Chapter 3

Determination of Magnetic Anisotropy by EPR

Andrej Zorko

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Abstract

Electron paramagnetic resonance (EPR) is a powerful spectroscopic technique, perfectly suited for determining magnetic anisotropy terms in spin Hamiltonians. Although solid foundations of the EPR theory were established by Kubo and Tomita (KT) more than half a century ago, especially in the last couple of decades, we have witnessed a rapid progress in the field due to the occurrence of enhanced computational capabilities. In this chapter, we overview this progress by summarizing the basic concepts of EPR in exchange-coupled systems. The review builds upon the standard KT theory and the exchange narrowing picture, which is however only suitable at high enough temperatures and for systems with dimensionality exceeding one. We also summarize the predictions of more modern approaches, including exact calculations on finite spin clusters, the Oshikawa-Affleck effective-field theory for 1D systems, and the recently developed EPR-moments approach. Many illuminating examples of the applicability of different approaches are also provided.

Keywords: EPR, ESR, EMR, Kubo-Tomita theory, exact diagonalization, Oshikawa-Affleck effective-field theory, EPR moments, exchange-coupled spin systems, magnetic anisotropy, Dzyaloshinskii-Moriya interaction, anisotropic exchange, single-ion anisotropy

1. Introduction

Since the pioneering demonstration of the electron paramagnetic resonance phenomenon in solids and liquids in 1944 by Zavoisky [1–3], EPR has become a well-established and broadly spread spectroscopic technique. Although the main principle of detecting microwave absorption by electronic magnetic moments at a fixed frequency and a sweeping applied magnetic fields has not changes from early days, the method has become one of the most sensitive local probes of magnetism.

The term electron paramagnetic resonance in a narrow sense applies to paramagnetic compounds containing transition-metal or rare-earth elements with incomplete inner shells, hence possessing paramagnetic electron moments. In a broader sense, the general term electron magnetic resonance (EMR) stands for magnetic resonance absorption experiments performed on an ensemble of magnetic moments corresponding to localized or itinerant electrons. In addition to paramagnets, EMR thus also covers absorption phenomena in ordinary metals and magnetically ordered systems, as well as absorption by imperfections in insulators and semiconductors, which may trap electrons or holes. In literature, also the term electron spin resonance (ESR) is often encountered. This is usually reserved for cases when the magnetic moment originates primarily from the spin momentum of the electron, like in iron-group metals where the orbital moment of the electron is usually quenched.

The EPR technique provides superior insight into magnetic properties of a particular sample compared to more conventional bulk magnetic techniques, e.g., bulk-magnetization or magnetic-torque measurements. A particular EPR experiment can provide information that help in characterization of local magnetic and electrostatic environments of a magnetic moment, as well as information about development of magnetic correlations and fluctuations [4–6]. The experiment can also help to determine magnetic coupling with other electronic and nuclear moments, etc. Due to these diverse and detailed information, EPR has earned reputation in various fields of science. Traditionally, it was in the domain of solid-state physics and chemistry, but lately it has become indispensable also in bio-oriented sciences and medical applications. Moreover, it has been recently highlighted for its strength in detecting unconventional magnetic phenomena, such as edge states in topological insulators [7], spinon excitations in spin liquids [8], and spin-nematic states [9].

For a general introduction to EPR the reader is advised to turn to one of many very good EPR monographs and reviews, like the Abragam and Bleaney "Electron Paramagnetic Resonance of Transition Ions" [4], the Pilbrow "Transition Ion Paramagnetic Resonance" [5], or the more recent Weil and Bolton "Electron Paramagnetic Resonance: Elementary Theory and Practical Applications" [6]. The purpose of this chapter is to review a specific problem of EPR in exchange coupled systems. This problem is particularly difficult to treat due to complications induced by the exchange interaction between neighboring moments. These interactions dramatically affect the way the moments respond to the external magnetic fields. In order to model this response properly, the use of modern theoretical concepts and advanced experimental approaches is required. These are review in this chapter.

The outline of the chapter is the following. We will start with a general overview of the Kubo-Tomita EPR theory (Section 2), which will first require the introduction of the spin-Hamiltonian concept. We will pay special attention to the exchange-narrowing limit, which is generally applicable to strongly-exchange-coupled spin systems. Next, a few successful applications of the KT theory will be demonstrated in Section 3. In Section 4, limitations of the KT approach will be summarized. Different approaches that can overcome these limitations and their specific applications will also be given. The concluding Section 5 will summarize this chapter.

2. KT theory of EPR in exchange-coupled systems

Dense magnetic insulators, i.e., systems that do not conduct electric current and where magnetic moments are localized at well-defined crystallographic sites (usually occupied by transition metals or rare earths), represent one of the major fields of research in condensed matter, where EPR is particularly powerful [10]. In this chapter, we shall focus on systems that are strongly exchange coupled, i.e., where magnetic moments communicate, and highlight particular information that EPR can provide in such cases.

EPR measures the absorption of microwaves by electrons, i.e., atomic magnetic moments, therefore, it provides a direct insight to the atomic magnetism. This is unlike some other local-probe techniques, such as nuclear magnetic resonance [11, 12] or muon spectroscopy [13] that can only provide indirect information about electron degrees of freedom. However, as we shall see below, this advantage of EPR at the same time turns out to be a drawback, since knowledge of four-spin correlations functions is required to accurately describe the EPR response of exchange-coupled magnetic moments at an arbitrary temperature. On the other hand, for indirect techniques, like NMR, two-spin correction functions suffice. This makes EPR an elaborate technique and prevents a routine analysis of the EPR spectra of exchange-coupled systems.

The beginnings of the EPR theory in exchange-couples magnetic systems go back to the seminal work by Kubo and Tomita (KT) entitled "General Theory of Magnetic Resonance Absorption" [14]. Although it rests on a perturbation approach and is therefore not exact, the KT theory still represents solid foundations in modern times. The EPR theory has seen some progress later on, especially in recent years with the advent of enhanced computational facilities. Within this chapter, we shall make a general overview of the KT theory and its successors that were developed for cases where the KT theory is not valid.

