Effective Spin-1/2 Moments on a Yb$^{3+}$ Triangular Lattice: an ESR Study

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We investigated the spin dynamics by electron spin resonance (ESR) of the Yb-based, effective spin-1/2 delafossites NaYbO$_2$, AgYbO$_2$, LiYbS$_2$, NaYbS$_2$, and NaYbSe$_2$ which all show an absence of magnetic order down to lowest reachable temperatures and thus are prime candidates to host a quantum spin-liquid ground state in the vicinity of long range magnetic order. Clearly resolved ESR spectra allow to obtain well-defined $g$ values which are determined by the crystal field of the distorted octahedral surrounding of the Yb-ions in trigonal symmetry. This local crystal field information provides important input to characterize the effective $S = 1/2$ Kramers doublet as well as the anisotropic exchange coupling between the Yb ions which is crucial for the nature of the groundstate. The ESR linewidth $\Delta B$ is characterized by the spin dynamics and is mainly determined by the anisotropic exchange coupling. We discuss and compare $\Delta B$ of the above mentioned delafossites focussing on the low temperature behaviour which is dominated by the growing influence of spin correlations.

KEYWORDS: spin dynamics, triangular lattice, quantum spin liquid, electron spin resonance

1. Introduction

Recently it was shown that Yb-based delafossite systems are an ideal platform to study spin-orbit entangled frustration effects on a perfect triangular lattice [1–3]. They are possible candidates to host a quantum spin-liquid (QSL) ground state [4] which is characterized by persistent magnetic fluctuations down to zero temperature accompanied by an absence of long range magnetic order. Especially for systems with strong spin-orbit interaction theory predicts new exotic spin states (including different QSLs) with unconventional excitations [5]. Electron Spin Resonance (ESR) was used to characterize the spin dynamics of potential QSL systems with Yb$^{3+}$ spins on a triangular lattice [6, 7] where anisotropic exchange interactions between the spins have a major impact on the ESR linewidth. A clear and well-resolved Yb$^{3+}$ spin resonance was recently reported for the delafossite system NaYbS$_2$ providing local information on the Yb$^{3+}$ $g$-factor and spin dynamics [7]. For theoretical treatments for instance on the anisotropic exchange of triangular-lattice Yb magnets [8] ESR-obtained $g$ factors are important parameters to compare with. Here we present ESR results on various Yb-based delafossite systems differing in their anisotropic exchange and crystal electric field splitting of the Yb Kramers doublets.
2. Experimental

2.1 Electron Spin Resonance

We used a standard continuous-wave ESR technique at X-band microwave frequencies ($\nu = 9.4$ GHz). The resonance signal was recorded in the field-derivative $dP/dB$ of the absorbed power $P$ of a transversal magnetic microwave field $b_{mw}$. The sample temperature was set with a helium-flow cryostat allowing for temperatures between 2.7 and 300 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 $B_{res}$ which is determined by the effective $g$-factor [$g = \hbar v / (\mu B_{res})$] and internal fields. The spectra of the powder samples were fitted by directional averaging the Lorentzians with uniaxial anisotropy. The ESR intensity $I_{ESR}$ is determined by the static spin-probe susceptibility $\chi_{ESR}$ along $b_{mw}$. Thus, $I_{ESR}$ provides a direct microscopic probe of the sample magnetization. Details on the determination of $I_{ESR}$ from the spectra are given in Ref. [7].

2.2 Sample preparation and characterisation

We investigated single crystals of NaYbSe$_2$ as well as polycrystalline material of NaYbO$_2$, AgYbO$_2$, LiYbS$_2$, NaYbS$_2$. All these compounds have a delafossite structure (space group $R\bar{3}m$) with Yb$^{3+}$ occupying a single crystallographic site having $\bar{3}m$ symmetry. The Ag-ion in AgYbO$_2$ is linearly coordinated with O, whereas Li- and Na-ions are octahedrally coordinated with the chalcogenides. Polycrystalline powders of NaYbS$_2$ and LiYbS$_2$ (ampule-based synthesis) were prepared according to the procedures reported in Ref. [1]. NaYbSe$_2$ single crystals were prepared following the method of Lissner and Schleid [9]. Polycrystalline NaYbO$_2$ and AgYbO$_2$ were synthesized by a solid state reaction and a cation-exchange reaction, respectively [10]. Magnetic and thermal properties were recently reported in Refs. [2, 3, 11].

