

Phase Transitions in $M^{II}TiF_6 \cdot 6H_2O$ ($M = Cd, Zn, Co$): An EPR Study

Geetha Jayaram

Physics Department, Osmania University, Hyderabad-500007, India

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Paramagnetic Mn^{2+} ions have been incorporated into $CdTiF_6 \cdot 6H_2O$, $ZnTiF_6 \cdot 6H_2O$ and $CoTiF_6 \cdot 6H_2O$ single crystals, and EPR spectra have been utilized to investigate the structural phase transitions in these crystals. They are first order in nature with a marked hysteresis in the case of $CoTiF_6 \cdot 6H_2O$ and are attributed to hindering of rotation of the $[M(H_2O)_6]$ as well as (TiF_6) groups.

Introduction

Many crystals of the type $ABF_6 \cdot 6H_2O$ and $ABF_6 \cdot 6D_2O$, where A represents a divalent and B a tetravalent metal ion, have been investigated using EPR, NMR, dielectric and heat capacity techniques. $ZnSiF_6 \cdot 6H_2O$ was the first in this family to be studied using EPR with the paramagnetic Mn^{2+} ion as probe [1]. Subsequent development of the theory of the forbidden hyperfine transitions ($\Delta m_s = +1$, $\Delta m_l = \pm 1$) was based on the extra lines that were seen when the magnetic field was rotated slightly away from the trigonal axis [2]. Since then Rubins [3–6], Hrabansky et al. [7–10], and Zaripov et al. [11] have investigated several compounds in this series. The structural transition in $ZnTiF_6 \cdot 6H_2O$ was originally found to occur near 180 K, as detected by an Ni^{2+} EPR study in this compound [12]. A ^{19}F NMR study of $ZnTiF_6 \cdot 6H_2O$ by Afanasyev et al. [13] showed splitting of ^{19}F resonances below 182 K. This suggested that the TiF_6 octahedron was distorted. Since no appreciable change was observed in the 1H resonances at the transition temperature, the authors postulated that a change in the $[Zn(H_2O)_6]$ symmetry caused a sudden decrease in the barrier height to $[TiF_6]$ reorientation.

The existence of more than one phase transition in $ZnTiF_6 \cdot 6H_2O$ was recognized by means of infrared, Raman, dielectric and thermal expansion measurements of Choudhary et al. [14–16]. The main trigonal to monoclinic transition is due to a rotational reorientation of the two complex ions making up the struc-

ture. The presence of a trigonal phase at high temperatures appears to be related to the rather large amount of reorientational motion of the complex ions which is present at ambient temperatures in these systems. These large scale motions could be the possible cause of the motional narrowing in NMR spectra. Each of these octahedra reorient via hindered rotations about the three-fold axis. In addition to geometrical considerations, barriers to such motions would definitely involve breaking and reforming of a number of hydrogen bonds. This would be affected by the motion of adjacent octahedra. All these processes are expected to be temperature dependent. Here we report a detailed study of the EPR spectra of Mn^{2+} ion in the three isomorphous lattices $CdTiF_6 \cdot 6H_2O$, $ZnTiF_6 \cdot 6H_2O$ and $CoTiF_6 \cdot 6H_2O$. This study was carried out with the aim of comparing the phase transitions in Cd, Zn and Co compounds. A preliminary report on the phase transition in Mn^{2+} : $ZnTiF_6 \cdot 6H_2O$ has already been published [17].

Experimental

All the crystals were grown from an aqueous solution obtained by reacting divalent metal carbonates, TiO_2 and 40% HF at room temperature. The solution was maintained at $pH < 2$. The Mn^{2+} content in the solution was 0.01% and the impurity content in the crystals, which grew as hexagonal rods of good quality, was found to be ca. 100 ppm. The possibility of any distortion of the lattice due to the presence of impurity ions was ruled out. EPR spectra were recorded on a Varian 4502 EPR spectrometer ($\nu = 9.0$ – 9.5 GHz) with 100 kHz magnetic field modu-

Reprint requests to Dr. Geetha Jayaram, Physics Department, Osmania University, Hyderabad-500007, India.