2.1. Spin Hamiltonian

We start the body of this review with introducing the concept of the spin Hamiltonian. In this framework the total Hamiltonian of a particular system with all degrees of freedom that are present, i.e., electron orbital, electron spin, nuclear, lattice, etc., is projected onto the spin space of the electrons. In an external magnetic field, the spin Hamiltonian comprises of the following terms [6]:

$$H = H_Z + H_{hf} + H_{ex} + H'. \tag{1}$$

Here, $H_Z = \mu_B \vec{B_0} \cdot \underline{g} \cdot \vec{S}$ is the Zeeman interaction of the electronic spin $\vec{S}$ with the applied magnetic field $\vec{B_0}$ (μ_0 denotes the Bohr magneton, $\underline{g}$ is the g tensor), H_{hf} is the electron-nuclear hyperfine coupling interaction,

$$H_{ex} = \sum_{i,\, j>i} J_{ij} \vec{S_i} \cdot \vec{S_j} \tag{2}$$

is the exchange Hamiltonian summing terms between electron spins at sites i and j coupled by an isotropic exchange interaction J_{ij}, and $H^{'}$ represents magnetic anisotropy. The latter,

$$H^{'} = H_{dd} + H_{zfs} + H_{AE} + H_{DM}, \tag{3}$$

includes the dipolar term between electronic spins H_{dd}, the zero-field splitting term H_{zfs}, which reflects a combined effect of the electrostatic crystal field and spin-orbit coupling on the energy levels in spin space, the symmetric anisotropic exchange (AE) term

$$H_{AE} = \sum_{i,\, j>i} \vec{S}_i \cdot \underline{\delta} \cdot \vec{S}_j \,, \tag{4}$$

where $\underline{\delta}$ is the symmetric part of the anisotropic exchange tensor, and the antisymmetric anisotropic exchange term

$$H_{DM} = \sum_{i,\, j>i} \vec{d}_{i,j} \cdot \vec{S}_i \times \vec{S}_j \,, \tag{5}$$

known as the Dzyaloshinskii-Moriya (DM) interaction ($\vec{d}$ is the DM vector) [15, 16]. We note that the dipolar term is important in diluted magnetic systems, but is usually negligible in dense magnetic insulators. The zero-field splitting term may be important for spins $S > 1/2$ and has, in the lowest order in spin, the following form

$$H_{zfs} = D\left(S_z^2 - S(\mathrm{S}+1)/3\right) + E\left(S_x^2 - S_y^2\right). \tag{6}$$

The exchange anisotropy is a relativistic effect due to the spin-orbit coupling. In transition metals, the Dzyaloshinskii-Moriya interaction is usually the dominant exchange anisotropy term. The reason is that it originates from the first-order perturbation in the spin-orbit coupling, while the symmetric anisotropic exchange results only from the second-order perturbation theory [15, 16]. Consequently, the DM term is proportional to $(\Delta g/g)J$, while the symmetric AE term is proportional to $(\Delta g/g)^2 J$, where the g-shift Δg from the free electron value of 2.0023 measures the amount of the orbital momentum in the ground crystal-field state due to mixing of higher crystal-field states. In copper-based magnets, for example, one typically finds $\Delta g/g \approx 0.15$ [4, 5].

2.2. EPR spectrum

In the high-temperature limit, where thermal energy is larger than the Zeeman energy splitting (in the conventional X-band at 9.5 GHz the Zeeman spitting corresponds to the temperature of 0.45 K), the EPR absorption spectrum is determined in the linear-response theory by thermal-averaged (denoted by $\langle \ldots \rangle$) fluctuations of the total transverse spin operator $\vec{S} = \sum_i \vec{S}_i$, as [14].

$$I(\omega) \propto \omega\chi''(\omega) \propto \frac{\omega}{T}\int_{-\infty}^{\infty}\left\langle S^{+}(t)S^{-}(0)\right\rangle \mathrm{e}^{-i\omega t}\mathrm{d}t, \tag{7}$$

where the spin ladder operators are given by $S^{\pm} = S^{x} \pm iS^{y}$ and $\chi''(\omega)$ represents the imaginary part of the uniform dynamical susceptibility. In the case when the Zeeman interaction is dominant, one can separate the Hamiltonian $H_0 = H_{ex} + H_Z$ from the other, perturbing terms H'. Rewriting $\chi''(\omega)$ in the interaction representation, which is given by the transformation $\tilde{S}(t) = \mathrm{e}^{-iH_0 t/\hbar}S(t)\mathrm{e}^{iH_0 t/\hbar}$, then yields

$$\chi''(\omega) \propto \int_{-\infty}^{\infty}\left(\left\langle \tilde{S}^{+}(t)S^{-}(0)\right\rangle \mathrm{e}^{-i(\omega-\omega_0)t} + \left\langle \tilde{S}^{-}(t)S^{+}(0)\right\rangle \mathrm{e}^{-i(\omega+\omega_0)t}\right)\mathrm{d}t. \tag{8}$$

Eq. (8) reveals an interesting result that the resonant absorption is peaked at the Larmor frequency $\pm\omega_0 = g\mu_B B_0/\hbar$, where $\hbar$ is the reduced Planck constant. Moreover, in the case of no anisotropy, there is no time dependence of the spin correlation functions in the interaction representation (Eq. (8)), therefore the EPR spectrum simply consists of two δ-functions. The time dependence of the correlation functions in Eq. (8), which is due to magnetic anisotropy H', is thus solely responsible for finite line widths of the EPR spectra and their shifts from the Larmor frequency. This is an essential results, as it demonstrates that magnetic anisotropy is directly reflected in the shape of the EPR line spectrum, unlike in all other techniques capable of detecting the anisotropy, e.g., inelastic neutron scattering, where the signal is a combined effect of multiple factors. Usually the EPR line width is small compared to the Larmor frequency and one can neglect the contribution peaked at the negative frequency $-\omega_0$.

According to the KT theory, the EPR spectrum can be expressed as the Fourier transform of the relaxation function $\varphi(t) = \left\langle \tilde{S}^{+}(t)S^{-}(0)\right\rangle / \left\langle \tilde{S}^{+}(0)S^{-}(0)\right\rangle$,

$$I(\omega) \propto \int_{-\infty}^{\infty}\varphi(t)\mathrm{e}^{-i(\omega-\omega_0)t}\mathrm{d}t. \tag{9}$$

Thus, spin correlations embedded into the relaxation function determine the EPR spectrum. The calculation of the relaxation function is however nontrivial. Therefore, approximation schemes are required. For Markovian random processes the relaxation function is approximated by [14]

$$\varphi(0) = \exp\left(-\int_{0}^{t}(t-\tau)\psi(\tau)\mathrm{d}\tau\right). \tag{10}$$

Here, the spin correlation function is defined as

$$\psi(\tau) = \frac{\left\langle \left[\tilde{H}'(0), S^{+}(0)\right]\left[S^{-}(0), \tilde{H}'(0)\right]\right\rangle}{\hbar^2\left\langle S^{+}(0)S^{-}(0)\right\rangle}, \tag{11}$$

where $[A, B]$ stands for the commutator between operators A and B. Within the KT theory a Gaussian decay of the spin correlation function is postulated,

$$\psi(0) = \psi(0)\mathrm{e}^{-\tau^2/2\tau_c^2}, \tag{12}$$

where the characteristic spin correlation time is determined by the dominant isotropic exchange J, $\tau_c \approx h/J$.

2.3. Exchange narrowing

Let us inspect two limiting cases of the correlation time with respect to the typical EPR time scale given by the Larmor frequency. For slow decay of correlations ($\omega_0\tau_c \gg 1$), i.e., in the quasi-static limit, $\psi(t)$ in Eq. (10) can be replaced by its zero-time value, which is proportional to the second moment of the absorption line

$$M_2 = \hbar^2\psi(0) = \frac{\left\langle \left[H'(0), S^+(0)\right]\left[S^-(0), H'(0)\right]\right\rangle}{\left\langle S^+(0)S^-(0)\right\rangle}. \tag{13}$$

This procedure yields a Gaussian relaxation function $\varphi(t)$ and, according to Eq. (9), also a Gaussian shaped EPR spectrum, with the width $\Delta B_G \propto \sqrt{M_2}$.

