

IMPROVED SPIN HAMILTONIAN PARAMETERS FOR Mn^{2+} DETERMINED BY EPR AT ZERO MAGNETIC FIELD

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EPR has been studied at zero magnetic field for high-spin Mn^{2+} in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and NH_4Cl . Significant differences have been found between high-field EPR spin hamiltonian parameters in the literature and those necessary to fit the complex zero-field spectra. Sources of the discrepancies are discussed in relation to the Mn^{2+} systems and more generally.

1 Introduction

Electron paramagnetic resonance (EPR) experiments have conventionally been described by the parameters of a spin hamiltonian. The operators are those of spin only, orbital operators of the original total hamiltonian having been cast into parametric form as tensor elements. Thus a typical set of parameters will include elements of a g tensor to describe the Zeeman effect, fine-structure parameters to describe spin and orbital electronic interactions which exist in zero magnetic field, and hyperfine structure parameters to represent electron-nuclear spin interactions. The parameters derived from an EPR experiment can be compared with calculated values to gain insight on these external and internal electronic interactions.

Only the g tensor requires the external field of a conventional EPR experiment, the other parameters would be evident in a zero-field resonance (ZFR) experiment. The technical difficulties of sweeping the frequency of a microwave spectrometer have largely prevented the fine structure and hyperfine structure being observed without simultaneous observation of the Zeeman effect. Our studies of optically detected EPR and ZFR in molecular crystal photoexcited triplet states [1] have led us to re-examine traditional EPR in some transition metal complexes. Other zero-field measurements on first-row transition metal ions have not shown any serious errors in the spin hamiltonian parameters as determined from conventional EPR experiments [2–7]. Most of these studies dealt

with Fe^{3+} of which 98% of the naturally occurring isotopes have zero nuclear spin and so there were no complications from nuclear hyperfine interactions. In the systems we have studied so far, significant differences have been found between the published EPR spin hamiltonian parameters and those obtained without the magnetic field. For transition ions of high electronic and nuclear spin (e.g. Mn^{2+} , $S = \frac{5}{2}$, $I = \frac{5}{2}$) we have found in some cases that the ZFR spectrum is unrecognisable when compared with that predicted from the EPR parameters. These discrepancies cast doubt on the magnitudes of some of the parameters of the spin hamiltonian obtained from EPR experiments. They suggest at the very least that these parameters include significant components due to crystal misalignments in EPR studies, and to errors in magnetic field measurement. More importantly, symmetry approximations in the larger interaction tensors such as \mathbf{D} and \mathbf{A} (for nuclei with large magnetic dipole moments) and the assumption of parallel tensor axes are expected to contribute to the smaller terms which then become little more than fitting parameters. Finally, in special cases inadequacies of the spin hamiltonian itself may mean that the parameters obtained at zero field cannot in principle be compared with the same parameters obtained from high-field EPR due to field mixing of states which are normally excluded in the choice of the hamiltonian's effective spin [8]. In the present paper, some typical examples of ZFR spectra are given and the spin hamiltonian parameters compared with those obtained from EPR experiments.

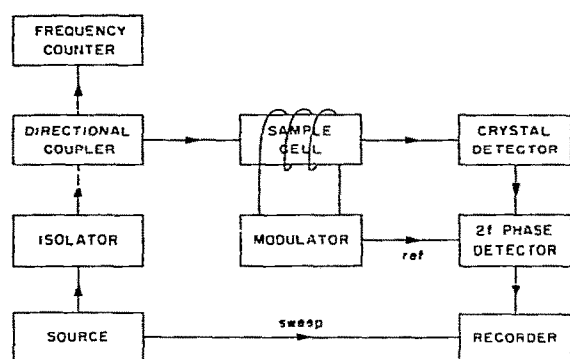


Fig. 1 Block diagram of zero-field resonance spectrometer

2. Experimental

The ZFR spectrometer is shown diagrammatically in fig. 1. The source is typically a backward wave oscillator although we have used motor driven klystrons. Frequency measurement is achieved with a transfer oscillator and counter, phase-locked to a secondary standard quartz oscillator. The magnetic modulation waveform is a bi-directional square wave and phase detection at the second harmonic of the modulation frequency produces the spectra shown in figs. 2b and 3b. They are in effect the differences between the detector crystal current with the modulating field on and off. Fig. 1 shows the spectrometer in the transmission mode. We have also used a reflection technique. This gives better signal-to-noise ratios but less reliable relative intensities. The sample cell is either a section of waveguide of appropriate size or a section of coaxial line with part of the dielectric replaced by the sample.

