A Single-crystal Electron Spin Resonance Study of Manganese(II)-doped Zinc Maleate Tetrahydrate†

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The electron spin resonance spectra of single crystals of manganese(II)-doped zinc maleate tetrahydrate have been investigated at room temperature. The transitions arise from a single type of site with $g_{xx} = 2.010$, $g_{yy} = 1.992$, and $g_{zz} = 2.035$. The g shifts from the free spin value have been attributed to an electron-transfer process from the ligands to the S state ion. The observed angular variation of the allowed hyperfine transitions is in good agreement with theory. The spin-Hamiltonian parameters $D = 360.5 \times 10^{-4}$, $E = 66.8 \times 10^{-4}$, $a = -8.9 \times 10^{-4}$, and $A = -87.0 \times 10^{-4}$ cm^{-1} have been deduced. From the A value an ionicity of 96.5% is derived for the metal–ligand bonding. The analysis of forbidden hyperfine transitions leads to $Q' = 1.58 \times 10^{-4}$ and $Q'' = 0.28 \times 10^{-4}$ cm^{-1} for the axial and rhombic components of the quadrupole coupling tensor respectively for the ^{55}Mn nucleus.

Structural and spectral investigations of complexes of carboxylic acids with metal ions are of great interest since the complexes exist as widely different structures, and exhibit features such as metal–metal interaction, hydrogen bonding, and marked differences in their thermal decomposition behaviour.[1–3] We have undertaken a systematic study of such aspects in these systems by X-ray diffraction, Mössbauer spectroscopy, and electron spin resonance spectroscopy (e.s.r.).[4–7] E.s.r. studies throw light on the nature of the site into which the impurity ion enters and its microsymmetry. We recently reported an e.s.r. study of copper(II)-doped zinc maleate tetrahydrate.[7] The present work pertains to a single-crystal e.s.r. study of manganese(II)-doped zinc maleate tetrahydrate {$[Zn(Hmale)_2]\cdot 4H_2O$, H_2male = maleic acid} at room temperature. Detailed single-crystal e.s.r. studies of Mn^{2+} are relatively rare in the literature, although they have several additional features of interest. For instance, one can study both the forbidden ($\Delta M_S = \pm 1$, $\Delta M_I = \pm 1$ or ± 2) and allowed ($\Delta M_S = \pm 1$, $\Delta M_I = 0$) transitions in favourable situations.[8–13] Even if the crystal structure is not precisely known, the principal axis can be fixed by the disappearance of the forbidden transitions. Further, the deviation of the g values from the free spin value in d^5 systems has been the subject of considerable discussion.[14,15] In the present case the single impurity ion site and the small linewidth encountered were found to be favourable for such a detailed study. We report here the analysis of the allowed and forbidden transitions for the above system and discuss the spin-Hamiltonian parameters in terms of the microsymmetry and nature of bonding of the impurity ion to the ligand atoms.

Experimental

A stoicheiometric amount of Zn^{2+}, in the form of zinc sulphate (AnalaR, BDH), was precipitated as hydroxide using ammonium hydroxide. After eliminating excess of ammonia by warming the solution, the resultant product was treated with a 100% excess of hot maleic acid (SD chemical) solution. Upon concentrating the solution, colourless crystals separated out. The $[Zn(Hmale)_2]\cdot 4H_2O$ was doped with 1% Mn^{2+}. Zinc(II) in the pure compound, *viz.* $[Zn(Hmale)_2]\cdot 4H_2O$, was estimated as the oxide (Calc. for $C_8H_{14}O_{12}Zn$: Zn^{2+}, 17.7; observed: Zn^{2+}, 17.1%). The e.s.r. measurements were carried out as reported earlier[7] on a JEOL-FE-3X spectrometer operating at X-band frequencies (*ca.* 9.45 MHz) with 100-kHz field modulation.