The fast decay limit ($\omega_0\tau_c \ll 1$) gives a completely different result. Here, the integral in Eq. (10) is approximated by

$$\int_0^t (t-\tau)\psi(\tau)\mathrm{d}\tau = \psi(0)\left(t\int_0^{t\to\infty} \mathrm{e}^{-\tau^2/2\tau_c^2}\mathrm{d}\tau - \int_0^{t\to\infty} \tau\mathrm{e}^{-\tau^2/2\tau_c^2}\mathrm{d}\tau\right) \approx \sqrt{\frac{\pi}{2}}\frac{M_2}{\hbar^2}\tau_c t, \tag{14}$$

which leads to an exponential decay of the relaxation function $\varphi(t)$. Consequently, the EPR spectrum has a Lorentzian shape. Its line width is $\Delta B_L \propto \tau_c M_2$. As $\tau_c \approx h/J$, this is known as the exchange-narrowing limit [17, 18], where the EPR broadening, which is given by magnetic anisotropy yielding finite M_2, is opposed by the isotropic exchange interaction causing narrowing of the EPR line. The spin correlation time $\tau_c \propto h\sqrt{M_2/M_4}$ is approximated by the second moment (Eq. (13)) and the fourth moment of the absorption line

$$M_4 = \frac{\left\langle \left[H - H_Z, \left[H', S^+(0)\right]\right]\left[H - H_Z, \left[H', S^-(0)\right]\right]\right\rangle}{\left\langle S^+(0)S^-(0)\right\rangle}, \tag{15}$$

which yields the full width at half maximum (FWHM) of the Lorentzian EPR line

$$\Delta B = \frac{C}{g\mu_B}\sqrt{\frac{M_2^3}{M_4}}. \tag{16}$$

The exchange-narrowing limit is typically applicable to real exchange-coupled system, except in cases of small couplings and high Larmor frequencies. We recall again that in the most

widespread X-band EPR experiment ($\omega_0 = 2\pi \times 9.5$ GHz) a typical temperature scale is 0.45 K. The exchange narrowing is straightforwardly confirmed in an EPR experiment by the Lorentzian line shape of the spectrum. However, strictly speaking, the experimental line shape is never truly Lorentzian, because the moments of the latter diverge, while the EPR moments, given by the commutators, such as those in Eq. (13) and Eq. (15), are always finite. In systems with strong isotropic exchange compared to magnetic anisotropy, deviations from the Lorentzian shape occur only in far wings of the EPR spectrum and are often not even observable. An approximate line shape that is a product of the Lorentzian and a broad Gaussian $\propto \exp\left(-(\mathrm{B}-\mathrm{B}_0)^2/2B_{ex}^2\right)$, with the exchange field $B_{ex} = k_B\sqrt{M_2/M_4}/g\mu_B$ [19], is then justified. This yields the constant $C = \sqrt{2\pi}$ in Eq. (16). The EPR line width is thus a fingerprint of magnetic anisotropy (Eq. (3)) present in a given exchange-coupled spin system, as the latter yields finite EPR moments (Eq. (13) and Eq. (15)).

3. Applications of the KT theory

Applications of the KT theory to experiments are numerous. Here, we will highlight a few cases from recent literature, where determination of the magnetic anisotropy turned out to be crucial for understanding the magnetic ground state. All examples concern magnetically frustrated spin lattices in 2D, where short-range spin interactions are incompatible with the underlying spin lattices, effectively suppressing long-range spin ordering and leading to unconventional states of matter. In such cases magnetic anisotropy, even if only being a small perturbation to the dominant isotropic exchange interaction, can tip the balance in favor of one or another competing ground state.

3.1. Kagome lattice

The first example is the 2D spin lattice in herbertsmithite, $ZnCu_3(OH)_6Cl_2$ [20], a compound that has earned the reputation of being the best experimental realization of a quantum kagome antiferromagnet (QKA) of corner-sharing triangles (**Figure 1**), where the geometrical frustration is the most severe [21]. Numerous theoretical studies that proposed various different ground states over the last two decades, now seem to have converged on a gapped quantum spin liquid (QSL) – a state that is disordered, yet highly entangled [21]. Experimental signatures of such a state have also been lately advocated, although the bulk of experiments on this and the majority of other known QKA representatives actually speaks in favor of a gapless QSL. This discrepancy may well be related to perturbations beyond the isotropic Heisenberg exchange model on the kagome lattice, such as magnetic anisotropy.

The magnetic anisotropy of herbertsmithite was successfully determined by EPR in Ref. [22]. Based on relatively small g-shifts (of the order of 15%, as typical for Cu^{2+} ions [4, 5]), it was argued that the antisymmetric DM interaction (Eq. (5)) dominates the magnetic anisotropy in this compound. The DM vector pattern (**Figure 1**), which is determined by the symmetry of the kagome lattice, then according to Eq. (16) predicts the following angular dependence of the EPR line width [22]

$$\Delta B(\theta) = \sqrt{2\pi}\frac{k_B}{2g(\theta)\mu_B J}\sqrt{\frac{\left(2d_z^2 + 3d_p^2 + \left(2d_z^2 - d_p^2\right)\cos^2\theta\right)^3}{16d_z^2 + 78d_p^2 + \left(16d_z^2 - 26d_p^2\right)\cos^2\theta}}, \tag{17}$$

where θ represents the polar angle between the normal to kagome planes and the applied magnetic field direction, while d_p and d_z are the in-plane and the out-of-plane components of the DM interaction. This expression is valid only in the infinite-temperature limit, therefore the authors applied it to fit the room-temperature EPR spectrum of herbertsmithite (**Figure 1**), where the EPR line width was shown to saturate to a constant value [22]. Thus the minute in-plane DM component $d_p/J \sim 0.01(3)$ and the dominant out-of-plane DM component $d_z/J \sim 0.08(1)$ could be determined. The magnitude of the extracted DM interaction agrees with another estimate $0.06 < d_z/J < 0.10$, later obtained from NMR measurements [23]. Importantly, this places the system to a QSL part of a phase diagram, however, quite close to a quantum critical point determined by the out-of-plane DM component, which according to theory should occur at $d_z/J \simeq 0.10$ [24]. This point separates the spin-liquid phase from a Néel ordered phase at larger DM values. A further in-depth EPR study has revealed that the establishment of the spin-liquid state in herbertsmithite induces macroscopic symmetry reduction of the crystal lattice [25].