The earth's magnetic field was found not to influence the position of the zero-field resonances within the accuracy of measurement and no attempt was made to cancel it. In complementary EPR studies, a Varian V4502 spectrometer with Q-band attachment

was used. The magnetic field was measured with a proton gauss meter and the microwave frequency with a wavemeter.

Both of the Mn^{2+} doped salts described in this paper were obtained by slow evaporation at room temperature of saturated aqueous solutions containing a small amount of Mn^{2+} as the appropriate salt. Dried (but not dehydrated) powdered materials were used in the ZFR spectrometer sample cell to allow the observation of transitions of all polarisations. The amounts of Mn^{2+} actually incorporated were measured by atomic absorption spectrophotometry.

3 Results

3.1 $\text{Mn}^{2+}/\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.63 mole%

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ crystallises in the orthorhombic space group $\text{P2}_1\text{2}_1\text{2}_1$. The asymmetric unit is one formula unit and consists of a magnesium ion in a slightly distorted octahedral arrangement of six coordinated water molecules with the seventh water molecule occupying a hole in the lattice [9]. The absence of any local symmetry requires a general spin hamiltonian with no necessary correspondence between any axes of any of the tensors. Only low anisotropy in \mathbf{g} and \mathbf{A} and the small size and/or general isotropy of fourth-order spin terms allows the assignment of a unique axis system determined by the electronic interactions contained in \mathbf{D} .

The most recent EPR work on this salt is by Janakiraman and Upreti [10] who used a spin hamiltonian for the z direction

$$\mathcal{H}_s = \mu_B g_z B_z S_z + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) + A_z S_z I_z + A_{\perp}(S_x I_x + S_y I_y) \quad (1)$$

This assumes axial symmetry for \mathbf{A} , but there is no

Table 1
Comparison of spin hamiltonian parameters (in MHz) for $\text{Mn}^{2+}/\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ at room temperature, obtained by EPR and ZFR

	D	E	A_z	A_{\perp}	a	Ref
EPR	1200	≈ 0	-265	-	-	[11]
	1154 ± 14	266 ± 28	-258 ± 14	-244 ± 28	-	[10]
ZFR	1181 ± 2	183 ± 2	-269 ± 2	-266 ± 2	12 ± 3	this work

evidence that this is not effectively the case. Their room-temperature (300 K) results are $D = 1155 \pm 14$ MHz, $|E| = 266 \pm 28$ MHz, $A_z = -258 \pm 14$ MHz and $A_{\perp} = 244 \pm 28$ MHz, the absolute sign of A_z being assumed. Parameters from some earlier work by Hayashi and Ono [11] are listed in table 1. The zero-field transition frequencies and intensities can fairly readily be calculated from given values of the parameters by exact diagonalisation of the matrix of a spin hamiltonian similar to eq. (1), but including a fourth-order term in a [12, p. 437] and without the external magnetic field term. These parameters predict a ZFR spectrum which bears no obvious resemblance to the observed spectrum except that the general region of the microwave spectrum is correct (see figs 2a and 2b). The ZFR spectrum is quite sensitive to small changes in the parameters since the lines can be located in most cases to within 5 MHz. However, we were unable to obtain a match by trial and error procedures nor to assign any transitions to eigenvector pairs of the 36×36 matrix diagonalisation and thus to begin an iterative refinement. We re-examined the EPR but used a powder in-

stead of their single crystal and Q-band (35 GHz) instead of their X-band. The powder has the advantage that there are no crystal orientation errors but the disadvantage that the singularities in the powder spectrum may not coincide exactly with the extrema of a perfectly oriented single crystal rotation diagram [13]. Nevertheless one would expect A_z and A_{\perp} to be little affected by this since they are obtained by averaging the successive spacings of similarly shaped features. We were particularly careful to establish that our proton gauss meter measured the same field as experienced by the sample and checked the spectrometer frequency using DPPH ($g = 2.0036$). We were able to assign all six singularities for each of the four outer fine-structure features of both parallel (z) and perpendicular (x or y , not both) transitions.