A detailed crystal structure of $[Zn(Hmale)_2]\cdot 4H_2O$ is not available. However, preliminary work shows that $[Zn(Hmale)_2]\cdot 4H_2O$ forms a triclinic system with space group $P1$. There is a slight difference in the unit-cell dimensions reported by two groups.[16,17] Antsyshkina *et al.*[16] have reported $a = 7.30$, $b = 9.82$, and $c = 5.28$ Å, $\alpha = 110.2$, $\beta = 77.1$, and $\gamma = 117°$, which may be compared with $a = 7.29$, $b = 9.73$, $c = 5.36$Å, $\alpha = 116.48$, $\beta = 63.18$, and $\gamma = 103.36°$ reported by Saroja and Raman.[17] There is one molecule of $[Zn(Hmale)_2]\cdot 4H_2O$ per unit cell. Experimentally, the principal axis in the laboratory co-ordinates was located by observing the spectra at different orientations and achieving that orientation which gives rise to only allowed transitions, free from forbidden transitions, satisfying the condition H parallel to Z axis.[18] Figure 1 shows such a spectrum with the morphology of the crystal shown in the insert. The insert indicates a convenient plane arbitrarily chosen, based on the crystal habit. The plane formed by the X' and Z axes coincides with the plane marked by shading and the angle indicates the rotation required to position the principal Z-axis parallel to the magnetic field. The spectra were subsequently recorded by rotating about two other axes such that $X'Y'Z$ form a mutually perpendicular co-ordinate system. The spectra were recorded at intervals of 10°.

Results and Discussion

The ground state of Mn^{2+}, with a d^5 configuration, is unique among d^n configurations in that there is only one state with maximum spin multiplicity ($^6S_{\frac{5}{2}}$). This splits into three Kramer's doublets ($\pm\frac{5}{2}$, $\pm\frac{3}{2}$, and $\pm\frac{1}{2}$) in an orthorhombic crystalline field, which are further split in the presence of the applied magnetic field. These six levels give rise to five fine-structure transitions. Each fine-structure transition will be split into six hyperfine components due to ^{55}Mn hyperfine coupling, giving, in all, 30 allowed transitions. Figures 1 and 2 show the e.s.r. spectra recorded in the $X'Z$ plane making an angle of $\theta = 0$ and $\theta = 5$ and 7° with the Z axis, respectively. The occurrence of not more than thirty lines indicates that Mn^{2+} occupies only one type of site. When the principal axis is parallel to the magnetic field the separation in energy levels, and hence the separation between the $M = -\frac{5}{2} \rightarrow -\frac{3}{2}$ and $M = \frac{3}{2} \rightarrow \frac{5}{2}$

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† *Non-S.I. unit employed:* G = 10^{-4} T.