In contrast to herbertsmithite, in another QKA representative, vesignieite, $BaCu_3V_2O_8(OH)_2$, a long-range magnetic order was observed [26], which could be due to the fact that this systems is positioned in the ordered part of the above-mentioned phase diagram. In order to

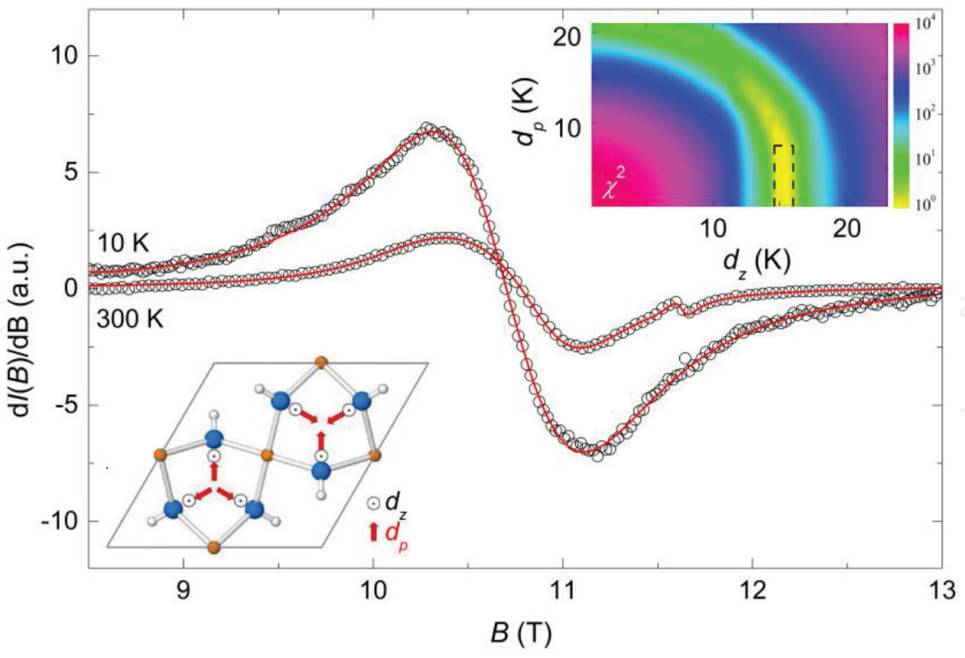

Figure 1. The EPR spectra of $ZnCu_3(OH)_6Cl_2$ at two different temperatures (symbols) and corresponding fits with a model based on the EPR line-width anisotropy given by Eq. (17). The lower inset shows the corresponding kagome lattice of Cu^{2+} $S = 1/2$ spins (orange) and the DM vector pattern. The upper inset shows the quality of the fit (reduced χ^2), where the dashed rectangle highlights the best fitting parameters. (Adapted from ref. [22].)

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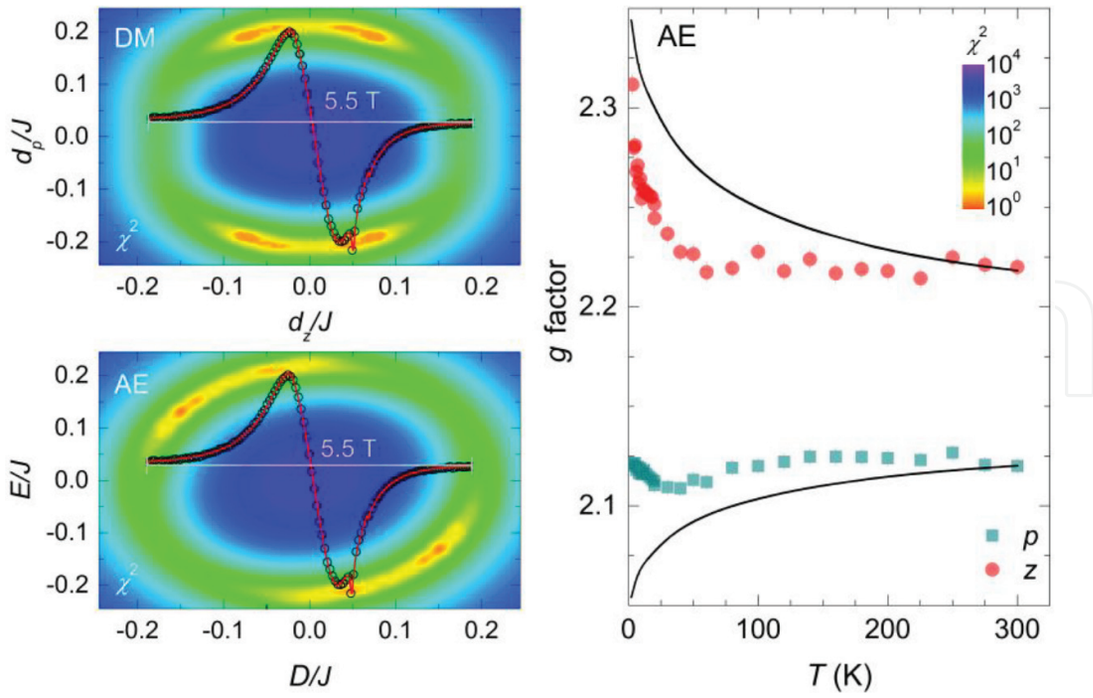

Figure 2. The 300-K EPR spectrum of $BaCu_3V_2O_8(OH)_2$ (symbols) fit with (top left) the DM model of Eq. (17) and (bottom left) the AE model [27] and the corresponding quality of the fits reflected in the reduced χ^2 in the parameter space of each model. (Right) the temperature dependence of the g factor (symbols) and the prediction of the AE model. (Adapted from ref. [27].)

verify this conjecture, the same EPR analysis (**Figure 2**) as the one presented above for herbertsmithite was performed in Ref. [27]. The derived DM components are somewhat different from those in herbertsmithite, as the in-plane component dominates in vesignieite, $d_p/J \sim 0.19(2)$ and $d_z/J \sim 0.07(3)$. Alternatively, the EPR line shape could be modeled also with the symmetric AE model (**Figure 2**). However, the extracted symmetric anisotropy parameters that, contrary to the DM interaction, are responsible also for temperature-dependent EPR shifts, significantly overestimated the measured shifts (**Figure 2**). Therefore, the conclusion was reached, that the DM interaction also dominates in vesignieite. Furthermore, it was argued that the condition $d_p > d_z$ could profoundly affect the quantum critical point because the in-plane DM component disfavors spin structures from the ground-state manifold of the isotropic J and should be much more efficient in suppressing quantum fluctuations than the out-of-plane DM component [27]. This could explain why magnetic ordering in vesignieite occurs at surprisingly high temperature for a frustrated system, $T_N/J \sim 0.17$ [26], despite d_z/J being very similar to the ratio in herbertsmithite.