We thus obtained $A_z = (-) 270 \pm 3$ MHz, and $A_{\perp} = (-) 267 \pm 4$ MHz, that is, isotropic within experimental error. D (and its relative sign) and a were then obtained directly from the parallel $M_s + \frac{5}{2} \leftrightarrow +\frac{3}{2}, +\frac{3}{2} \leftrightarrow +\frac{1}{2}, -\frac{1}{2} \leftrightarrow -\frac{3}{2}$ and $-\frac{3}{2} \leftrightarrow -\frac{5}{2}$ features [14] noting that the rhombic correction terms [15] shift fine-structure groups of lines with the same $|M_s|$ by the same amount (≈ 1 G) at 35 GHz. D and a were 1177 ± 6 and 12 ± 4 MHz respectively. Going back to the ZFR spectrum with a prediction based on these new values for A_z, A_{\perp}, D and a but the old EPR determined E value, it was possible to recognise a group of transitions near 5.9 GHz which we believed would merge if E was fitted by trial and error. This proved to be the case but required a large change in E from the published 266 ± 28 MHz to 183 MHz. To check this value the perpendicular transitions in the powder spectrum were analysed and $E = 182$ MHz obtained. It was then straightforward to perform an iterative refinement of the parameters, D, E, a, A_z , and A_{\perp} to obtain a best fit to sixteen of the most intense features in the ZFR spectrum. The spectrum is very sensitive to these parameters and leads to the quite small estimated standard deviations on them. Table 1 compares the results and the simulation is shown in fig. 2c. This calculated spectrum uses the second derivative of the absorption lineshape (evidently very close to lorentzian). It has been normalised to account for the changing Boltzmann distribution as a function of frequency. We do not regard the intensity anomalies as being serious since power levelling across the three bands (1–2, 2–4 and 2–8 GHz) is approximate only, and we have not sought to eliminate

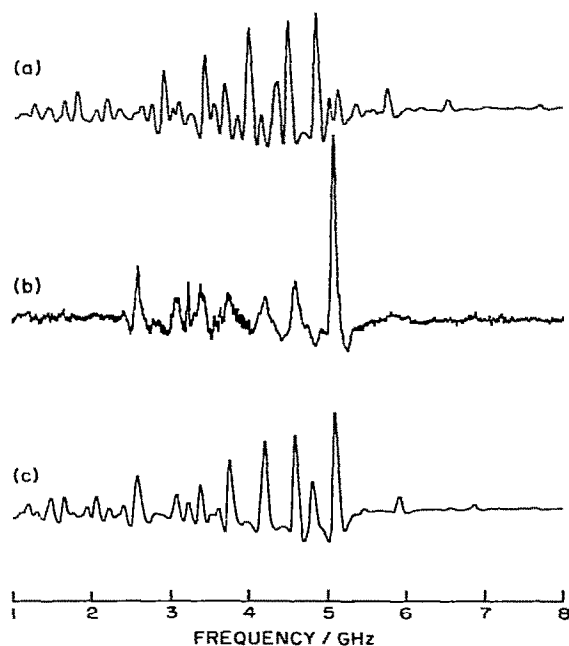


Fig. 2 (a) ZFR spectrum predicted for $\text{Mn}^{2+}/\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ from parameters of ref. [10] (b) Observed ZFR spectrum (reflection technique) (c) Theoretical spectrum, this work. All data correspond to measurements at room temperature.

minor frequency-dependent reflections which are a feature of swept frequency microwave measurements. For the computed spectra, a fixed line width was used and thus can result in further discrepancies in the spectral profile since the experimental zero-field transitions have somewhat variable line widths.

3.2 Mn^{2+}/NH_4Cl , 0.08 mole%

Analysis of the ZFR spectrum (see fig. 3b) was more straightforward in the case of Mn^{2+} in NH_4Cl . EPR measurements on this system have been analysed in terms of a spin hamiltonian of axial symmetry [16–20] and are of interest because the magnitude of D is much larger than is usual for Mn^{2+} . Under the crystal growth conditions we used, the bulk of the evidence [17,18,21,22] favours a structure in which Mn^{2+} occupies an interstitial site at the centre of a cube face defined by four chloride ions in the body centred cubic structure of NH_4Cl . Two NH_4^+ ions originally at the centres of the adjacent unit cells which contain the impurity ion are replaced by two water molecules, resulting in Mn^{2+} being in a strongly axial electric field.