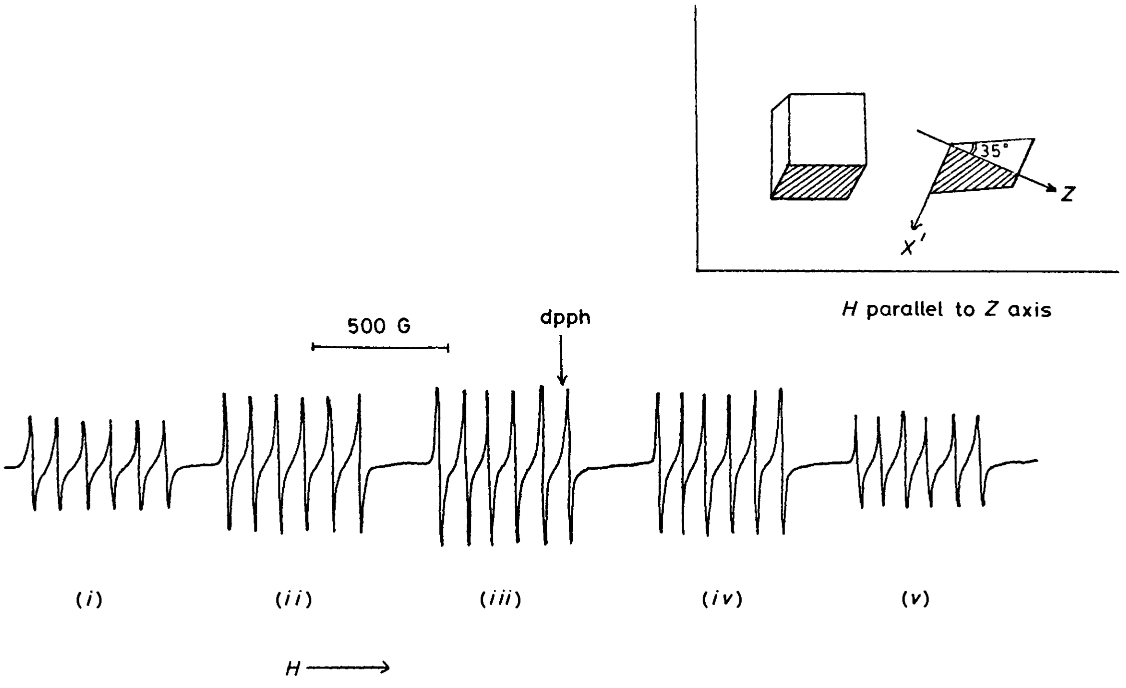

Figure 1. Room temperature e.s.r. spectrum of Mn^{2+}–$[Zn(Hmale)_2]\cdot 4H_2O$ in the $X'Z$ plane at $\theta = 0°$, dpph = diphenylpicrylhydrazyl; transitions (*i*) $\frac{5}{2} \rightarrow \frac{3}{2}$, (*ii*) $\frac{3}{2} \rightarrow \frac{1}{2}$, (*iii*) $\frac{1}{2} \rightarrow -\frac{1}{2}$, (*iv*) $-\frac{1}{2} \rightarrow -\frac{3}{2}$, (*v*) $-\frac{3}{2} \rightarrow -\frac{5}{2}$

