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Characterization of the high-spin Mn^{2+} -functional center in
 BaTiO_3 by means of right-angle wiggling electron paramagnetic
resonance spectroscopy

dedicated to Arthur Schweiger († January 4th, 2006)

intended publication in **Mol. Phys.**

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Abstract

The recently introduced *right-angle wiggling* (RAW) EPR technique is applied to enhance the resolution of complicated high-spin EPR spectra. In particular, the RAW-EPR technique allows for a considerable resolution enhancement of orientationally disordered systems with anisotropic magnetic interactions and provides direct access to spin-Hamiltonian parameters without the need of numerical spectrum simulation. As an example of application, the Mn^{2+} -functional center in polycrystalline BaTiO_3 is studied.

Keywords: barium titanate, manganese doping, right-angle wiggling EPR

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I. INTRODUCTION

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2 Polycrystalline compounds, as ceramics, powders or glasses, represent an important class
3 of materials. However, electron paramagnetic resonance (EPR) spectroscopic information is
4 often lost under anisotropically broadened resonance lines. One approach to overcome such
5 kind of problems is to spread EPR spectra into a second dimension, providing an enhanced
6 spectral resolution. Recently, two classes of experiments have been introduced that invoke
7 a modulation of the external magnetic field during an electron spin-echo pulse sequence.
8 On the one-hand side, the magnitude of the external magnetic field is varied in the so-
9 termed *electron-Zeeman* (EZ) resolved EPR experiment [1, 2], where the second dimension
10 represents the electron g -value. On the other hand, the orientation of the external field may
11 be altered by means of the *right angle wiggling* (RAW) EPR technique [3, 4]; an alternative,
12 and technically less demanding method as compared to the formerly introduced *right-angle*
13 *spinning* (RAS) EPR technique [5, 6]. Both methods provide a means for disentangling
14 complicated EPR spectra. Furthermore, these experiments provide building blocks for more
15 complex pulsed EPR techniques, such as orientation-filtered inversion-recovery [7] or electron
16 spin echo envelope modulation (ESEEM) schemes [8]. More generally, the outlined concept
17 is analogous to nuclear-Zeeman resolved ESEEM [9].

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31 So far the applications of RAW and RAS have been restricted to $S = \frac{1}{2}$ centers with
32 anisotropic hyperfine and electron Zeeman interactions. In this work, the RAW-EPR tech-
33 nique is applied to demonstrate its mode of operation on high-spin systems. As an example
34 of application, the Mn^{2+} -functional center in polycrystalline barium titanate is studied.
35 Generally, ferroelectric BaTiO_3 is widely used as the base ingredient for the construction
36 of ceramic miniature capacitors because of its high dielectric constant and by exploiting
37 the positive temperature coefficient (PTC) of the resistivity for the construction of PTC
38 devices [10]. In particular aliovalent doping (Mn_{Ti}'') and defect diffusion processes exhibit
39 a strong impact on the physical properties of the material. In order to investigate these
40 influences and to understand the involved mechanisms, EPR may be used as a sensitive
41 spectroscopic tool [11]. Subtle changes of the local symmetry at particular crystal sites
42 may be probed by means of the sensitive electron fine-structure (FS) interaction present for
43 high-spin paramagnetic centers, such as the manganese functional center [12–15].

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54 The aim of this study is to demonstrate the versatility of RAW-EPR for the study of high-

spin paramagnetic centers. Therefore, a number of model RAW-EPR spectrum simulations for spin systems of different complexity illustrate the principal characteristics of RAW-EPR spectra, along with an example of application for the Mn^{2+} high-spin functional center in BaTiO_3 .

II. THEORETICAL DESCRIPTION

In order to analyze EPR spectra for high-spin systems ($S > \frac{1}{2}$), the corresponding spin-Hamiltonian typically is used

$$\mathcal{H} = g_e \beta_e \mathbf{B}_0 \cdot \mathbf{S} + \sum_{k=2}^{-k \leq q \leq k} B_k^q O_k^q(S_x, S_y, S_z) \quad (1)$$

in which g is the electron g -matrix, β_e denotes the Bohr magneton, \mathbf{B}_0 the external magnetic field, B_k^q are the FS spin-Hamiltonian parameters, and O_k^q are the extended Stevens spin operators [19, 20]. The standard FS parameters B_k^q are related to the also used parameters b_k^q by the scaling factors f_k ($f_2 = \frac{1}{3}$, $f_4 = \frac{1}{60}$) via $B_k^q = f_k b_k^q$ [19]. These values are related to the conventional spectroscopic parameters by $B_2^0 = \frac{b_2^0}{3} = \frac{D}{3}$, $B_2^2 = \frac{b_2^2}{3} = E$, $B_4^4 = \frac{b_4^4}{60} = \frac{5a}{120}$, and $B_4^0 = \frac{b_4^0}{60} = \frac{F}{180} + \frac{a}{120}$ [21, 22]. In principle all conceivable B_k^q parameters, resulting from 3rd, 4th and 5th-rank tensors, have to be considered [23].