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lation and Varian low temperature (300 K–110 K) accessories. DSC recordings were made with a Mettler instrument. The detailed crystal structure of the three fluotitanates is not known, but early crystallographic data indicate that they belong to the R3 space group with $Z = 1$ [18–20].

Theory

EPR spectra of Mn^{2+} ions in sites of trigonal symmetry have been investigated, and the theory is well developed. The spectra can be fitted to the following spin-Hamiltonian:

$$\begin{aligned} \mathcal{H}_{\text{trigonal}} = & g \beta H + D [S_z^2 - 1/3 S(S+1)] \\ & + (1/6) a [(S_x^4 + S_y^4 + S_z^4) - (1/5) S(S+1) (3S^2 + S - 1)] \\ & + (1/180) F [35 S_z^4 - 30 S(S+1) S_z^2 + 25 S_z^2 - 6 S(S+1) \\ & + 3 S^2 (S+1)^2] + A S I \\ & + P [I_z^2 - (1/3) I(I+1)]. \end{aligned} \quad (1)$$

The spectra recorded at $T < T_c$ can be fitted after

$$\mathcal{H}_{\text{rhombic}} = E (S_x^2 - S_y^2) \quad (2)$$

is added to (1).

The expression for the forbidden doublet separation in the $m_s: +1/2 \leftrightarrow -1/2$ transition is obtained from third order perturbation theory under the approximation $g \beta H \gg D, E$, and A [21], and is given by

$$\begin{aligned} \Delta H = & H_{|1/2, m_I+1\rangle \leftrightarrow | -1/2, m_I\rangle} - H_{|1/2, m_I\rangle \leftrightarrow | -1/2, m_I+1\rangle} \\ = & (17 A^2 / 2 H_0) \\ & + 2(\gamma \beta_N / g \beta) H_0 - (2 m_I + 1) [2 P - (8 A^2 \sigma / H_0^2) \\ & + (25/2) (A^3 / H_0^3) + (\gamma \beta_N / g \beta) A], \end{aligned} \quad (3)$$

where

$$\sigma = (1/2) [D (3 \cos^2 \theta - 1) + 3 E \sin^2 \theta \cos 2 \phi], \quad (4)$$

$$P = (1/2) [Q' (3 \cos^2 \theta - 1) + 3 Q'' \sin^2 \theta \cos 2 \phi], \quad (5)$$

and $(\gamma \beta_N / g \beta) = 0.37 \times 10^{-3}$ from the NMR Table [22].

Theoretically, the relative intensities of the forbidden to the allowed lines are given by

$$\begin{aligned} (I_F / I_A) = & (3 D \sin 2 \theta / 4 H_0)^2 \\ & \cdot [1 + \{S(S+1) / 3 m_s (m_s - 1)\}] \\ & \cdot [I(I+1) - m_I (m_I + 1)], \end{aligned} \quad (6)$$

showing that the forbidden lines should not appear at $\theta = 0$. In (6) a small quadrupolar term has been ignored.

The separation between lines in a given doublet, determined from the eigenvalues calculated by DeWijn and van Balderen [23] but modified to allow for anisotropy, is given at $\theta = 0$ by

$$\begin{aligned} \Delta H(m_I) = & (17 A^2 / 2 H_0) + 2(\gamma \beta_N / g \beta) H_0 \\ & + [(-67 A^3 / 4 H_0^2) \\ & + (8 A^2 D / H_0^2) - 2 P] (2 m_I - 1), \end{aligned} \quad (7)$$

where P is the electric quadrupole interaction.

If the fine-structure line separations are experimentally determined, the parameters can be evaluated using the following expressions valid for H along the trigonal axis:

$$\begin{aligned} m_s: & \pm 5/2 \leftrightarrow \pm 3/2, \\ H = & H_0 \pm [4 D - (4/3) (a - F)], \end{aligned} \quad (8)$$

$$\begin{aligned} m_s: & \pm 3/2 \leftrightarrow \pm 1/2, \\ H = & H_0 \pm [2 D + (5/3) (a - F)], \end{aligned} \quad (9)$$

$$\begin{aligned} m_s: & \pm 1/2 \leftrightarrow -1/2, \\ H = & H_0. \end{aligned} \quad (10)$$