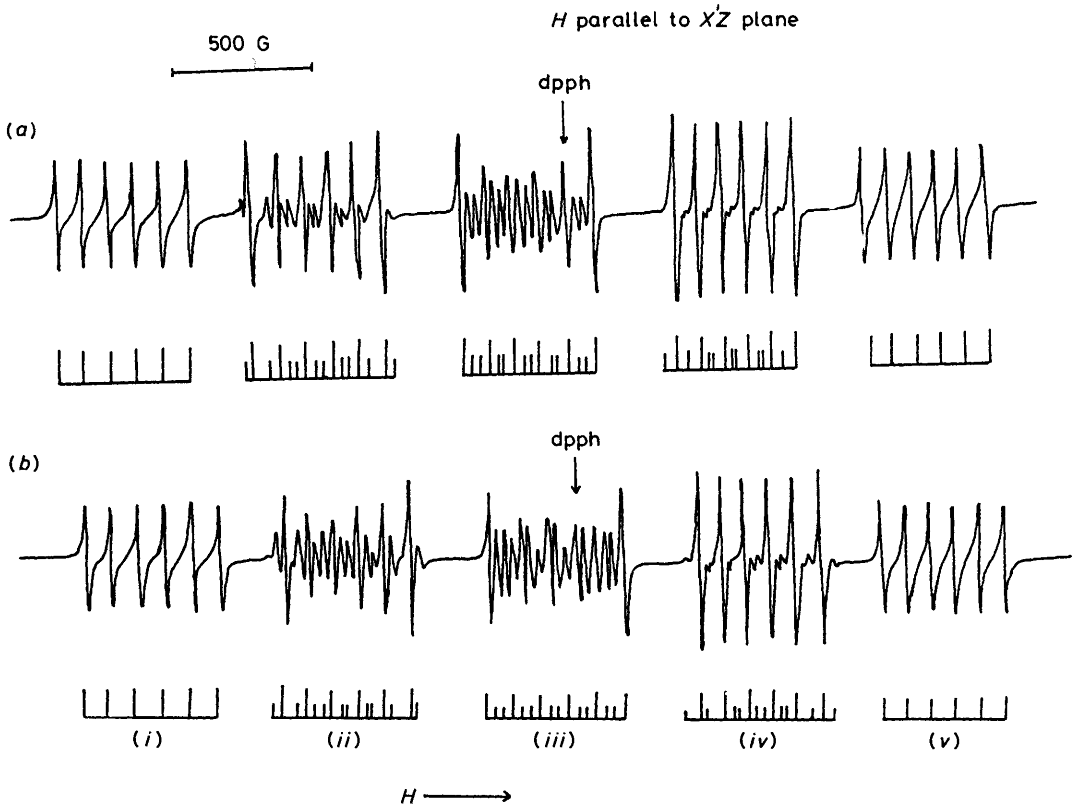

Figure 2. Room temperature e.s.r. spectrum of Mn^{2+}–$[Zn(Hmale)_2]\cdot 4H_2O$ in the $X'Z$ plane at (*a*) $\theta = 5$ and (*b*) $\theta = 7°$; long vertical lines correspond to $\Delta M_I = 0$ and small vertical lines to $\Delta M_I = \pm 1$ transitions respectively; transitions (*i*) $\frac{5}{2} \rightarrow \frac{3}{2}$, (*ii*) $\frac{3}{2} \rightarrow \frac{1}{2}$, (*iii*) $\frac{1}{2} \rightarrow -\frac{1}{2}$, (*iv*) $-\frac{1}{2} \rightarrow -\frac{3}{2}$, (*v*) $-\frac{3}{2} \rightarrow -\frac{5}{2}$

transitions, will be a maximum. The ratios of peak heights in derivative curves of the five sextets are close to the theoretical intensity ratios, 5:8:9:8:5.[18]

The angular variation of the fine-structure transitions corresponding to $M \rightarrow M \pm 1$ depends on the term $(3\cos^2\theta - 1)$ when higher order terms are neglected. The field for all the sextets will be the same at the magic angle. However, if the higher order terms are also included, all five curves do not coincide.[19] Figure 3 shows the angular variation of these transitions in the $X'Z$ plane with the theoretical curves obtained using the appropriate expressions.[8] The agreement between the theoretical curves and the experimental points is fairly good. The e.s.r. spectra have been analysed using the spin-Hamiltonian[20] in equation (1), where the first term represents the Zeeman energy, and the second and third terms represent the axial and rhombic components of the zero-field splittings respectively. The fourth and fifth terms represent the cubic field and the hyperfine interaction respectively. The parameters Q' and Q'' represent the axial and rhombic components of the quadrupole coupling tensor respectively. For fine structure, only the first four terms in the spin-Hamiltonian contribute. The following expressions [equations (2)—(5)], obtained using perturbation theory, were used to calculate the D, E, a, and A parameters.[8,21]

$$\begin{aligned}\mathscr{H} = {} & \beta H\cdot g\cdot S + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + \\ & \tfrac{a}{6}[S_x^4 + S_y^4 + S_z^4 - \tfrac{1}{5}S(S+1)(3S^2 + 3S - 1)] + \\ & S\cdot\tilde{A}\cdot I - \gamma\beta_N H\cdot I + Q'[I_z^2 - \tfrac{1}{3}I(I+1)] + Q''(I_x^2 - I_y^2) \quad (1)\end{aligned}$$

For fine structure (in G) with H parallel to Z.

$$H_{i=1,5}(M = \pm\tfrac{5}{2} \rightarrow \pm\tfrac{3}{2}) = H_0 \pm 4D' + \frac{9E'^2}{(H_i \pm D')} - \frac{5E'^2}{(H_i \pm 3D')} \pm 2a' \quad (2)$$

$$H_{i=2,4}(M = \pm\tfrac{3}{2} \rightarrow \pm\tfrac{1}{2}) = H_0 \pm 2D' - \frac{9E'^2}{(H_i + D')} \pm \frac{9E'^2}{(H_i - D')} - \frac{5E'^2}{(H_i \pm 3D)} \pm \tfrac{5}{2}a' \quad (3)$$

$$H_3(M = \tfrac{1}{2} \rightarrow -\tfrac{1}{2}) = H_0 - \frac{9E'^2}{(H_3 - D')} + \frac{5E'^2}{(H_3 + 3D')} + \frac{5E'^2}{(H_3 - 3D')} - \frac{9E'^2}{(H_3 + D')} \quad (4)$$

For hyperfine structure (in G) with H parallel to Z.

$$H(m \rightarrow m) = -A'm - (A'^2/2H)[I(I+1) - m^2 + (2M-1)m] \quad (5)$$

The constants D', E', a', and A' in the above equations are expressed in gauss and related to D, E, a, and A expressed in wavenumbers by a factor $g\beta_e$ ($D = g\beta_e D'$, *etc.*), where β_e is the electronic Bohr magneton.