3.2. Triangular lattice

A regular triangular lattice of edge-sharing triangles is another example of a highly frustrated spin lattice in 2D. Contrary to the kagome lattice, where each spin in surrounded by four nearest neighbors, on the triangular lattice there are six such neighbors, which reduces the

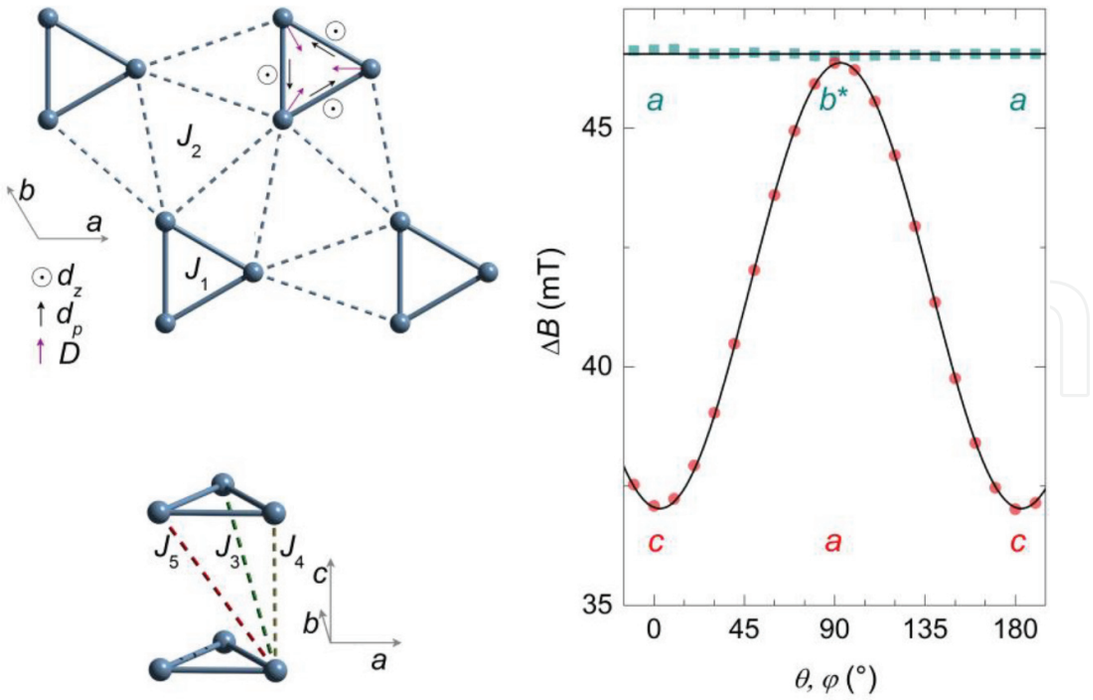

Figure 3. (Left) The 2D triangular arrangement of the Fe^{3+} S = 5/2 spins in $Ba_3NbFe_3Si_2O_{14}$ and the corresponding isotropic exchange interactions $J_1 - J_5$. The basic motif of anisotropic DM and AE interactions is also shown. (Right) The angular dependence of the EPR line width at 500 K (symbols) and the fits (lines) with the model of Eq. (18). (Adapted from ref. [29].)

amount of frustration. Consequently, the triangular lattice exhibits a magnetically ordered ground state, which is, however, much more complex than on ordinary bi-partite spin lattices.

A slightly more complicated triangular lattice is realized in Fe-langasite, $Ba_3NbFe_3Si_2O_{14}$ [28]. Here the Fe^{3+} (S = 5/2) spins reside on vertices of equilateral triangles arranged into a 2D triangular lattice (**Figure 3**). Quite interestingly, the magnetically ordered ground state below T_N = 26 K is doubly chiral, as the same 120° spin configuration on each triangle is helically modulated from plane to plane [28].

To identify the anisotropy term that is responsible for such chirality of the magnetic ground state, an EPR study was again conducted [29]. The room-temperature EPR signal was found to exhibit a pronounced angular dependence of the EPR line width and line position. The former could be related either to zero-field-splitting anisotropy (Eq. (6)) or DM exchange anisotropy (Eq. (5)), with the anisotropy patterns as shown in **Figure 3**. The two models could not be distinguished solely based on the EPR response of the system. However, a combined study of the EPR spectra and antiferromagnetic resonance (AFMR) modes observed below T_N suggested the DM interaction as the dominant source of anisotropy and thus to be responsible for the observed chiral behavior of Fe-langasite. The out-of-plane DM component $d_z/J \sim 0.004$ and the in-plane component $d_p/d_z = 2.6$ were estimated from the combined fits of the EPR and AFMR data. For the EPR line width in accordance with Eq. (16), the DM anisotropy yielded the EPR line width of the form [29]

$$\Delta B(\theta) = \sqrt{2\pi}\frac{k_B}{2g(\theta)\mu_B}\sqrt{\frac{105\left(5d_p^2 + 6d_z^2 + \left(d_p^2 - 2d_z^2\right)\cos 2\theta\right)^3}{32\left(35J_{DM}^2 d_p^2 + 6J_{DM}^{'2} d_z^2 + \left(2J_{DM}^{'2} d_z^2 - 7J_{DM}^2 d_p^2\right)\cos 2\theta\right)}}, \quad (18)$$

which was fit to the experimentally determined line-width anisotropy at 500 K (**Figure 3**). Here the constants $J_{DM}^2 = 3J_1^2 + 2J_2^2 + J_3^2 + J_4^2 + J_5^2$ and $J_{DM}^{'2} = 18J_1^2 + 14J_2^2 + 7J_3^2 + 7J_4^2 + 7J_5^2$ are defined by the five strongest exchange interaction depicted in **Figure 3**.

A later study combining EPR, AFMR and inelastic neutron scattering refined the anisotropy model in Fe-langasite and showed that actually both the DM anisotropy ($d_z/J \sim 0.033$, $d_p/d_z = 2.6$), and the zero-field-splitting anisotropy ($D/J \sim 0.052$) are of very similar size [30].

4. Pitfalls of the KT theory and alternative approaches

Although the above examples nicely demonstrate the value of the KT theory, this theory should be applied to each particular case with caution, because it is limited in several aspects. Firstly, the KT approach does not take into account a possible hidden symmetry of the DM interaction (Section 4.1) and diffusional decay of spin correlations in low dimensional spin systems (Section 4.2). Secondly, the EPR moments (Eq. (13) and Eq. (15)) implicitly employ four-spin correlation functions, which can be explicitly evaluated only in the infinite-temperature limit, where spin correlations between neighboring sites are negligible. On the other hand, the analysis of the EPR line width at temperatures of the order of the dominant exchange coupling J and below requires different approaches, like the Oshikawa-Affleck effective-field-theory (Section 4.3). Lastly, one should keep in mind that the KT theory is perturbative, therefore the cases of large (or even dominant) magnetic anisotropy should be treated with different approaches (Section 4.4).

4.1. Reducibility of the DM interaction

It was found theoretically that the DM interaction may in some cases possess a hidden symmetry [31], in the sense that it can be effectively transformed into a term with the symmetry of the anisotropic exchange and with reduced magnitude of d^2/J, by applying a nonuniform spin rotation [32]. Consequently, the exchange narrowing KT theory becomes inadequate for describing the effect of the DM interaction on the ESR line width. However, this is true only for certain spin lattices and certain components of the DM interaction [33]. The components that can be eliminated in the first order in d are those that sum up to zero within any closed loop on a spin lattice; for example, for the kagome lattice, the in-plane DM component D_p is reducible, while the out-of-plane component D_z is irreducible. The KT theory remains applicable for the irreducible components of the DM interaction.