Results

I. Cadmium Hexafluotitanate Hexahydrate ($CdTiF_6 \cdot 6H_2O$)

The room temperature EPR spectra consist of one prominent set of 30 lines which show a maximum spread for $H \parallel c$, the trigonal axis (Figure 1). The rotation of the crystal from $H \parallel c$ to $H \perp c$ followed a $(3 \cos^2 \theta - 1)$ variation with a total collapse at $\theta = 54^\circ$. For $H \perp c$ the spectrum showed a secondary maximum. The rotation about c -axis resulted in an invariant spectrum. All these features are in complete agreement with Mn^{2+} substituting for an M^{II} site in a trigonal crystal. The spectrum for $H \parallel c$ showed five sets of hyperfine sextets with the predicted intensity ratios, viz., 5:8:9:8:5, and the central hyperfine sextet, corresponding to the $m_s = -1/2 \leftrightarrow +1/2$ transition, showed five pairs of forbidden transition. As the c -axis was rotated away from the H -direction, the forbidden transitions were found to grow in intensity. The room temperature spectra were fitted to an axial spin-Hamiltonian, while the low temperature ($T < T_c$) spectra were fitted to a rhombic spin-Hamiltonian, (1) and (1, 2), respectively. The room temperature parameters are given in Table 1.

On gradually cooling the crystal with H along c -axis, no change in the position of the lowest as well

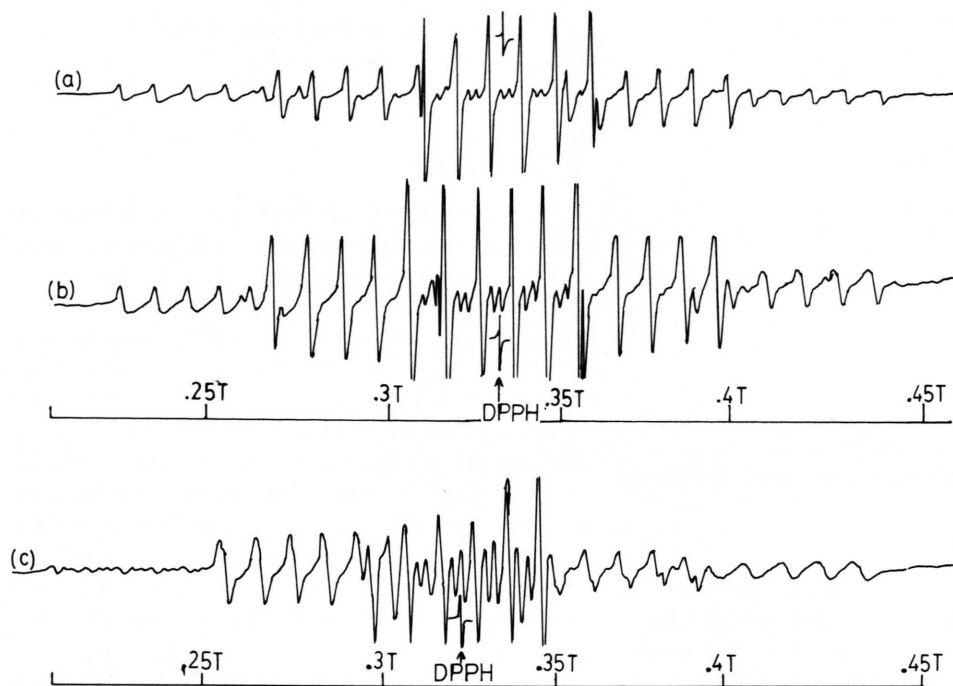


Fig. 1. EPR spectra of Mn^{2+} : $CdTiF_6 \cdot 6H_2O$, for $H \parallel c$ axis at a) 295 K, b) 153 K, and c) 133 K.

Table 1. Spin-Hamiltonian parameters for $M^{II}TiF_6 \cdot 6H_2O$ ($M^{II} = Cd, Zn, Co$) with Mn^{2+} impurity at room temperature, $T > T_c$.