The experimental H values and the calculated field positions of the sextets H_i are given in Table 1 along with the D, E, a, and A values used. An indirect check on the relative sign of D is as follows. If the separations between the sextets decreases on the high field side when the direction of the magnetic field is parallel to the Z-axis, then D/A will be positive. In all the systems so far studied A is negative[9—13] and is assumed to be so for the present case. In the present measurements the separations of the sextets increase towards the high field side and hence D/A is negative which implies that D is positive. The sign and magnitude of D give information regarding the microsymmetry of the metal ion. A positive value for D is associated with a tetragonal compression or trigonal elongation.[22,23] In the present case the positive D value and a finite E value taken together may therefore be identified with a compressed octahedron which is orthorhombically distorted. This is also in

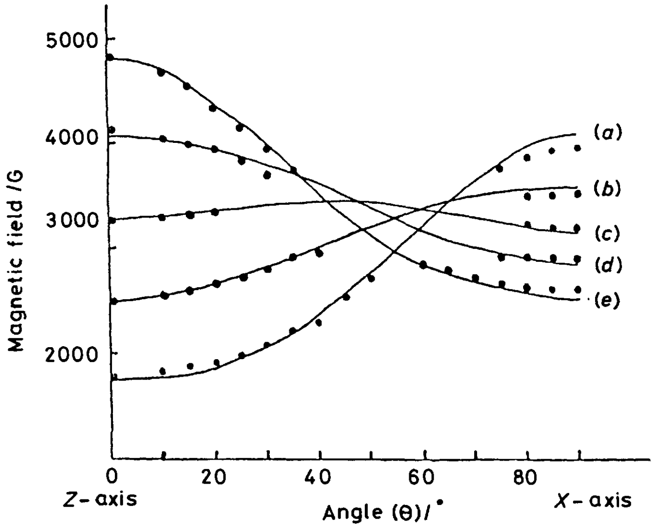

Figure 3. Angular variation in $X'Z$ plane of the allowed transitions in the e.s.r. spectrum of Mn^{2+}–$[Zn(Hmale)_2]\cdot 4H_2O$ at room temperature; (——) theoretical; (●) experimental: transitions (*a*) $\tfrac{5}{2}\rightarrow\tfrac{3}{2}$, (*b*) $\tfrac{3}{2}\rightarrow\tfrac{1}{2}$, (*c*) $\tfrac{1}{2}\rightarrow -\tfrac{1}{2}$, (*d*) $-\tfrac{1}{2}\rightarrow -\tfrac{3}{2}$, (*e*) $-\tfrac{3}{2}\rightarrow -\tfrac{5}{2}$

Table 1. Observed and calculated H_i values for H parallel to Z axis in Mn^{2+}–$[Zn(Hmale)_2]\cdot 4H_2O$ along with D, E, a, and A values

	Calc.	Obs. (±3)	10^4D/ cm^{-1}	10^4E/ cm^{-1}	10^4a/ cm^{-1}	10^4A/ cm^{-1}
H_1	1 668.7	1 664.0	360.5 ± 1	66.8 ± 1	−8.9 ± 1	−87.0 ± 1
H_2	2 330.5	2 332.4				
H_3	3 075.6	3 016.6				
H_4	3 804.8	3 809.5				
H_5	4 501.3	4 505.0				

Table 2. Observed and calculated doublet separations (ΔH, in gauss) of the forbidden hyperfine transitions ($\Delta M_I = \pm 1$) for various transitions ($\Delta M_S = \pm 1$) in the $X'Z$ plane of the complex Mn^{2+}–$[Zn(Hmale)_2]\cdot 4H_2O$ at room temperature

