange correlation time gets longer which narrows the ESR line. This can be clearly seen on the last data point at 4.7 K, where the linewidth is only around a quarter of the value for lowest temperatures. Also here the curves vary for different angles of the metallic block inside the resonator box. The change of the linewidth at 41 mK amounts to 12%.

Compared to literature [5] our ESR linewidth seems to be enlarged by a factor of two to four, although one has to consider that the experiments in Ref. [5] were carried out for frequencies of 74.4 MHz rather than our 1.5 GHz. However a possible reason for this can be the wide distribution of the DPPH on the resonator (Fig. 1) considering possible field distortions by the superconducting chip [2]. In our data we notice a flattening of the curves towards the lowest temperatures, which was not reported in [5].

One possible cause of error in such ESR experiments is saturation. To investigate this, we used different powers of the microwaves ranging from -23 dBm down to -40 dBm as the output power of the VNA. The power arriving at the resonator is lower due to the large damping in the coaxial cables. In Fig. 4a we show the experimentally determined $g$ factors for three different powers. No dependence is noticeable within the error bars. This indicates that even with highest used power no heating is observed.

In Fig. 4b the experimentally determined $g$ factors are shown as color plot as a function of temperature and magnetic field. For this plot the ESR was measured for the first three resonator modes with the frequencies 1.5 GHz, 3 GHz and 4.5 GHz. The corresponding magnetic fields are 52 mT, 104 mT and 156 mT. For decreasing temperatures the $g$ factor is increasing as well as for decreasing resonance fields.
4 Conclusion and Outlook

We used a superconducting coplanar resonator, mounted in a $^{3}$He/$^{4}$He dilution refrigerator, to study the ESR response of a DPPH powder directly attached to the resonator chip. We covered temperatures down to 30 mK (and up to 4.7 K) and magnetic fields up to 170 mT, corresponding to ESR frequencies between 1.5 GHz and 4.5 GHz. A transition from a disordered paramagnetic to an ordered state was observed and the ESR line was still present down to 30 mK. We find a pronounced dependency of the $g$ factor on temperature and magnetic field. Surprisingly, the geometry of the cavity inside the metal box into which the superconducting resonator is mounted also affected the ESR resonance fields and thus the experimentally determined $g$. This observation underlines our previous notion that ESR experiments of this kind, using planar superconducting resonators, require an independent determination of the static magnetic field at the sample position if precise values of the $g$ factor are desired. Our experiments document that DPPH might indeed be used for this task, as it displays a pronounced ESR line throughout our complete parameter range of temperature and magnetic field. But the strong temperature dependence of the ESR of DPPH at temperatures below 1 K requires a detailed characterization of the mK properties of DPPH before this material can conveniently be employed as a reference for high-precision ESR at mK temperatures using our experimental scheme.

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References


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