The most accurate EPR analysis of this system to date appears to be that quoted by Lupei et al. [20] which is based on previous work by Lupei et al. [19] and Zaripov and Chirkun [18]. They used a tetragonal spin hamiltonian which included fourth-order parameters a and F [12, p. 437] and a nuclear quadrupole term Q [12, p. 166]. The ZFR powder spectrum predicted from their spin hamiltonian parameters is shown in fig. 3a and the observed ZFR spectrum of the powder at 296 K is shown in fig. 3b. In this case most of the line positions could be measured to within 2 MHz. Because $D \gg A$ the spectrum has recognisable first-order features, in the limit $D/A \rightarrow \infty$ and for isotropic hyperfine interaction zero-field resonance consists of two groups centred at $2D$ and $4D$, the $4D$ group being split into six lines with a separation of A whereas the

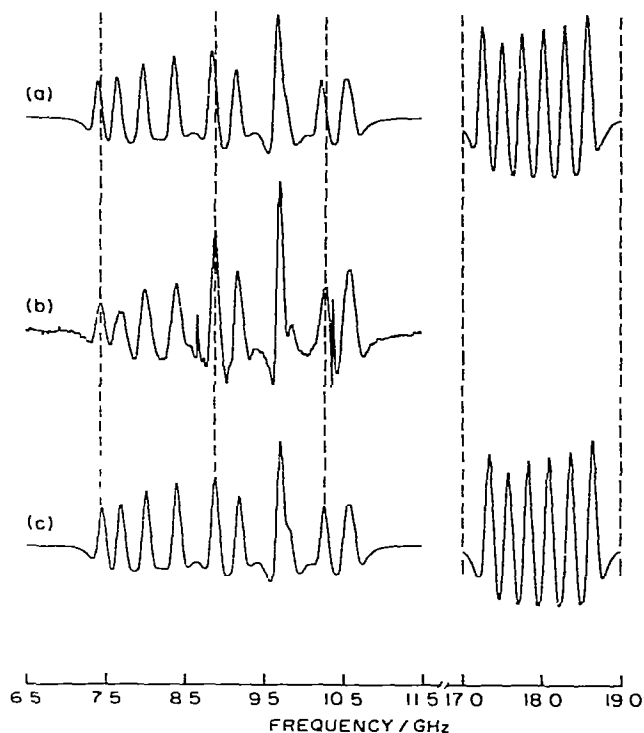


Fig. 3 (a) ZFR spectrum predicted for $[MnCl_4(H_2O)_2]^{2-}$ in NH_4Cl from parameters of ref. [20] (b) Observed ZFR spectrum (transmission technique) (c) Theoretical spectrum, this work. All data correspond to measurements at room temperature. Two sharp lines in (b) at 8.7 and 10.3 GHz are spurious.

$2D$ group splits into eleven lines of uneven separation. Although the predicted and observed transitions do not coincide, the observed pattern is immediately recognisable. Nevertheless in this case of high and known symmetry, significant improvement in the fine-structure parameters is afforded by the ZFR spectrum. Since we do not as yet have sources to observe the transitions between 17 and 19 GHz, separate refinement of the D and a parameters is not possible from the ZFR spectrum. Adjustment of either parameter

Table 2

Comparison of spin hamiltonian parameters (in MHz) for Mn^{2+}/NH_4Cl at room temperature, obtained by EPR and ZFR/EPR of this work.

	D	A_z	A_{\perp}	a	F	Q	Ref
EPR	-4491.8 ± 1.5	-247.3 ± 0.6	-253.3 ± 0.6	15.0 ± 1.5	2.1 ± 1.5	2.1 ± 0.15	[20]
ZFR/EPR	-4509.3^a	-245.0 ± 2.7	-253.1 ± 2.7	15.3^a	—	—	this work

^a) Errors not given because of the empirical relationship between D and a in our analysis, see text.

moves the whole group of lines which lie in the range 7–11 GHz. However, it was possible from this group of lines to obtain values for the principal values of the hyperfine interaction by least-squares iterative refinement (table 2), the quantities D and a being kept as close as possible to EPR derived values. These principal values of A are in reasonable accord with the EPR derived values [20]. With these values for the hyperfine interaction a best fit to the ZFR spectrum requires the empirical relationship (at 296 K)

$$a = 0.8027D + (3635.1 \pm 2) \text{ MHz},$$

$$-4600 > D > -4400 \text{ MHz} \quad (2)$$

A unique solution from this group of ZFR lines alone is not possible. The values of D and a given by Lupei et al. [20] (see table 2) are not consistent within the accuracy of eq. (2).