M_I	$M = \tfrac{1}{2}\leftrightarrow -\tfrac{1}{2}$, $\Delta M_I = \pm 1, \theta = 5°$		$M = \tfrac{3}{2}\leftrightarrow\tfrac{1}{2}$, $\Delta M_I = \pm 1, \theta = 10°$		$M = -\tfrac{1}{2}\leftrightarrow -\tfrac{3}{2}$, $\Delta M_I = \pm 1, \theta = 5°$		$M = \tfrac{5}{2}\leftrightarrow\tfrac{3}{2}$, $\Delta M_I = \pm 1, \theta = 15°$		$M = -\tfrac{3}{2}\leftrightarrow -\tfrac{5}{2}$, $\Delta M_I = \pm 1, \theta = 25°$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$-\tfrac{5}{2}$	23.8	24.7	201.6	202.8	149.2	152.5	369.2	377.0	330.1	339.4
$-\tfrac{3}{2}$	24.5	25.0	205.8	207.1	155.8	158.5	372.3	383.2	341.3	350.2
$-\tfrac{1}{2}$	24.9	25.3	210.8	211.5	163.1	164.8	379.2	389.7	350.9	362.4
$+\tfrac{1}{2}$	25.0	25.5	215.8	216.0	168.3	171.2	388.3	396.4	362.3	374.4
$+\tfrac{3}{2}$	25.1	25.8	217.5	220.8	174.2	177.7	395.5	403.5	377.0	386.7

accord with the compressed octahedral geometry reported for the parent $[Mn(Hmale)_2]\cdot 4H_2O$ and the close similarity in the unit-cell dimensions and co-ordination reported for $[Zn(Hmale)_2]\cdot 4H_2O$ and $[Mn(Hmale)_2]\cdot 4H_2O$.[16,17,24] A survey of the literature shows that Mn^{2+} invariably enters Zn host lattices substitutionally.[25–27] This may be attributed to comparable ionic radii for Mn^{2+} and Zn^{2+} ($Mn^{2+} = 0.82$, $Zn^{2+} = 0.75$ Å). In such cases Mn^{2+} has a microsymmetry identical to that of the parent complex. However, whether such a microsymmetry is also dictated by the host lattice can only be stated if a detailed knowledge of the crystal structure of $[Zn(Hmale)_2]\cdot 4H_2O$ is available. The magnitude of D is a function of overlap, covalency, and separation of the ^4P excited state from the ^6S ground state.[28] Comparatively, a large D value is obtained, *viz.* 360.5×10^{-4} cm^{-1} (Table 1), in the present case indicating a low lying ^4P excited state.

The g values, *viz.* $g_{xx} = 2.010$, $g_{yy} = 1.992$, and $g_{zz} = 2.035$, show large anisotropy. The deviation from the free spin value (2.0023) has been observed in distorted octahedral systems such as manganese(II)-doped tris(ethylenediamine)zinc(II),[25] zinc acetate dihydrate,[27] and lithium ammonium tartrate monohydrate.[29] The large observed shift of the g values from the free spin value for $Cu^{2+}(3d^9)$ in low symmetry can be well accounted for by mixing excited states into the ground state.[7] However, admixtures of excited quartet levels into the ground state ^6S by spin–orbit coupling produce only a small negative g shift. A more significant contribution leading to a positive g shift, as observed, arises due to the electron-transfer process through spin–orbit interaction from the ligands to the S-state ion.[15] An estimate of the covalency in the present case may be obtained from the hyperfine splitting constant A. The values of A_{xx}, A_{yy}, and A_{zz} were found to be the same within experimental error. The relation between A and the local bonding of Mn^{2+} and the nearest neighbour ligands has been derived phenomenologically on a quantitative basis by plotting A *vs.* the Pauling covalency parameter.[30,31] From this curve we obtained, for $A = -87 \times 10^{-4}$ cm^{-1}, an ionicity of 96.5% for Mn^{2+}–$[Zn(Hmale)_2]\cdot 4H_2O$. Similar values have been found for manganese(II)-doped acetate and oxalate systems.[13]

The forbidden transitions, which occur in pairs, have been analysed using perturbation expressions.[8,12] The magnitude of the splitting in these pairs depends on the angle θ. The intensities of the forbidden lines are significantly less, when θ is small, increase with θ (reaching a maximum when $\theta = 45°$), and then decrease.[32] For all the sextets the doublet separations for the forbidden transitions have been calculated and are given in Table 2, along with the experimental doublet separations. A good fit is obtained for $Q' = 1.58 \times 10^{-4}$ cm^{-1} and $Q'' = 0.28 \times 10^{-4}$ cm^{-1} which are the axial and rhombic components of the quadrupole coupling tensor of the ^{55}Mn nucleus respectively. The relatively large deviation between the observed and calculated doublet separations in $M = +\frac{5}{2} \rightarrow +\frac{3}{2}$ and $M = -\frac{5}{2} \rightarrow -\frac{3}{2}$ sextets may be attributed to the large angle ($\theta = 15$ and $25°$) at which the comparison is made where the perturbation theory gives results which are less accurate.[33]