For the Mn^{2+} with $S = \frac{5}{2}$ and a hyperfine interaction with $I^{55} = \frac{5}{2}$ in principal the Hamiltonian in its most general form should include FS terms up to fourth-order. However, former studies justified considerable simplifications [13, 14], yielding an isotropic g_{iso} value, an isotropic hyperfine structure constant a_{iso}^{55} and axial symmetry of the crystal field ($B_2^2 = 0$). Furthermore, the higher-order FS parameters $B_{k>2}^q$ can be neglected. In particular, we found no evidence for the possible contribution of the inherently field-dependent odd-rank tensor contributions in our spectral analysis.

$$\begin{aligned} \mathcal{H} = & g_{\text{iso}} \beta \mathbf{B}_0 \cdot \mathbf{S} + 3B_2^0 \left[S_z^2 - \frac{1}{3} S(S+1) \right] + a_{\text{iso}}^{55} \mathbf{S} \cdot \mathbf{I} \\ & - g_n \beta_n \mathbf{B}_0 \cdot \mathbf{I} + Q \left[I_z^2 - \frac{1}{3} I(I+1) \right] \end{aligned} \quad (2)$$

III. EXPERIMENTAL

RAW-EPR is a two-dimensional (2D) pulsed EPR method where the orientation of the external field B_0 is varied during an electron spin-echo pulse sequence, deflecting the ori-

1 entation between sample and external field by an angle ρ and thus changing the resonance
2 frequency by $d_\rho\omega$. Therefore, conventional B_0 field-swept EPR spectra can be disentangled
3 into a second dimension, which represents the anisotropy of magnetic interactions, providing
4 considerably better resolved EPR spectra. In particular slices for $d_\rho\omega = 0$ are substantially
5 better resolved than conventional B_0 field-swept EPR spectra, because all spectral features
6 that do not belong to the canonical orientations are shifted to values $d_\rho\omega \neq 0$, yielding
7 single-crystal like spectra even for polycrystalline samples.
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10 Experimentally, the RAW technique uses an orientational modulation of the external field
11 during a stimulated or primary spin echo sequence, which is performed by an additional si-
12 nusoidal field of variable amplitude, perpendicular to the orientation of B_0 . Pulses and spin
13 echo are placed at subsequent zero crossings of the sinusoidal field modulation, as schemat-
14 ically illustrated in figure 1. As a function of the resonance-frequency shift imposed by the
15 wiggling magnetic field perpendicular to the orientation of the static magnetic field, the
16 amplitude of the spin echo oscillates. In one dimension of an RAW-EPR experiment, field-
17 swept echo-induced EPR spectra are recorded. In the second dimension, the oscillation of the
18 spin-echo is measured as a function of the deflection ρ from the initial orientation between
19 sample and external field for each B_0 -field setting. After baseline correction, apodization,
20 zero-filling and Fourier-Bessel transformation with respect to the deflection angle ρ , the
21 RAW-EPR spectrum is finally obtained.
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33 The RAW-EPR experiments were performed on a homebuilt X-band spectrometer [16],
34 operating at a Larmor frequency of $\nu_{mw} = 9.15$ GHz, with a homebuilt dielectric-ring TE_{001}
35 resonator [6] at a temperature of $T \approx 15$ K. The Hahn-echo pulse-sequence consisted of
36 microwave pulse lengths of $t_{\pi/2} = t_\pi = 20$ ns and an evolution time of $\tau = 980$ ns (cf. figure
37 1). The magnetic field was modulated with a frequency of 500 kHz and the amplitude A_{raw}
38 was varied in a range of $[0 ; 15]$ mT in steps of 0.2 mT.
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46 IV. ILLUSTRATIVE EXAMPLES OF RAW-EPR SPECTRA

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48 RAW-EPR spectra manifest in a very different way compared to conventional EPR spec-
49 tra, which particularly holds for spectra of disordered systems. To become more familiar with
50 the appearance of 2D RAW-EPR spectra of polycrystalline samples, a number of numerical
51 spectrum simulations is presented in the following section. Figure 2 illustrates model-type
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high-spin RAW-EPR spectra for $S = 1, \frac{3}{2}$ and 2, respectively.