Since the discrepancy between the calculated and observed ZFR spectra (figs. 3a and 3b) was seen to be due to error in either or both D and a , we attempted to obtain better values of these two parameters which might fit eq. (2) more exactly by remeasuring the EPR spectrum of a single crystal at Q-band. Analysis of the spectrum obtained with the external magnetic field directed along a [100] direction (z axis of a Mn^{2+} centre) to third order [23] in D and A yielded values for the parameters D and a of -4505 and 10.3 MHz respectively, the ZFR values of A being regarded as known. This represents an improvement over the previously published values, the sum of squares of differences between nine observed and calculated ZFR line positions ($\Sigma \Delta^2$) decreasing from 10365 MHz^2 in the case of the parameters obtained by Lupei et al. [20] to 3703 MHz^2 from our ZFR and EPR determinations. These improved values of D and a still do not satisfy eq. (2) and hence do not minimise $\Sigma \Delta^2$ in the ZFR spectrum. Our final values, given in table 2, represent a best fit to the ZFR spectrum, the final values of D and a being obtained from eq. (2) such that the difference from our EPR derived values was minimised. The absolute sign of D was taken from Zaripov and Churkin's work [18]. The ZFR spectrum predicted from these values is shown in fig. 3c and the agreement with the experimental spectrum shown in fig. 3b is very good with $\Sigma \Delta^2 = 208 \text{ MHz}^2$. Such a procedure does not warrant separate standard errors for D and a as they are linearly dependent, but the error quoted in eq. (2) is valid.

In the case of $\text{Mn}^{2+}/\text{NH}_4\text{Cl}$ we believe that the main source of discrepancy between the ZFR spectrum and that predicted from analyses of EPR spectra (ref. [20] and this work) lies in insufficient accuracy in the perturbation analysis of EPR resonant fields. Even analysis to fourth order [19] in D is not enough and to get adequate accuracy from such an EPR spectrum some type of iterative least-squares fit to the resonant fields involving exact diagonalisation of the spin hamiltonian matrix would be desirable. A complete ZFR spectrum is much more simply analysable. Our values of D and a are only a fit to the low-frequency part of the ZFR spectrum and should not be regarded as definitive values. Such values would require measurement of the high-frequency part of the ZFR spectrum or exact EPR analysis. Inclusion of small nuclear quadrupole and low-symmetry fourth-order spin terms is not yet justified in the ZFR analysis.

3.3 Other systems

In other materials we have examined, the ZFR spectrum is not correctly predicted by EPR data within experimental error and our ZFR refined parameters generally fall well outside error limits on EPR derived parameters in the literature. So far these include $\text{Mn}/\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, copper acetate monohydrate and copper benzoate. These studies will be published in detail later. An exception is ruby [24] (Cr^{3+} in $\alpha\text{-Al}_2\text{O}_3$) which, as in other cases of satisfactory agreement with EPR data, has a particularly simple spin hamiltonian for the 90% zero nuclear spin isotopes of chromium.

4 Conclusions

We believe that except in the most painstaking work, some of the parameters of the spin hamiltonian at present in the literature must be viewed with caution. We expect that in general they include in no small measure the accumulated systematic errors of a typical EPR experiment. Such errors include those of crystal alignment; frequency and particularly field measurement errors are also very likely to contribute. Other errors may creep in through analytical procedures. We have already commented on the use of perturbation calculation of resonant fields. Even at high orders, significant errors remain for large values of D as in the

case of $\text{Mn}^{2+}/\text{NH}_4\text{Cl}$. Frequently an approximate spin hamiltonian is used either by leaving out higher terms or by choosing a symmetry which is too high, and there is the common assumption of parallel tensors in situations of low symmetry. More importantly, the various approximations made in the calculation of a spin hamiltonian from a total hamiltonian for the system can perhaps be explored through the ZFR experiment which is free of many errors in the EPR situation such as those of crystal orientation, field measurement, and assuming parallelism of the g tensor with other tensor interactions. We note also that the ZFR experiment confers benefits not only for systems with $S \geq 1$, including exchange coupled ions, but also for doublet systems with large hyperfine or large quadrupole interactions.

We conclude that a ZFR study has value both in its own right and as a complement to the conventional EPR experiment. In the case of $\text{Mn}^{2+}/\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ analysis of the ZFR spectrum was certainly made easier by accurate EPR measurements. For $\text{Mn}^{2+}/\text{NH}_4\text{Cl}$ a complete ZFR spectrum would readily have yielded accurate values for the parameters D , A and a , the EPR data only being required because of our current frequency limitation in the ZFR experiment. The ZFR technique promises to provide considerably finer insight into the properties of electron and nuclear paramagnetic materials.

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