Simulating frequency-swept magnetic resonance spectra of V_{15}.

The transmission coefficient of a plane parallel sample as a function of frequency (hereafter called transmission spectrum) depends on both the complex dielectric permittivity (ε^*) and the complex magnetic permeability of the sample ($\mu*$). These are defined as Eqs. 1 and 2, respectively:

$$\varepsilon^*(\nu) = \varepsilon'(\nu) + i\varepsilon''(\nu) \qquad (1)$$
$$\mu*(\nu) = \mu'(\nu) + i\mu''(\nu). \qquad (2)$$

In these equations, the $\varepsilon'(\nu)$ is the effective dielectric constant and $\varepsilon''(\nu)$ is the dielectric absorption. Likewise, $\mu'(\nu)$ is the magnetic permeability and $\mu''(\nu)$ is the magnetic absorption. In the general case of an anisotropic system, $\varepsilon^*(\nu)$ and $\mu*(\nu)$ are tensors. The magnetic permeability tensor also includes gyrotropic (antisymmetric) components for magnetized media. The interference of radiation inside the plane parallel slab of the finite thickness causes oscillations in the baseline of the transmission spectrum, of which the period is determined by $\varepsilon'(\nu)$ and the thickness d of the sample. The damping of these oscillations and the slope of the baseline are determined by $\varepsilon''(\nu)$. In our analyses the complex dielectric permittivity is assumed to be independent on radiation frequency in the narrow range of the magnetic absorption. Around the resonance frequency, i.e. where the radiation frequency is equal to the energy difference between two adjacent spin sublevels (M_S states in the absence of transverse terms in the spin Hamiltonian), strong absorption of radiation occurs due to the magnetodipolar transition. Outside this region the $\mu'(\nu)$ is assumed 1 and $\mu''(\nu)$ is taken as being 0. Experimentally, two parameters are available, namely the transmission coefficient, Tr, and the phase change, φ. The dielectric permittivity parameters are calculated from Tr and φ, outside the magnetic dispersion region. The obtained values are then used in the region of the magnetic resonance line, and finding the magnetic permeability parameters are obtained by solving two equations with two unknowns. However, in this study only Tr was measured, and the following procedure was used: 1) The complex dielectric permeability parameters were fitted rather than calculated in the region outside the magnetic resonance. 2) Furthermore, an assumption was made about the lineshape of the magnetic resonance line, for which a Lorentzian was used. In the following, first the general dependence of the transmission coefficient on the dielectric and magnetic permeabilities is shown, which is then followed by the formulas used in our studies, which assume a Lorentzian lineshape and where the powder nature of the sample has been taken into account.

The transmission coefficient is a rather complicated function of the complex dielectric and magnetic permeabilities, which can be deduced from the Fresnel equations in optics.(see for instance [1]) In most textbooks, the magnetic permeability is not considered, and μ' is taken as 1 and μ'' as 0. In the case of magnetodipolar transitions this is obviously no longer true, and the most general case has to be used, as given in Eq. 3 and following:[2]

$$Tr(v) = E \frac{(1-R)^2 + 4R\sin^2 \psi}{(1-RE)^2 + 4RE\sin^2(N+\psi)} \tag{3}$$

In this equation E and N are functions of the extinction coefficient (k), the real refractive index (n), the resonance frequency (v), and the thickness of the sample (d), as given by Eqs. 4 and 5, respectively:

$$E = e^{-4\pi k v d} \tag{4}$$

$$N = 2\pi n v d \tag{5}$$

The complex refractive index, given by Eq. 6, can be expressed in terms of the complex dielectric and magnetic permeabilities according to Eqs. 7 and 8:

$$n^* = n + ik \tag{6}$$

$$n = \frac{\theta_2}{2k} \tag{7}$$

$$k = \sqrt{\frac{-\theta_1 + \sqrt{\theta_1^2 + \theta_2^2}}{2}} \tag{8}$$

In Eqs. 7 and 8, the θ_1 and θ_2 quantities are functions of the complex dielectric and magnetic permeabilities, given by Eqs. 9 and 10:

$$\theta_1 = \varepsilon'\mu' - \varepsilon''\mu'' \tag{9}$$

$$\theta_2 = \varepsilon'\mu'' - \varepsilon''\mu' \tag{10}$$

The quantity R in Eq. 3 is a function of, ultimately, the complex dielectric and magnetic permeabilities, as given in Eq. 11:

$$R = \frac{(a-1)^2 + b^2}{(a+1)^2 + b^2} \tag{11}$$

where a and b are given in Eq 12 and 13 respectively:

$$a = \sqrt{\frac{\gamma_1 + \sqrt{\gamma_1^2 + \gamma_2^2}}{2}} \tag{12}$$

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$$b = \frac{\gamma_2}{2a} \tag{13}$$

In Eqs. 12 and 13 the γ_1 and γ_2 quantities are given by Eqs. 14 and 15 respectively:

$$\gamma_1 = \frac{(\mu'\varepsilon' + \mu''\varepsilon'')}{\varepsilon'^2 + \varepsilon''^2} \tag{14}$$

$$\gamma_2 = \frac{(\mu''\varepsilon' + \mu'\varepsilon'')}{\varepsilon'^2 + \varepsilon''^2} \tag{15}$$

The remaining parameter in Eq. 3, ψ, again depends on the complex dielectric and magnetic permeabilities, according to Eq. 16:

$$\psi = \arctan\left(\frac{2b}{a^2 + b^2 - 1}\right) \tag{16}$$

with a, and b defined in Eqs. 12 and 13 respectively.