Because the systems studied with RAW-EPR have to possess of at least one anisotropic interaction, closed-form perturbation-theory expressions for the solution of the spin Hamiltonian in general exist. For numerical spectrum simulation, using these formulae is advantageous with respect to exact diagonalization methods, which holds especially for the case of rather complex systems. It is common practise of simulation programs to terminate the calculation at a stage of second-order corrections to the energy. In this work it has turned out, that third-order corrections are particularly useful for high-spin systems. The linewidth is introduced by convolution in both, the B_0 -field and the anisotropy dimension [18].

We will start with the simplest case of zero-field splitting, a triplet-state spin system. For axial symmetry ($B_2^2 = 0$), as the field changes its orientation from $\theta = 0$ to $\theta = \frac{\pi}{2}$, the line positions are varied from $\frac{3|B_2^0|}{g\beta_e}$ to $-\frac{3|B_2^0|}{2g\beta_e}$. Neglecting second-order terms, the separation between the outer vertical lines is $\frac{6|B_2^0|}{g\beta_e}$, corresponding to resonances from species lying in such a position that the external field is directed along the laboratory z -axis, while the separation between the two inner parallel lines is $\frac{3|B_2^0|}{g\beta_e}$, corresponding to resonances from species in which the external field lies in the xy -plane (figure 2(a)). The two transitions cross at an angle of $\theta = 54^\circ 44'$ [19].

As these features may be compared with those corresponding to g_{\parallel} and g_{\perp} in the case of g anisotropy, EPR spectra of triplet-state spin systems are often described in terms of two overlapping pseudo $S = \frac{1}{2}$ spin systems with anisotropic effective g -value g' . These overlapping subspectra are resolved in an RAW-EPR spectrum (figure 2(b)), which consists of two anisotropy ellipses for each subsystem that is mirrored by an axis parallel to the anisotropy dimension. The two anisotropy ellipses corresponding to the two subspectra reveal 'opposite orientation'. Using the description based on anisotropic g -values, for one subspectrum $g'_{\parallel}{}^{(1)} > g'_{\perp}{}^{(1)}$, whereas for the other subspectrum $g'_{\parallel}{}^{(2)} < g'_{\perp}{}^{(2)}$. The g'_{\perp} -value of one circle is shifted by $\frac{3}{2}B_2^0$ with respect to the g'_{\parallel} -value of the other circle, and the two effective perpendicular g' -values are separated by $3B_2^0$.

Under axial symmetry the absorption line reveals turning points at $\theta = 90^\circ$ and $\theta = 41^\circ 48'$, which give rise to significant amplitudes in the EPR spectrum. Because $\theta = 90^\circ$ is the most probable orientation in a polycrystalline sample, the field positions of the more intense signals in the powder spectrum correspond to those for the $\theta = 90^\circ$ orientation of a single crystal.

For rhombic symmetry ($B_2^2 \neq 0$) more turning points for all of the transitions will occur, and the spectra will become more complicated. In this case the lines do not cross any more but have a turning point instead, which gives rise to new steps in the EPR absorption spectrum. The peaks at $\pm \frac{3B_2^0}{2g\beta_e}$ are each split into two new features. The separation of the outermost lines is again $\frac{6|B_2^0|}{g\beta_e}$ for molecules with the field along the z -axis, whereas that of the intermediate and inner pairs is $\frac{3|B_2^0+B_2^2|}{g\beta_e}$ for the y -axis and $\frac{3|B_2^0-B_2^2|}{g\beta_e}$ for the x -axis. In almost all systems of application it has been found that the values for B_2^2 are an order of magnitude smaller than those of B_2^0 . Thus, in the following, we will restrict to axial symmetry and neglect B_2^2 .

In order to determine the absolute signs of the FS parameters B_2^0 and B_2^2 , RAW-EPR at low temperatures has to be performed, analogous to conventional EPR where the relative intensity of different transitions is observed owing to polarization effects [24, 25]. Then, the RAW-circle corresponding to the lowest transition in energy will become more intense than the RAW-circle corresponding to the highest transition. However, for X-band frequencies the corresponding 'polarization temperature' $T = \frac{h\nu_{mw}}{k_B}$ amounts to 0.5 K.