4.2. Spin diffusion

In low-dimensional magnetic systems it may happen that the Gaussian approximation of the decay of the spin correlation function in Eq. (12) is not justified due to a diffusional contribution to the decay. This dictates slower time dependence of the form [34].

$$\psi(\tau) \propto \tau^{-D/2}, \tag{19}$$

where D represents the dimensionality of the spin system. For $D \leq 2$ this leads to a divergent integral in Eq. (14), which in reality leads to broadening of the EPR spectra and changes their shape from the Lorentzian shape [34].

When the secular part of the anisotropy Hamiltonian (Eq. (3)), i.e., the part commuting with the Hamiltonian H_0, dominates the anisotropy in one-dimensional systems, the relaxation function is given by $\varphi(t) = \exp\left(-(\Gamma t)^{3/2}\right)$, where $\Gamma = \left(4M_2/3\hbar^2\right)^{2/3}\tau_c^{1/3}$ [34]. The Fourier transform in Eq. (9) then yields an absorption spectrum decaying somewhere in-between the Lorentzian and the Gaussian line shape (**Figure 4**). The line width of the spectrum is of the order of Γ. On the other hand, there exists no universal picture for two dimensions. Nevertheless, deviations of the experimentally observed EPR spectra from the Lorentzian shape in 2D were observed in the past and successfully ascribed to the presence of spin diffusion [35]. Quite generally, the spin-diffusion effect in two dimensions is usually much less pronounced than in one dimension.

Finally, we note that the diffusional decay of the electronic spin correlation functions is often not detectable by EPR at all, even in low dimensional systems. Although these systems may be

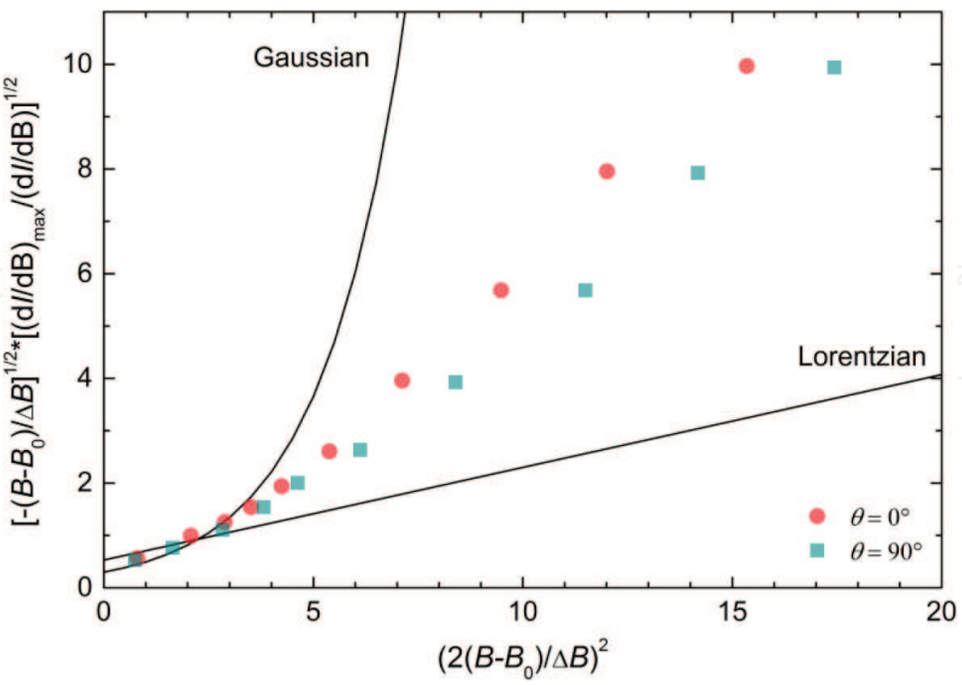

Figure 4. Analysis of the line shape in the one-dimensional spin system $(CH_3)_4NMnCl_3$ (TMMC) for two different directions of the magnetic field. (Adapted from ref. [34].)

characterized as being low dimensional due to the dominant exchange interaction along a chain or within a plane, also inter-chain/inter-layer exchange couplings can still be large compared to the magnetic anisotropy terms regulating the linewidth of the EPR absorption spectra. In such cases the decay of spin correlations is effectively taking place in three dimensions and the spin-diffusion problem is absent.

4.3. Exact calculations on finite clusters

The postulate of the Gaussian decay of the spin correlation function in the KT theory (Eq. (12)) has no theoretical background and is not necessarily valid, as explained in Section 4.1. However, this assumption is not needed at all if the EPR line shape is calculated from the basics, i.e., from Eq. (7). This can be done only on finite clusters of spins. Such a limitation then requires an extrapolation to the thermodynamic limit if these calculations are to be applied to macroscopic samples.

Exact calculations of the EPR line shape on finite clusters were performed by El Shawish et al. [36] for certain 1D and 2D spin lattices. For a spin chain, the results showed a noticeable transformation of the decay of the spin correlations from the Gaussian shape at early times to a much slower decay of diffusional characteristics at longer times. The resulting line broadening and the deviation from the Lorentzian line shape were, however, later shown to be effectively short-cut by inter-chain exchange [37].

The situation is very different in 2D, e.g., for the kagome spin lattice. Namely, the finite-cluster calculations revealed that, at least for the irreducible DM component d_z the line width indeed scales with d_z^2/J [36], as predicted by the KT theory. Although no clear signature of the diffusional decay of spin correlations was observed, an interpolation to the spin-diffusional assumption still caused a moderate increase of the line width and a slight deviation from the Lorentzian line shape. For herbertsmithite, such an assumption would then slightly decrease the amplitude of the DM vector compared to the above-presented results based on the KT approach, namely to $0.04 \leq d_z/J \leq 0.08$ [36].

We note that the finite-cluster approach is severely limited, as the extrapolation to the thermodynamic limit, which is usually of interest in experiments, is highly nontrivial and depends on a particular spin lattice [36]. However, since the results are exact, this approach may still be very interesting for small systems, such as molecular magnets. An interesting prediction of a double-peak EPR spectrum was also given (**Figure 5**). The spectrum should thus strongly differ from the usual Lorentzian line shape, which still awaits experimental confirmation.