The phase change also depends on the dielectric and magnetic permeabilities (Eq. 17):

$$\varphi = N + \arctan\left(\frac{ER \sin 2(N+\psi)}{1 - ER \cos 2(N+\psi)}\right) + \arctan\left(\frac{b}{a^2 + b^2 + a}\right) - \arctan\left(\frac{b}{a+1}\right) \tag{17}$$

with all parameters as defined above.

In the present study, the phase change was not measured and instead the lineshape was assumed to be Lorentzian (Eq. 18).

$$\mu^*(\nu) = 1 + \frac{\Delta\mu \nu_H^2}{(\nu_H^2 - \nu^2 - i\nu\Delta\nu)} \tag{18}$$

This equation can be rewritten in terms of μ' and μ'' as in Eqs. 19 and 20, respectively:

$$\mu'(\nu) = 1 + \Delta\mu \frac{\left(1 - \dfrac{\nu^2}{\nu_H^2}\right)}{\left(1 - \dfrac{\nu^2}{\nu_H^2}\right)^2 + \left(\dfrac{\nu\Delta\nu}{\nu_H^2}\right)^2} \tag{19}$$

$$\mu''(\nu) = \Delta\mu \frac{\left(\dfrac{\nu\Delta\nu}{\nu_H^2}\right)}{\left(1 - \dfrac{\nu^2}{\nu_H^2}\right)^2 + \left(\dfrac{\nu\Delta\nu}{\nu_H^2}\right)^2} \qquad (20)$$

In this equation $\Delta\mu$ is the mode contribution, which determines the intensity of the absorption line. The parameter ν_H is the resonance frequency as given by the difference in energies of the spin states and $\Delta\nu$ is the linewidth of the absorption line.

The transition between the spin states is due to the oscillating magnetic field of the radiation. The Hamiltonian describing the interaction between this field and the paramagnetic system contains the magnetic moment operator, which is given by (Eq. 21).

$$\hat{\boldsymbol{\mu}} = \mu_B \mathbf{g} \cdot \hat{\mathbf{S}} \qquad (21)$$

Although in our system the **g** tensor is axial, for the calculation of $\Delta\mu$, we have used the average g factor in view of the small anisotropy of the g tensor. This approximation was supported by the quality of the fits that were obtained eventually.

In general, the mode contribution, $\Delta\mu$ is determined by the square of the matrix elements coupling the initial and final states by the magnetic moment operator, the energy difference between initial and final states, the number of molecules per cm^3 (the density of the sample) and a Boltzmann weighting factor accounting for the population difference between initial and final states.

The mentioned matrix element is then (Eq. 22):

$$\langle m | \hat{\boldsymbol{\mu}} | n \rangle = g\mu_B \langle m | \hat{\mathbf{S}} | n \rangle \qquad (22)$$

in the case of an isotropic g value. Since $\hat{\mathbf{S}}_z$ does not couple states with $\Delta M_S \neq 0$, only the $\hat{\mathbf{S}}_x$ and $\hat{\mathbf{S}}_y$ play a role. The Boltzmann weighting factor is given by (Eq. 23):

$$\frac{e^{-E_m/kT} - e^{-E_n/kT}}{\sum_i e^{-E_i/kT}} \qquad (23)$$

where E denotes the energy of a spin state with respect to the ground state and the denominator is the partition function that sums over all available energy levels.

The total mode contribution to the magnetic permeability for the magnetodipolar transition m $\rightarrow$ n with the frequency $h\nu_{nm} = E_n - E_m$ is then given by (Eq. 25):

$$\Delta\mu(m \to n) = 8\pi N g^2 \mu_B^2 \left|\langle m|\hat{S}_{x,y}|n\rangle\right|^2 \frac{e^{-E_m/kT} - e^{-E_n/kT}}{\left(\sum_i e^{-E_i/kT}\right)(E_n - E_m)} \quad (25)$$

where $N = \rho N_A/M$, with ρ the density of the sample in g cm^{-3}, M the molecular weight of the system, and N_A is the Avagadro number.