Compound	g	A	D	$(a-F)$	Q'	Ref.
$CdTiF_6 \cdot 6H_2O$ *	2.001	-86.0	-192.5	7.9	0.5	This work
$ZnTiF_6 \cdot 6H_2O$ *	2.003	-86.4	-172.8	7.3	0.2	This work
$CoTiF_6 \cdot 6H_2O$ *	2.008	-87.0	-182.2	8.8	-	This work
$ZnTiF_6 \cdot 6H_2O$	2.001	-90.7	-182.0	8.0	-	[6]
$ZnGeF_6 \cdot 6H_2O$	2.001	-88.8	-178.5	8.0	-	[11]
$ZnNbOF_5 \cdot 6H_2O$	2.0037	-90.9	-168.8	9.0	-	[27]
$CoNbOF_5 \cdot 6H_2O$	2.0095	-90.7	-176.8	4.0	-	[27]
$MgSiF_6 \cdot 6H_2O$	2.000	-91.6	-213.0	7.5	-	[7]

A , D , $(a-F)$, and Q' are in units of 10^{-4} cm^{-1} .

* Errors: g (± 0.001), A (± 1) and D (± 2). Parameters evaluated from spectra recorded at 298 K and $\nu = 9.46 \text{ GHz}$.

Table 2. Spin-Hamiltonian parameters for $M^{II}TiF_6 \cdot 6H_2O$ ($M^{II} = Cd, Zn, Co$) with Mn impurity at low temperature, $T < T_c$.

Compound	Ref.	g	A	D	E	$(a-F)$	α	Q'	Q''
$CdTiF_6 \cdot 6H_2O$	*	2.000	-88.8	-238.3	31.8	7.9	20	1.3	-
$ZnTiF_6 \cdot 6H_2O$	*	2.001	-88.3	-262.5	67.7	8.1	16	1.2	1.35
$CoTiF_6 \cdot 6H_2O$	*	2.007	-87.8	-207.4	-	-	22	-	-
$ZnTiF_6 \cdot 6H_2O$	[1]	2.001	-90.7	-218.0	≈ 40	8.0	15	-	-
$ZnGeF_6 \cdot 6H_2O$	[2]	2.000	-89.9	-245.7	46.7	7.5	-	-	-
$CoNbOF_5 \cdot 6H_2O$	[3]	2.013	-91.0	-270.0	-	14.0	28	-	-
$MgSiF_6 \cdot 6H_2O$	[4]	2.001	-93.3	-273.0	31.0	7.0	-	-	-

A , D , E , $(a-F)$, Q' , and Q'' are in units of 10^{-4} cm^{-1} . Microwave frequency $\nu = 9.037 \text{ GHz}$.

* This work. Error: g (± 0.001), A (± 1), D (± 2), E (± 2).

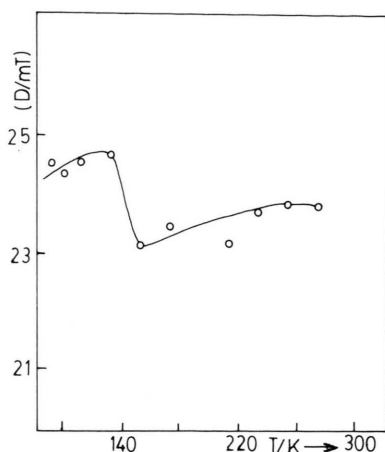


Fig. 2. Variation of the ZFS parameter D with temperature in $CdTiF_6 \cdot 6H_2O$.

as the highest field line was observed. However, the forbidden hyperfine transitions within the central sextet were found to grow by a factor of three in intensity in a continuous manner in the temperature range 295 K to 138 K.

At 133 ± 2 K the spectrum showed an abrupt change in the fine structure spread indicating a first-order structural phase transition. This was found to be reversible within a very narrow range of temperatures. The hysteresis was within the limits of experimental error, unlike in $CoTiF_6 \cdot 6H_2O$, where it was prominent. The addition of a rhombic component to the axial crystal field resulted in an asymmetry in the spectrum. On rotating the c -axis away from the magnetic field direction, the lines were found to split into two, indicating the presence of two inequivalent sites rotated with respect to each other by 20° . The axis of either of the octahedra was rotated by 10° from the c -axis. The low temperature phase was most probably monoclinic, as was reported for $CoSiF_6 \cdot 6H_2O$ by Kodera et al. [24]. Below T_c , the high temperature c -axis was still retained as one of the crystallographic axes. The intensity of the forbidden transitions increased again by a factor of three in going through T_c . The variation of the ZFS parameter, D , with temperature is shown in Figure 2. The influence of the phase transition on D is clearly seen. The rotation pattern just below T_c showed the existence of two extrema, each making an angle of $10 \pm 1^\circ$ with the c -axis. Parameters evaluated for the low temperature phase are given in Table 2. From the observed forbidden doublet separation within the central hf sextet above

and below T_c , Q' and Q'' were evaluated (Table 1 and 2).