![Typical ESR spectra of NaYbSe$_2$ for two crystal orientations. Dashed lines denote Lorentzian shapes with $g$ factors as indicated. The structure near 0.33 T is a background feature. Inset: $g$ factor dependence on the angle $\Theta$ between the external field $B$ and the crystallographic $c$-axis with the microwave field $b_{mw} \perp c$. Dashed line indicates $g(\Theta) = \sqrt{g^2_\perp \cos^2 \Theta + g^2_\parallel \sin^2 \Theta}$ with $g_\perp$ and $g_\parallel$ given in the main frames.](image)

Fig. 1. Typical ESR spectra of NaYbSe$_2$ for two crystal orientations. Dashed lines denote Lorentzian shapes with $g$ factors as indicated. The structure near 0.33 T is a background feature. Inset: $g$ factor dependence on the angle $\Theta$ between the external field $B$ and the crystallographic $c$-axis with the microwave field $b_{mw} \perp c$. Dashed line indicates $g(\Theta) = \sqrt{g^2_\perp \cos^2 \Theta + g^2_\parallel \sin^2 \Theta}$ with $g_\perp$ and $g_\parallel$ given in the main frames.
3. Results

We obtained and analyzed the ESR data of the above mentioned compounds in the same way as previously reported for NaYbS\(_2\) [7]. All spectra are well-resolved and reveal a common characteristics for a \(J = 7/2\) state of Yb\(^{3+}\) in an crystal electric field environment with a \(R\bar{3}m\) space group symmetry.

3.1 NaYbSe\(_2\) single crystal

Similar to NaYbS\(_2\) [7], the ESR spectra of NaYbSe\(_2\), shown in Fig. 1, have very clear amplitudes and relatively narrow linewidths as compared to the ESR spectra of YbMgGaO\(_4\) [6]. The magneto-crystalline anisotropy of Yb\(^{3+}\) in an uniaxial crystalline-electric field yields the large anisotropy of the \(g\)-factor illustrated in the inset.

Fig. 2 demonstrates the temperature dependence of the ESR parameters being again very similar to NaYbS\(_2\) [7]. The linewidth \(\Delta \nu\) and the relaxation rates \(\Gamma\) show characteristic low- and high temperature behaviors: towards low temperatures a power law increase \(\Delta \nu(T) \propto 1/T^3/4\) and towards high temperatures an Orbach process \(\Delta \nu \propto 1/\exp(\Delta/k_B T) - 1\) which includes population of the first excited crystalline-electric field doublet at an energy \(\Delta\) above the ground state [7]. Within data accuracy, no clear temperature dependence of the \(\Gamma\) anisotropy could be resolved. Similar to NaYbS\(_2\) [7] we obtained a small anisotropy of the Weiss temperatures from the temperature dependencies of ESR intensity and \(g\)-factor (Fig. 2 right frame). For \(g_\parallel(T)\) and \(g_\perp(T)\) we used the equations given in Ref. [7] with the parameters \(g_\perp \approx 3.12\) and \(g_\parallel \approx 1.03\), in good agreement with the values describing the anisotropy (Fig.1).

![Fig. 2. Temperature dependencies of ESR parameters of NaYbSe\(_2\) for two orientations of the external field \(B\) to the \(c\)-axis. Left: ESR linewidth \(\Delta \nu\), relaxation rate \(\Gamma = \nu \Delta \nu / B_{\text{res}}\) and ratio of \(\Gamma\) along the two directions of the field. Dashed lines describe \(\Delta \nu(T)\) towards higher temperatures as a relaxation via the first excited crystalline electric field level of Yb\(^{3+}\) at \(\Delta = 160 \pm 30\) K. Inset: Linewidth without a residual contribution (\(\Delta \nu_0\) from the dashed lines in the \(\Delta \nu\)-frame). Solid lines suggest a power law behavior as indicated. Right: ESR intensity \(\chi_{\text{ESR}}\) and \(g\) factor for the external field \(B\) and the microwave field \(b_{\text{mw}}\) aligned to the \(c\)-axis as indicated. Dashed lines denote Curie-Weiss fits for the intensity and fits of \(g_\parallel(T)\) and \(g_\perp(T)\) using the equations given in Ref. [7].](image-url)
3.2 Polycrystalline NaYbO$_2$, AgYbO$_2$, LiYbS$_2$, and NaYbS$_2$

As shown in Fig. 3 the investigated polycrystalline samples all show well-defined powder-shaped Lorentzian ESR spectra with no dependence on the orientation of the field - as expected for arbitrarily oriented microcrystallites. The ESR intensity follows a Curie-Weiss law fairly well below about $T = 30$ K as suggested by the red dashed lines in the right frame of Fig. 3.