In the case of a magnetised medium, the magnetic permeability becomes gyrotropic , and the resulting permeability becomes a tensorial quantity, described by Eq. 26, for the magnetisation along the z-axis:[3]

$$\mu = \begin{pmatrix} \mu_\perp & i\mu_a & 0 \\ -i\mu_a & \mu_\perp & 0 \\ 0 & 0 & \mu_\parallel \end{pmatrix} \quad (26)$$

This expression can be used both for powder samples and single crystalline ones with axial (hexagonal, tetragonal) symmetry and for H$\parallel$ the symmetry axis. The parallel component of the effective magnetic permeability does not contribute to the effective permeability, since in the case of weak anisotropy, the spins precess around the magnetisation direction (z axis), and therefore the magnetisation does not oscillate in the z direction.

For transversely magnetized media (i.e. H$\parallel$M$\perp$k, Voigt geometry) the magnetic permeability, which determines the transmission coefficient (as outlined above) becomes (Eq. 27):

$$\mu_{\mathrm{eff}}(\nu) = \mu_\perp(\nu) - \mu_a(\nu)^2/\mu_\perp(\nu) \quad (27)$$

Here the off-diagonal elements μ_a are often neglected; however, they were shown to have some importance in V15 in our Voigt geometry experiment.

So far we suggested only a single orientation of the molecule with respect to the magnetic field (H$\parallel$symmetry axis). In a polycrystalline sample comprised of axially anisotropic molecules, their contribution to the magnetic permeability has to be averaged with respect to the angle θ_H between the magnetic field and anisotropy axis. The average of a function that depends on θ_H is (Eq. 27):

$$\langle f(\theta_H)\rangle = \tfrac{1}{2}\int_0^\pi f(\theta_H)\sin\theta_H d\theta_H \quad (27)$$

Therefore, assuming a Lorentzian lineshape of the resonance mode in the single molecules, the beforementioned actual components of the effective magnetic permeability become (Eqs. 28 and 29) :

$$\mu_\perp(\nu) = \langle \mu_\perp(\nu, \theta_H) \rangle = 1 + \frac{1}{2} \int_0^\pi \Delta\mu \frac{\nu_H^2 \sin\theta_H d\theta_H}{\nu_H^2 - \nu^2 + i\nu\Delta\nu} \tag{28}$$

$$\mu_a(\nu) = \langle \mu_a(\nu, \theta_H) \rangle = \frac{1}{2} \int_0^\pi \Delta\mu \frac{\nu\nu_H \sin\theta_H d\theta_H}{\nu_H^2 - \nu^2 + i\nu\Delta\nu} \tag{29}$$

where $\nu_H(\theta_H) = (\mu_B H /h)(g^2_{\perp c}\sin^2\theta_H + g^2_{\|c}\cos^2\theta_H)^{1/2}$, $\Delta\nu$ and $\Delta\mu$ are the resonance frequency, the intrinsic linewidth and the mode contribution to the permeability of the single molecule, respectively. Here $\Delta\nu$ and $\Delta\mu$ are also functions of θ_H, however this dependence is small due to the weak anisotropy of V15. The most important contribution in the integrals (27), (28) is due to the resonance frequency $\nu_H(\theta_H)$. Thus $\Delta\mu$ in (28), and (29) is considered independent of θ_H and can be replaced by its value at the average g factor.

For finite temperatures we have to take into account the contributions of all five magnetodipolar transitions. Asuming their frequencies are equal to each other and summing their individual contributions $\Delta\mu(m\to n)$ we can calculate that the mode contribution becomes (Eq. 30), using equalities of the type ½(exp(z)+exp(-z))=cosh(z):

$$\Delta\mu(T,H) = 4\pi \frac{2N\bar{g}^2\mu_B^2}{h\bar{\nu}_H} \frac{1}{4} \tanh(\beta h\bar{\nu}_H/2) \frac{1 + e^{-\beta E_0}(2 + 3\cosh(\beta h\bar{\nu}_H))}{1 + e^{-\beta E_0}\cosh(\beta h\bar{\nu}_H)} \tag{29}$$

where $N = \rho N_A/M_{V15}$, $\rho = 2.77$ g cm^{-3}. $\beta = 1/k_B T$. As said above, we did not take into account the g value anisotropy in this formula, but rather used the average g value and the average resonance frequency that is derived from that (Eq. 30):

$$\bar{g}^2 = (g^2_{\perp c} + g^2_{\|c})/2 \quad ; \quad \bar{\nu}_H = \bar{g}\mu_B H/h \tag{30}$$

The g value anisotropy is taken into account in the resonance frequency (ν_H) in Eq. 28 and 29.

References:
1   M. Dressel and G. Grüner, *Electrodynamics of Solids*, Cambridge University Press, Cambridge 2002.
2   G.V. Kozlov and A.A. Volkov, in G. Grüner (Ed.): *Millimeter and Submillimeter Wave Spectroscopy of Solids*, Springer, Berlin 1998.
3   B. Lax and K.J. Button, *Microwave ferrites and ferrimagnets*, McGraw-Hill, New York 1962.