II. Zinc Hexafluorotitanate Hexahydrate, $ZnTiF_6 \cdot 6H_2O$

The room temperature EPR spectrum along c -axis showed features that are similar to the Cd compound. g , A , $(a-F)$ and D were evaluated from the spectra for $H \parallel$ and \perp to the c -axis. These are given in Table 1. A comparison of the relative intensities of the five fine-structure groups indicated that there was an appreciable broadening within the $\pm 5/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 1/2$ groups. The linewidths varied from ca. 15 G for the $\pm 3/2 \leftrightarrow \pm 1/2$ sextets to about 20 G for the $\pm 5/2 \leftrightarrow \pm 3/2$ sextets. The variation has been ascribed to statistical fluctuations in the local crystalline field caused by the strains in the crystal. The large linewidths were also due to contributions from the local magnetic moments of the protons of the water molecules.

With the magnetic field oriented along c -axis, the lowering of temperature caused a sudden change in the extreme line field positions (Figure 3) at 173 ± 2 K. This is typical of a first order phase transition. The transition occurred within a narrow range of temperature and was found to be reversible with a hysteresis of 2° . This is less than that observed in $CoTiF_6 \cdot 6H_2O$ (see III). No coexistence of the two phases was observed, which is in contrast to what was observed in $CoSiF_6 \cdot 6H_2O$ [24]. It is also seen from Figure 3 that the variation in the position in the extreme low and high field lines with temperature did not reflect the presence of the phase transition observed at 230 K in 2D NMR studies [25, 26]. The presence of 'the undetermined unimolecular intermediate phase' reported in the above work was not detected in this study. The spin-Hamiltonian parameters reported by Rubins [6] show a marked disagreement with those evaluated in this work, in particular for the low temperature axial (D) and rhombic (E) components of ZFS tensor. The room temperature c -axis is retained as one of the crystallographic axes analogous to the cadmium compound. However, the principal axis of either of the $[Zn(H_2O)_6]$ octahedra was rotated from the c -axis by $(8 \pm 1)^\circ$.

Another weaker set of lines, shown in Figure 4, was seen flanking the extreme low and high field hf lines of the prominent spectrum. These could either be due to i) Mn^{2+} occupying a Ti^{4+} site or ii) the forbidden

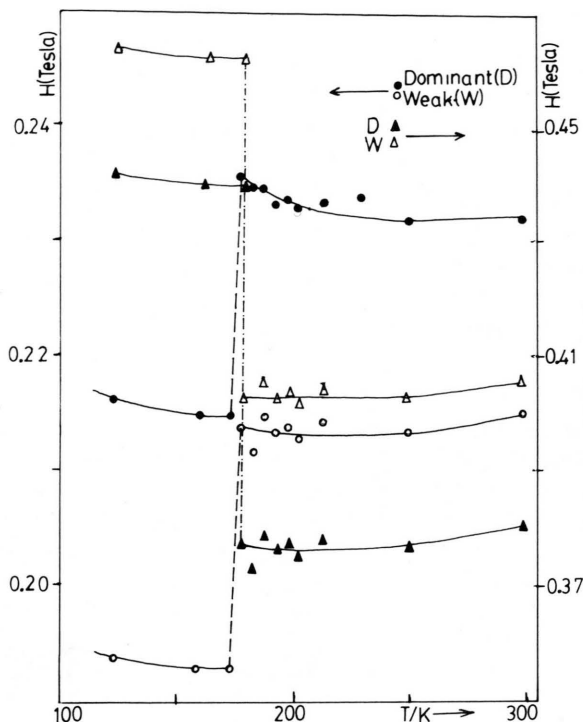


Fig. 3. Variation in the position of the extreme low and high field hf line positions with temperature in Mn^{2+} : $ZnTiF_6 \cdot 6H_2O$

transitions $\Delta m_s = +1$, $\Delta m_l = \pm 1$ for the $\pm 5/2 \leftrightarrow \pm 3/2$ fine structure transitions. The doublet separations for the forbidden hyperfine lines within the $\pm 5/2 \leftrightarrow \pm 3/2$ fine-structure transitions were of the order of '3A'. This would result in the presence of one of the doublet components at field positions below the lowest and above the highest field hf component of the outer sextets.