![Fig. 3.](image)

Figure 3. Left frame: Typical ESR spectra of the investigated polycrystalline powder samples at indicated temperatures. Dashed lines indicate a powder-averaged Lorentzian lineshape (except for AgYbO$_2$: single Lorentzian line). Right frame: inverse ESR intensity with dashed lines corresponding to a Curie-Weiss behavior as indicated.

Figure 4 compiles the temperature dependence of the linewidth for the polycrystalline samples. Again, as indicated by the dashed red lines, at high temperatures the first excited crystalline electric field level at $\Delta$ dominates (left frame). For NaYbO$_2$ the ESR-obtained $\Delta = 350 \pm 30$ K roughly agrees with the value $\Delta \approx 400$ K obtained from neutron scattering [12]. Towards low temperatures the linewidth increases with a power law behavior $\Delta B(T) \propto 1/T^{3/4}$ (right frame).

![Fig. 4.](image)

Fig. 4. Left frame: Temperature dependence of ESR linewidth $\Delta B$ of the investigated polycrystalline powder samples. Dashed lines describe $\Delta B(T)$ towards higher temperatures as a relaxation via the first excited crystalline electric field level of Yb$^{3+}$ at $\Delta$ K. Right frame: Linewidth without a residual contribution ($\Delta B_0$ from the dashed lines in the left frame). Dashed lines suggest a power law behavior as indicated.

4. Discussion and Summary

All investigated samples show a quite comparable characteristics of their Yb$^{3+}$ spin resonance, noteworthy a large g factor anisotropy, a clear influence of the first excited crystal-field split level on the linewidth and (at least for the investigated single crystals) a weak anisotropy of the local susceptibility obtained from the intensity. Table I compiles the main parameters extracted from the ESR data presented in the sections above.
Table I. ESR parameters with two uniaxial components: $g$-factor obtained from fitting the spectra by a Lorentzian shape, Weiss temperature $\theta$ obtained from the ESR intensity $x_{\text{ESR}} \propto (T + \theta)$, and first excited crystalline electric field level $\Delta (\pm 30 \text{ K})$ obtained from the high temperature behavior of the linewidth.

| compound     | $g_\parallel$ | $g_\perp$ | $\theta_\parallel (\text{K})$ | $\theta_\perp (\text{K})$ | $\Delta (\text{K})$ | remark       |
|--------------|---------------|-----------|-------------------------------|---------------------------|---------------------|--------------|
| NaYbSe$_2$  | 1.01(1)       | 3.13(4)   | 14.3                          | -                         | 14.0                | 160          |
| NaYbS$_2$   | crystal       | 0.57(3)   | 3.19(5)                       | 15.2                      | -                   | 14.8         |
| NaYbS$_2$   | polycrystal   | 0.6       | 3.21(5)                       | 15                        | -                   | 200          |
| NaYbO$_2$   | polycrystal   | 1.75(3)   | 3.28(8)                       | 9                         | -                   | 350          |
| AgYbO$_2$   | polycrystal   | -         | 3.1(5)                        | 2                         | -                   | 290          |
| LiYbS$_2$   | polycrystal   | 1.5(3)    | 2.9(4)                        | 25                        | -                   | 200          |

The anisotropy in the Weiss temperatures obtained from the single crystal ESR intensity of about 0.4 K is rather weak when compared with magnetization results [1, 11]. Note, however, that the exchange anisotropy provides a considerable contribution to the linewidth. As was estimated for NaYbS$_2$ [7] hyperfine and dipolar broadening yield less than 1 mT whereas the smallest observed linewidth amounts to 3.6 mT (in polycrystalline NaYbS$_2$).

Regarding a putative presence of a QSL ground state the low-temperature behavior of the linewidth is worth to be considered, keeping in mind that for none of the investigated samples magnetic order was observed. For NaYbO$_2$ the onset of the low-temperature increase of $\Delta B$ occurs in a similar temperature region where also the muon spin relaxation rate increases, tracking the onset of correlations between Yb$^{3+}$ pseudospins [12]. Below $T = 20 - 30 \text{ K}$ down to the lowest accessible temperatures (2.7 K) a power law increase $\Delta B(T) \propto 1/T^{3/4}$ seems reasonable for all investigated samples (see Figs. 2, 4). Such power law behavior indicates a suppression of exchange narrowing by classical critical fluctuations of a 3D order parameter [13].

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