4.4. Oshikawa-Affleck theory

Exact calculations of the second and fourth moments of the EPR absorption spectra (Eq. (13) and Eq. (15)) are possible within the KT framework for infinite lattices, but only in the limit of infinite temperature. In this case, static spin correlations of the products of spin operators acting on different lattice sites can be neglected. In general, in Eq. (13) and Eq. (15), one is dealing with the computation of four-spin correlation functions since the magnetic anisotropy

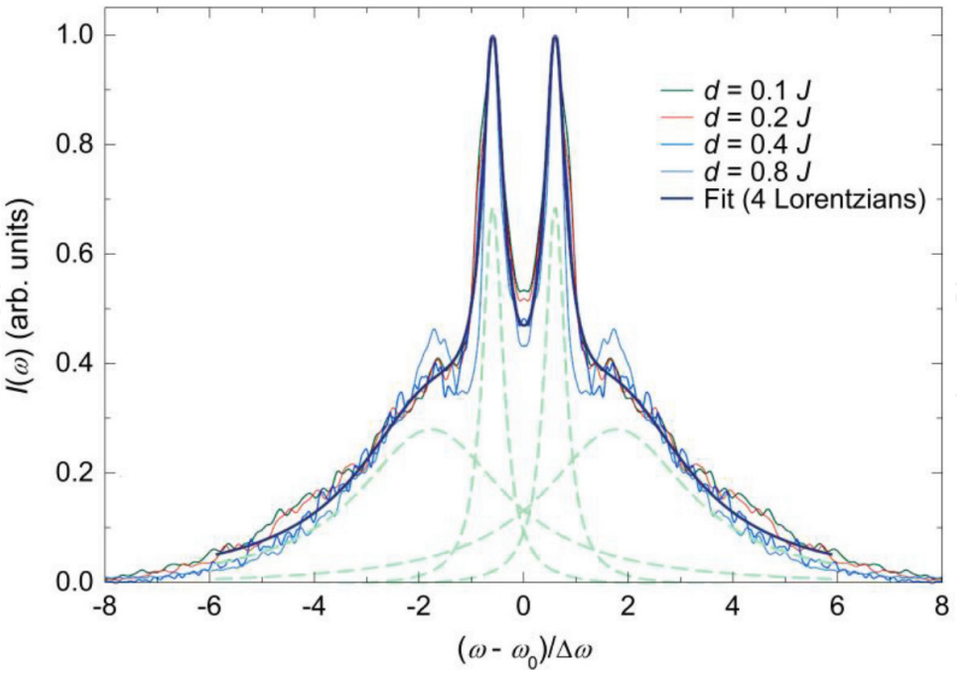

Figure 5. The EPR line shape of a finite 16-spin chain for different values of the staggered DM interaction d. The curves are rescaled with the half width $\Delta\omega$. (Adapted from ref. [36].)

Hamiltonian is quadratic in spin operators. Therefore, special schemes of disentangling the four-spin correlation functions into products of two-spin correlation functions need to be applied [14, 19]. Further complications emerge at finite temperatures, i.e., at $T \sim J$, when spin correlations between adjacent spin sites become important.

The problem of how finite temperatures (finite spin correlations) affect the EPR line width is treated within the Oshikawa-Afflect effective-field-theory approach that is applicable to spin chains [38, 39]. The spin diffusion picture, which predicts a non-Lorentzian line shape in 1D, does not apply to the OA theory. In contrast to the KT theory, this approach works well at intermediate and low temperatures, $T_N \ll T \ll J$, where, in general, all classical theories break down due to many-body correlation effects. The lower limit is given by the Néel temperature of 3D spin ordering, where 3D critical spin correlations develop. The AO theory allows to differentiate between the symmetric-exchange-anisotropy broadening and the antisymmetric DM broadening, as different scalings with temperature and magnetic field are predicted. The AE contribution scales like [38–40]

$$\Delta B_{AE}(T) = \varepsilon \frac{2k_B(\delta/J)^2}{g\mu_B\pi^3} T, \tag{20}$$

where the constant $\varepsilon = 2$ applies for the direction of the external magnetic field along the anisotropy axis and $\varepsilon = 1$ for the perpendicular directions. This contribution does not depend on the magnitude of the applied field and scales linearly with temperature. The DM contribution to the EPR line width is characterized by the staggered field $h_s = c_s B_0$, where the

staggered field coefficient c_s originates from the DM interaction and/or from a staggered g factor. This broadening is of the form

$$\Delta B_{DM}(T, B_0) = 0.69 g \mu_B \frac{k_B J}{(k_B T)^2} h_s^2 \sqrt{\ln\left(\frac{J}{T}\right)}. \tag{21}$$

The temperature dependence of the DM broadening is inverse to the AE broadening, as the former decreases with increasing temperature while the latter increases. Moreover, while the AE broadening effect is independent of the applied field, the DM broadening increases with the square of the applied field.

If both the AE and the DM term are of similar magnitude in a particular system, one can expect to observe both EPR broadening mechanisms simultaneously. Such is, for instance, the case in the $CuSe_2O_5$ spin-chain compound [40]. There, simultaneous modeling of the angular, temperature, and frequency-dependent EPR line width with the OA theory (the sum of contributions in Eq. (20) and Eq. (21)) allowed Herak et al. to extract both the AE and the DM anisotropy constants [40]. The simultaneous fits of the AO theory to multiple experimental datasets are presented in **Figure 6**.

At the end, it should be stressed that the OA approach still relies on the perturbation theory (in magnetic anisotropy). So, cases, where the anisotropy is of the order of the isotropic exchange interactions or larger are untreatable within this theory.

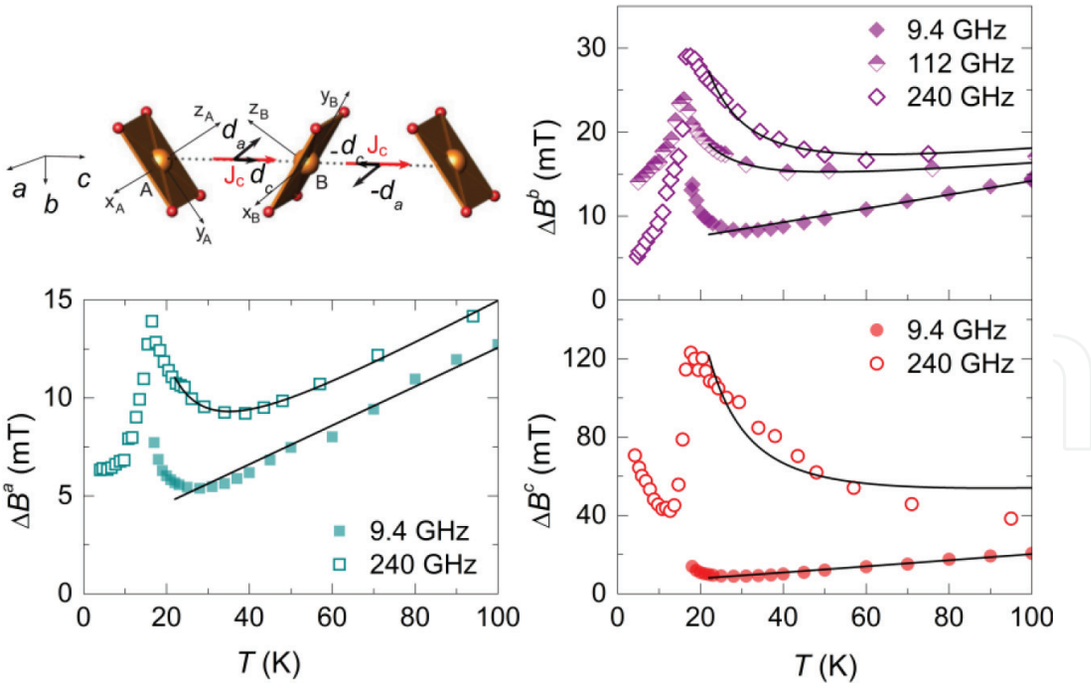

Figure 6. (top left) A 1D chains of Cu^{2+} S = 1/2 spins (orange) in $CuSe_2O_5$. Other panels show the temperature dependence of the EPR line width in three crystallographic directions at different frequencies. The solid lines are fits to the OA theory of the data (symbols) corrected for high-temperature phonon-induced broadening. (Adopted from ref. [40].)