The ionic radius of Mn^{2+} (0.80 Å) is much larger than that of Ti^{4+} (0.48 Å). This would make the substitution of Mn^{2+} in Ti^{4+} site improbable. Therefore, the second alternative appears more likely and is supported by an additional observation. On lowering the temperature below T_c , a rotation by 8° from the c -axis resulted in the hf lines splitting into two. A similar splitting was observed for the weak lines also. This feature of simultaneous splitting would support the second possibility mentioned above. However, for an unequivocal assignment more evidence would be required.

Differential scanning calorimetry was used to verify the existence of the phase transition in $ZnTiF_6 \cdot 6H_2O$.

The DSC thermogram of the sample showed a pronounced endothermic peak at 181 K, which was reproducible. This confirmed the transition detected by EPR. The heat of transition per mole was calculated to be 712 cal/mole, using cyclo hexane as the reference.

III. Cobalt Hexafluotitanate Hexahydrate, $CoTiF_6 \cdot 6H_2O$

As expected for a trigonal crystal with a unimolecular unit cell, a single set of 30 lines was observed at room temperature for Mn^{2+} : $CoTiF_6 \cdot 6H_2O$ crystal as shown in Figure 5. The angular variation in the plane containing the c -axis showed the expected $(3 \cos^2 \theta - 1)$ variation. The following aspects marked the room temperature spectra in $CoTiF_6 \cdot 6H_2O$ in contrast to those in the isomorphous Cadmium and Zinc Fluotitanate Hexahydrates:

- the linewidths in the cobalt compound were larger by a factor of two,
- the relative intensities of the different fine-structure sextets did not follow the theoretically predicted ratio of 5:8:9:8:5. All the sets appeared to have the same intensity.

The room temperature spin-Hamiltonian parameters are given in Table 1. The hyperfine tensor is nearly isotropic. Any departure from isotropy is found to be due to the larger linewidth and the consequent error in measurement. The g -value calculated, using DPPH ($g = 2.0036$) as the internal reference, showed a small anisotropy, absent in the diamagnetic analogous. A similar anisotropy has been reported for $CoNbOF_5 \cdot 6H_2O$ and $CoSiF_6 \cdot 6H_2O$ [27, 28].

Keeping in view the retention of the c -axis as the symmetry axis of the low temperature monoclinic phase in the Cd and Zn compounds, the temperature was lowered with $H \parallel c$ in $CoTiF_6 \cdot 6H_2O$ also. The following observations were made:

- The spectral lines are observed to gradually broaden, unlike in the diamagnetic analogs.
- At 253 ± 2 K the spectrum indicated a change of phase in the form of an increased fine-structure spread. At T_c there was a sudden increase in the microwave absorption, leading to a detuning of the cavity. Such a feature is characteristic of a sudden change in the dielectric properties of the crystal. On approaching T_c , the room temperature spec-