For magnetic species with $S > 1$, additional terms should in principle be added to the spin Hamiltonian. These usually only make relatively small contributions to the total energy of the system and manifest in a shift of the line positions and a correction of the line intensities. In figure 2(c,d), two RAW-EPR spectra with $S = \frac{3}{2}$ and $S = 2$ are shown, being representative for Cr^{3+} , Mn^{4+} ($S = \frac{3}{2}$) and Mn^{3+} , Fe^{2+} ($S = 2$).

In the conventional B_0 field-swept EPR spectrum it becomes already difficult to assign the peaks to the corresponding transitions. The RAW-EPR spectrum consists of one circle for each 'allowed' EPR transition ($\Delta m_S = \pm 1$). The transitions and therewith the RAW-circles are unequal in intensity, which corresponds to the projection of the magnetic moment on the direction of the applied magnetic field that is larger for small values of $|m_S|$ than for higher values of $|m_S|$. The intensity of the $|m_S\rangle \leftrightarrow |m_S - 1\rangle$ transition is proportional to $S(S + 1) - m_S(m_S - 1)$ [19].

V. RESULTS AND DISCUSSION

As an example of application, the high-spin Mn^{2+} -functional center in BaTiO_3 is studied. The corresponding echo-induced EPR spectrum is shown in figure 3 (a). The shape of the

EPR spectrum is governed by the intense lines of the central FS transition $|m_S = +\frac{1}{2}\rangle \leftrightarrow |-\frac{1}{2}\rangle$. The weaker lines at the low and high-field end of the spectrum correspond to the 'higher' $m_S = |\pm\frac{5}{2}, \pm\frac{3}{2}\rangle \leftrightarrow |\pm\frac{3}{2}, \pm\frac{1}{2}\rangle$ transitions, respectively. Due to the random orientation of the different crystallites with hyperfine structure and FS splitting, the existence of 'allowed' ($\Delta m_S = \pm 1, \Delta m_I = 0$) and 'forbidden' ($\Delta m_S = \pm 1, \Delta m_I = \pm 1$) transitions, the spectrum is considerably broadened. Consequently, the determination of spin-Hamiltonian parameters is rather difficult.

The corresponding RAW-EPR spectrum is represented in figure 4(d). Mainly contributions from the central transitions are observed. For each of the six hyperfine transitions within the central FS transition a closed ring is observed. Second-order effects due to the FS interaction are proportional to $\frac{1}{B_0}$ and are present at all orientations, except $\theta = 0$. These second-order effects include shifts in the 'centre of gravity' of the FS transitions and the appearance of 'forbidden' transitions. Hence, the even spacing of FS transitions, which is a purely first-order effect of the zero-field splitting, occurs only at $\theta = 0$ orientations. Because of the $\frac{1}{B_0}$ dependence of the second-order effects, differences in the spacings of $\theta = \frac{\pi}{2}$ features in powder spectra for different frequency bands are expected.

The electronic transitions have a first-order displacement proportional to $B_2^0(3\cos^2\theta - 1)$, except for the central transition which has only second-order displacement of order $\frac{(3B_2^0)^2}{g\beta B}$. In a powder consisting of randomly oriented crystallites, the outer transitions are therefore smeared out, while the central transition still gives a well resolved hyperfine structure. Due to the spin-Hamiltonian symmetry with isotropic Zeeman and hyperfine terms, a peak is expected in the absorption EPR spectrum for $\theta = 0^\circ$, and steps are attributed for angles of $\theta = 41.9^\circ$ and $\theta = 90^\circ$. In the $d_\rho\omega$ slices also the steps will transform into peaks. The distance between the outer peaks ($\theta = 90^\circ, \theta = 41.9^\circ$) is determined by the second-order term $\frac{(3B_2^0)^2}{B_0}$. Due to third-order terms, an additional weak dependence on m_I is superimposed. This manifests in a difference in angular dependence for each hyperfine structure line within the central FS transition; with increasing nuclear quantum number m_I , the angular dependence becomes more pronounced, meaning a larger anisotropy. In the RAW-EPR spectrum this effect results in a scaling of the RAW rings, which become larger to the high-field end of the spectrum (cf. figure 4(d)).