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References

1 C. Oldham, *Prog. Inorg. Chem.*, 1969, **10**, 223.
2 J. Catterick and P. Thornton, *Adv. Inorg. Chem. Radiochem.*, 1977, **20**, 291.
3 M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.
4 N. Ravi and R. Jagannathan, *Hyperfine Interactions*, 1982, **12**, 167.
5 N. Ravi, R. Jagannathan, B. Rama Rao, and Raza Hussain, *Inorg. Chem.*, 1982, **21**, 1019.
6 M. Vithal and R. Jagannathan, *Transition Met. Chem.*, 1984, **9**, 73.
7 M. Vithal, R. Jagannathan, and C. S. Sunandana, *Spectrochim. Acta, Part A*, 1985, **41**, 861.
8 B. Bleaney and D. J. E. Ingram, *Proc. R. Soc. London, Ser. A*, 1951, **205**, 336.
9 J. M. Baker, B. Bleaney, and W. Hayes, *Proc. R. Soc. London, Ser. A*, 1958, **247**, 141.
10 V. J. Folen, *Phys. Rev., A*, 1965, **139**, 1961.
11 T. Takeda, *J. Phys. Soc. Jpn.*, 1967, **23**, 1314.
12 G. C. Upreti, *J. Magn. Reson.*, 1974, **13**, 336.
13 M. Korkmaz, M. Dupont, and B. Aktas, *J. Phys. Chem. Solids*, 1984, **45**, 465.
14 I. Fidone and K. W. H. Stevens, *Proc. Phys. Soc., London*, 1959, **73**, 116.
15 H. Watanabe, *J. Phys. Chem. Solids*, 1964, **25**, 1471 and refs. therein.
16 A. S. Antsyshkina, M. A. Parai-Koshits, and M. G. Guseinov, *Izv. Akad. Nauk, SSSR, Ser. Khim.*, 1974, 237.
17 K. Saroja and S. V. Raman, *Curr. Sci.*, 1972, **41**, 599.
18 A. Abragam and B. Bleaney, 'Electron Paramagnetic Resonance of Transition Ions,' Clarendon Press, Oxford, 1970, p. 158.
19 Ref. 18, p. 437.
20 W. Low, 'Paramagnetic Resonance in Solids,' Academic Press, New York, 1960.
21 B. V. R. Chowdari and P. Venkateswarulu, *J. Chem. Phys.*, 1968, **48**, 318.
22 M. Gerloch, J. Lewis, and R. S. Salde, *J. Chem. Soc. A*, 1969, 1422.
23 J. G. Hampel, *J. Chem. Phys.*, 1976, **64**, 4307.
24 M. P. Gupta and B. Mahanta, *Cryst. Struct. Commun.*, 1978, **8**, 179.
25 R. A. Palmer, M. Chim-Lam Yang, and J. C. Hampel, *Inorg. Chem.*, 1978, **17**, 1200.
26 H. Morigaki and H. Abe, *J. Phys. Soc. Jpn.*, 1967, **23**, 462.
27 S. K. Misra and M. Kahrizi, *Phys. Rev., B*, 1984, **30**, 2920.
28 R. R. Sharma, T. P. Das, and R. Orbach, *Phys. Rev., B*, 1984, **30**, 2920.
29 A. K. Jain and G. C. Upreti, *J. Chem. Phys.*, 1981, **75**, 1623.
30 O. Matumura, *J. Phys. Soc. Jpn.*, 1959, **14**, 108.
31 E. Simaneck and K. A. Muller, *J. Phys. Chem. Solids*, 1970, **31**, 1207.
32 Ref. 18, p. 188.
33 D. H. Lyons and R. W. Kedzie, *Phys. Rev.*, 1966, **145**, 148.

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