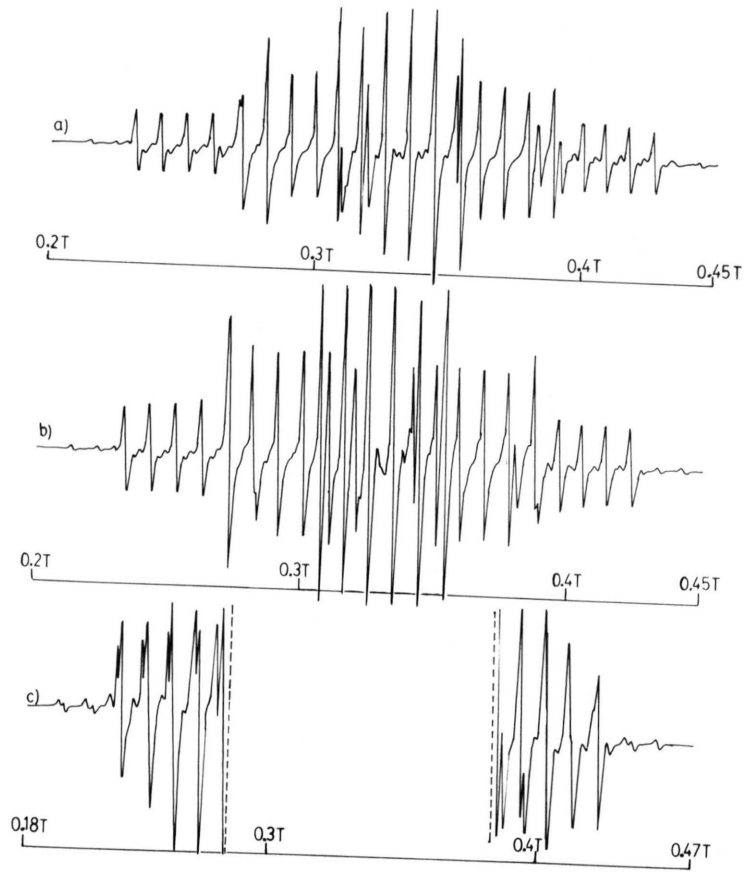


Fig. 4. EPR spectra of $Mn^{2+}: ZnTiF_6 \cdot 6H_2O$, for $H \parallel c$ axis at a) 300 K, b) 178 K, and c) 173 K.

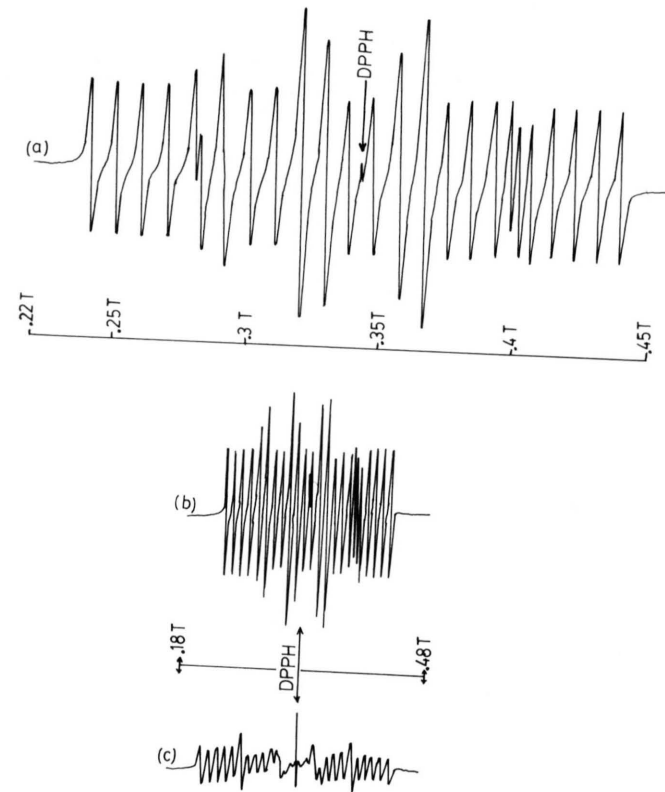


Fig. 5. EPR spectra of $Mn^{2+}: CoTiF_6 \cdot 6H_2O$, for $H \parallel c$ axis at a) 300 K, b) 258 K, and c) 252 K.

trum disappeared and subsequently the spectrum that reappeared was characteristic of the low temperature phase (Figure 6). This change was sudden, unlike in $CoSiF_6 \cdot 6H_2O$ where the two phases co-existed over an 8° temperature interval [28].