4.5. EPR moments

The EPR-moments approach [41] described in this section is more direct, i.e., non-perturbative. Within this approach the line width (and line shift) in the "frequency domain," where the frequency is varied in a fixed Zeeman field, can be calculated for an arbitrary strength of magnetic anisotropy. Moreover, exact calculations at any temperature are possible for spin chains. In general, the EPR line width is given by the four lowest shifted moments

$$m_n^{\omega} = J^{-n} \int_{-\infty}^{\infty} (\omega - h)^n \chi''(\omega - h) \mathrm{d}\omega, \tag{22}$$

where $h = g\mu_B B_0/\hbar$, as [41]

$$\Delta\omega = J^2 \frac{Jm_3^{\omega} + hm_2^{\omega}}{Jm_2^{\omega} + hm_1^{\omega}} - \left(J \frac{Jm_2^{\omega} + hm_1^{\omega}}{Jm_1^{\omega} + hm_0^{\omega}} \right)^2. \tag{23}$$

The moments in the frequency domain (Eq. (22)) represent static correlations that can be calculated in the case of 1D spin chains to arbitrary precision for any temperature and applied field [41]. The agreement of this approach with fully numerical calculation for finite chain Hamiltonians is shown in **Figure 7**.

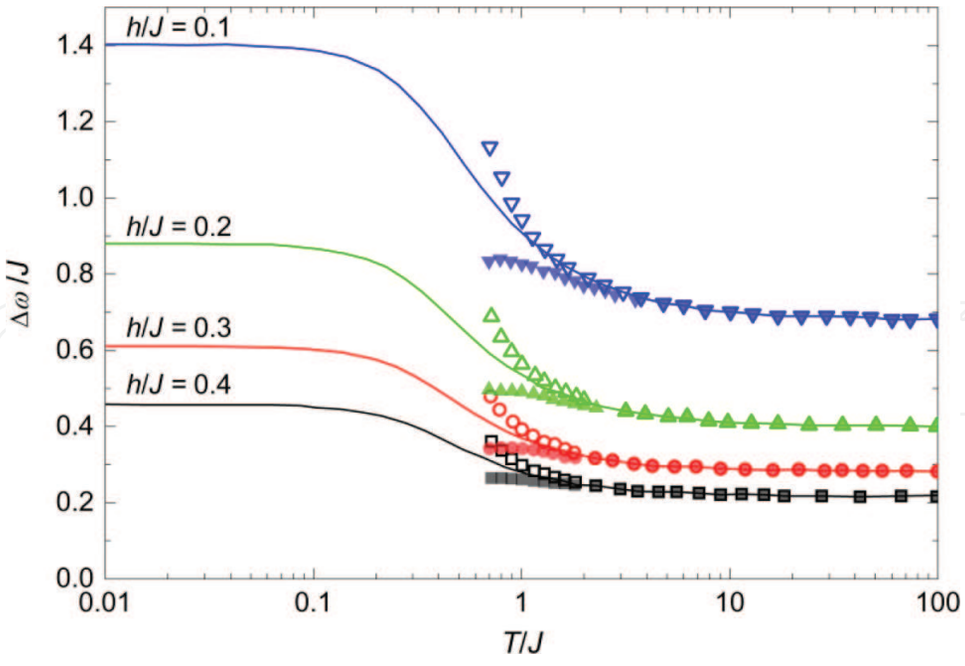

Figure 7. The temperature dependence of the EPR line width in the frequency domain of a spin chain predicted by the EPR moments approach (Eq. (23)) for the AE anisotropy δ = 0.1 J at various fields $h = g\mu_B B_0/k_B$ (lines). The symbols represent numerical calculations on finite chains with the length of N = 16 spins (full symbols) and N = 24 spins (open symbols). (Adopted from ref. [41].)

In a typical EPR experiment, however, the frequency is kept constant and the magnetic field is swept. It turns out that the calculation of the shifted moments in the field domain,

$$m_n^h = J^{-n} \int_{-\infty}^{\infty} (\omega - h)^n \chi''(\omega - h) \mathrm{d}h, \tag{24}$$

requires the knowledge of infinitely many moments in the frequency domain. Therefore, the experimental line width cannot be calculated exactly at arbitrary temperature and field [40].

We should stress that the fact the EPR spectrum is measured in a field-sweet experiment is actually neglected in almost all theoretical treatments. Furthermore, a complication that arises when applying the EPR-moments approach to an experiment is that "long tails" of the EPR line may considerably contribute to the moments, while these are usually not properly accounted for by the experimentally determined FWHM due to noise [42]. Therefore a cutoff of high-frequency tails is necessary, as it was recently demonstrated for the case of the quasi-one-dimensional magnet $Cu(py)_2Br_2$ [42].

5. Conclusions

This chapter reviews the development of the treatment of the EPR absorption line in strongly exchange-coupled spin systems. The starting point is the Kubo Tomita general theory of magnetic resonance absorption, which demonstrates how the line width can be approximated by two lowest even moments of the EPR line, M_2 and M_4. We note that the knowledge of all the moments, $M_n = \int_{-\infty}^{\infty} \omega^n I(\omega) \mathrm{d}\omega$, is equivalent to the knowledge of all the derivatives of a particular absorption line and, therefore, exactly determines the line shape. A particularly enlightening result of the KT theory is the phenomenon of exchange narrowing, according to which the EPR line width scales with the square of the magnetic anisotropy and is inversely proportional to the isotropic exchange interaction.

The KT approach was successfully applied to various spin lattices in the past, including the geometrically frustrated kagome and triangular lattices, which are exemplified here. However, when the theory is applied to a particular system special attentions needs to be made a) to a possible reducibility of the asymmetric Dzyaloshinskii-Moriya exchange anisotropy, b) to the diffusional decay of spin correlations, which may occur in low-dimensional spin systems, c) to finite correlations among spins at different sites, which typically develop below the temperature of the order of the dominant isotropic exchange, and d) to the size of the magnetic anisotropy, which is only treated as a perturbation in the KT theory. All these drawbacks of the KT theory can be overcome, at least in special cases. In this review, special approaches that were developed in this vein have been summarized. These include a) exact calculations of the EPR line on finite clusters, the Oshikawa-Affleck effective-field theory for 1D spin systems, and the recently developed EPR-moments approach. For each approach a representative example has been provided in this review.

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Conflict of interest

The author declares no conflict of interests.

Author details

Andrej Zorko

Address all correspondence to: andrej.zorko@ijs.si

Jožef Stefan Institute, Ljubljana, Slovenia

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