The allowed transitions have maximum intensity for orientations parallel or perpendicular to the symmetry axis, $\theta = 0, \frac{\pi}{2}$, and partly vanish for intermediate angles, whereas the

forbidden angles vanish for the canonical orientations $\theta = 0, \frac{\pi}{2}$ and their intensity becomes strongest for $\theta = \frac{\pi}{4}$ [29]. This behavior can also be observed in the RAW-EPR spectrum. 'Forbidden' transitions, in which the nuclear quantum number m_I changes by ± 1 , arise from second-order effects due to cross terms in the spin Hamiltonian between the FS splitting and the hyperfine structure splitting terms. These forbidden transitions are strongest in the electronic $|-\frac{1}{2}\rangle \leftrightarrow |+\frac{1}{2}\rangle$ transition, at which the $\Delta m_I = \pm 1$ lines occur as doublets, with splitting $2g_n\beta B_0$, centered on the points midway between the main lines. For the outer transitions, half of the $\Delta m_I = \pm 1$ lines are displaced by an amount $2a_{\text{iso}}^{55}$ towards higher fields, while the other half are equally displaced in the opposite sense. Hence, one line at each end of a hyperfine set falls outside the main hyperfine structure lines [30].

A particular advantage of RAW-EPR spectra is that a slice for $d_\rho\omega = 0$ corresponds to a field-swept EPR spectrum of considerably increased resolution (figure 3(b)). It consists of a well resolved multiplet of six non-equidistant allowed and five forbidden hyperfine structure doublets centered at $g \approx 2.002$, corresponding to the central FS transition. Obviously this sextet arises from the ^{55}Mn -hyperfine interaction. The broadened outer features correspond to the non-central FS transitions. g_{iso} is taken as the centre of central FS transition and a_{iso}^{55} as the distance between the third and fourth line of the central transition. The obtained g -value and hyperfine splitting, given in table I, are typical for Mn^{2+} ions incorporated in BaTiO_3 single crystals [26, 27]. The axial FS parameter B_2^0 is in good agreement with the respective value of ceramic samples [28].

The FS term exhibits a strong angular variation for all allowed transitions, except for the central transition $|m_S = +\frac{1}{2}\rangle \leftrightarrow |-\frac{1}{2}\rangle$ where it is eliminated by cancellation in first order. Hence, in the powder pattern the outer transition lines tend to be smeared out due to B_2^0 -strain, while the central lines remain well resolved. In order to represent the full Mn^{2+} RAW-EPR spectrum, a numerical spectrum simulation is shown in figures 4(a-c). The different sections represent the different EPR transitions.

VI. CONCLUSION AND OUTLOOK

In summary, it has been demonstrated that RAW-EPR spectroscopy facilitates a considerable improvement of resolution also for FS-broadened high-spin systems. With this respect, the RAW-EPR technique may also serve as an alternative to high-frequency EPR

studies on high-spin centers [31–33].

VII. ACKNOWLEDGMENTS

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Appendix A: TABLES

Table I: Spin-Hamiltonian parameters for polycrystalline Mn^{2+} doped BaTiO_3 for different transitions.

g_{iso}	a_{iso}^{55} [mT]	$ B_2^0 $ [mT]
2.002 ± 0.001	8.64 ± 0.02	8.15 ± 0.05

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Appendix B: FIGURES

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3 Figure 1: Timing diagram of the coherence-transfer RAW EPR experiment. The pulses and the
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5 electron spin echo occur at subsequent zero crossings of the magnetic field modulation $\Delta B_0^\perp(t)$.
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Appendix C: FIGURES

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Figure 2: Numerically simulated EPR spectra for high-spin systems with $S = 1, \frac{3}{2}, 2$. (a,b) - triplet-spin system ($S = 1$) with $|E| = 0$ for $|D| = 1$ GHz. (a) - orientation dependence of the 'allowed' EPR transitions ($\Delta m_S = \pm 1$) and (b) - corresponding RAW-EPR spectrum. (c) - quartet-spin system ($S = \frac{3}{2}$). (d) - quintet-spin system ($S = 2$). For comparison, the corresponding conventional field-swept EPR spectra are depicted on top of each 2D spectrum.

Figure 3: EPR spectra of Mn^{2+} -modified BaTiO_3 . (a) - conventional echo-induced EPR spectrum.

(b) - RAW-EPR slice for $d_\rho\omega = 0$ exhibiting only contributions from canonical orientations.

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Figure 4: RAW-EPR spectra of Mn^{2+} -modified BaTiO_3 . (a-c) - numerically simulated RAW-EPR spectra of allowed and forbidden transitions, showing regions of the centrals (c) and higher FS transitions. (d) - experimentally obtained Mn^{2+} RAW-EPR spectrum of the central FS transition region.

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