- 3) A marked hysteresis of ca. 8° was seen in $CoTiF_6 \cdot 6H_2O$, with the transition temperature shifting to a higher value on heating the crystal from below T_c . The hf lines were found to broaden before shifting to the high temperature phase. The transition in either direction was abrupt and the changes occurred in a very narrow range of temperatures.
- 4) On moving away from the c -axis, the hf lines were seen to split into two. The extrema for the two inequivalent sites in the low temperature phase were found to be rotated on either side of the c -axis by $(11 \pm 1)^\circ$. The magnetic equivalence of the two sites along the c -axis clearly showed that it was a symmetry axis in the low symmetry monoclinic structure too.
- 5) The Mn^{2+} hf lines were considerably broadened even at 253 K and continued to broaden further with lowering the temperature.

At 77 K the Mn^{2+} spectrum was completely broadened. The spin-Hamiltonian parameters evaluated just below T_c are given in Table 2. In $CoTiF_6 \cdot 6H_2O$, the observation of fairly narrow lines at room temperature and the broadening accompanying the lowering of temperature has been rationalised in terms of the fast spin-lattice relaxation of the host lattice [29–31]. The fast relaxing host ions effectively average out the dipolar field which the Mn^{2+} experiences due to the paramagnetic host ions. This narrowing of the dipolar broadened lines at ambient temperature is due to the relatively short spin-lattice relaxation time of the host ion and the more efficient modulation of the dipolar fields. In keeping with this argument, the hf lines were found to narrow above room temperature, i.e., 353 K, because T_1 decreases with increasing temperature. The linewidths of the hf lines in all the five fine-structure groups is ca. 35 G. The considerable broadening at low temperatures could be attributed to cross-relaxation between Mn^{2+} and Co^{2+} ions [32–34]. Further quantitative studies must be carried out before any conclusion can be drawn with regard to the $Mn^{2+} - Co^{2+}$ interaction.

An endotherm was observed in the DSC trace at 256 ± 1 K and was found to be reproducible as well as

reversible with a hysteresis in T_c of the same order as found in EPR. The high temperature traces for both $ZnTiF_6 \cdot 6H_2O$ as well as $CoTiF_6 \cdot 6H_2O$ did not show any phase transition upto 550 K. The changes observed were only due to the decomposition of the compound due to the loss of water molecules, as was evident from their irreversible nature. The change in enthalpy associated with the transition in $CoTiF_6 \cdot 6H_2O$ was calculated to be 1098 cal/mole.

Discussion

In the case of $CdTiF_6 \cdot 6H_2O$, the forbidden transitions observed along the c -axis for $T > T_c$ and along the symmetry axis of one of the sites for $T < T_c$ were analysed using (7). For the zinc analog the analysis was made with spectra recorded with the c -axis making an angle of 8° with H ($\theta = 8^\circ$ in (3)) at room temperature and at 173 K. Suitable values for Q' and Q'' (Tables 1 and 2) were invoked to arrive at a satisfactory agreement between experimental and calculated separations to within 1 G. This led us to believe that the quadrupole coupling is sensitive to the immediate ligand field around the Mn^{2+} ion. Apart from the six water molecules which form a trigonally distorted octahedron around the Cd^{2+} and Zn^{2+} ions, the six fluorines forming the (TiF_6) octahedron are hydrogen bonded to the protons of the water molecules. The bulky Cd atom opposes any rotation of the $[Cd(H_2O)_6]$ octahedron. This leads to a small Q' even at room temperature due to weak hydrogen bonds, $O-H \cdots F$, due to the rotation of the (TiF_6) octahedron. Consequently forbidden transitions are observed along the symmetry axis of the D -tensor. As the temperature is lowered, the rotation of the (TiF_6) octahedron is gradually arrested, and this results in an increase in the distortion of the efg at the Mn^{2+} ion site. Therefore one observes an increase in the intensity of these forbidden transitions. Another possible explanation is that a small but increasing deviation of the crystal from pure trigonal symmetry on cooling, viz., small changes in bond distances and a small twist about the c -axis results in changes in bond angles. Mn^{2+} , a 6S state ion, is extremely sensitive to even small changes in symmetry. This would result in a systematic increase or decrease in D . Such a change was definitely not observed (Figure 3). In contrast, in $ZnTiF_6 \cdot 6H_2O$ the $[Zn(H_2O)_6]$ octahedron also executes rotational motion along with the (TiF_6) group. Therefore, the efg at the paramagnetic ion site is ex-

pected to be negligible, resulting in the absence of forbidden transitions along the symmetry axis.

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