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## An EPR study of a single crystal of the solid-state-laser material $\text{Mn}^{5+}$ -doped $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$

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**Abstract.** A single crystal of the solid-state-laser material  $\text{Mn}^{5+}$ -doped  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ , wherein the  $\text{Mn}^{5+}$  ion substitutes for the tetrahedrally coordinated  $\text{P}^{5+}$  ion, has been investigated by X-band (9.6 GHz) EPR at 296, 190 and 120 K. The fine- and hyperfine-structure spin-Hamiltonian parameters have been estimated rigorously from a simultaneous fitting of the EPR line positions observed for several orientations of the external magnetic field in the various magnetic planes. The increase in EPR linewidths suggests enhanced vibrations of  $\text{MnO}_4^-$  tetrahedra, and/or strain effects, with increasing temperature.

### 1. Introduction

There is currently a great interest in materials suitable for lasers that are tunable and capable of lasing at room temperature. Quite recently, the ions  $\text{Cr}^{4+}$  and  $\text{Mn}^{5+}$ , which are isoelectronic to each other ( $3d^2$  configuration) and stabilized in the tetraoxo-coordination, have been found to be lasing by Petricevic *et al* (1988a, b, 1989) ( $\text{Cr}^{4+}$ ), Verdún *et al* (1988) ( $\text{Cr}^{4+}$ ) and Capobianco *et al* (1992a, b) ( $\text{Mn}^{5+}$ ). The  $\text{Mn}^{5+}$  ion substitutes for the  $\text{P}^{5+}$  ion in the tetrahedrally coordinated sites in the spodosite structure (e.g.,  $\text{Ca}_2\text{PO}_4\text{Cl}$ ) and apatite structure (e.g.,  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ ). A broader examination of these laser materials, containing  $3d^2$  ions in tetrahedral coordination, by various different techniques is thus desirable at present.

Electron paramagnetic resonance (EPR) of the  $\text{Mn}^{5+}$  ion has not been frequently reported. However,  $\text{Mn}^{5+}$  has been studied in the tetraoxo-coordination by optical and EPR techniques in several arsenates, phosphates and vanadates. Recently, Capobianco *et al* (1992a, b) published their studies on near-infra-red emission from  $\text{Mn}^{5+}$ -doped  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$  and  $\text{Ca}_2\text{PO}_4\text{Cl}$ , similar to those of Herren *et al* (1991) on  $\text{Mn}^{5+}$ -doped  $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$  and  $\text{Ca}_2\text{VO}_4\text{Cl}$ . The near-infra-red emission was found to be due to the  ${}^1\text{E} \rightarrow {}^3\text{A}_2$  transition from  $\text{Mn}^{5+}$  ions located at tetrahedral sites.

Borromei *et al* (1977, 1981) and Milstein and Holt (1969) reported single-crystal electronic spectra of tetrahedral  $\text{Mn}^{5+}$  in host lattices with apatite and spodosite structures. Reinen *et al* (1986) published their electronic reflection and powder EPR data in apatite mixed crystals, estimating only the values of the zero-field splitting parameters ( $D$ ,  $E$ ) and  $\mathbf{g}$  tensor (isotropic) from powder EPR data at various temperatures. Single-crystal EPR investigations were performed by Lachwa and Reinen (1989) on  $\text{Mn}^{5+}$  in apatite- and spodosite-type host

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lattices. As for  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ , they did not analyse the data in detail, only evaluating the zero-field splitting parameters  $D$  and  $E$ , and the isotropic  $g$  tensor from powder EPR spectra at various temperatures. Further, not being able to analyse the angular dependence of the  $D$  tensor, they speculated that the principal components of the  $D$  tensor,  $D_x'$ ,  $D_y'$ , and  $D_z'$ , did not follow the approximate  $C_{3v}$  symmetry of the three magnetically inequivalent  $\text{MnO}_4^{3-}$  polyhedra in the unit cell.

A detailed X-band EPR study in the temperature range 120–296 K on an  $\text{Mn}^{5+}$ -doped  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$  (SPC, hereafter) has been presented in this paper. From a simultaneous fitting of the EPR line positions obtained for several orientations of the external magnetic field ( $B$ ) in the various magnetic planes the spin-Hamiltonian parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $D$ ,  $E$ ,  $A$  and  $B$  are evaluated using a rigorous least-squares fitting procedure employing the eigenvalues and eigenvectors of the spin-Hamiltonian matrix on a digital computer.

## 2. Sample preparation, crystal structure and experimental arrangement

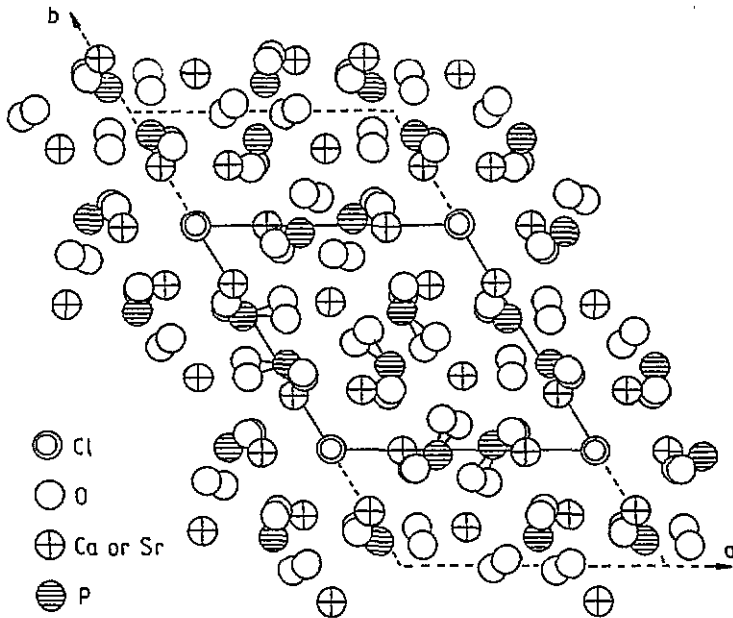
Single crystals of  $(\text{MnO}_4^{3-})$ -doped SPC were grown by the flux technique following modifications of the procedures described by Kingsley *et al* (1965) and Borromei and Fiscaro (1979). The concentration of  $\text{Mn}^{5+}$  was determined to be 0.033 wt%, equivalent to  $4.145 \times 10^{18}$  ions  $\text{cm}^{-3}$ .

The SPC crystal is hexagonal, with the space group  $P6_3/m$  and the unit-cell parameters  $a = 0.9859(1)$  and  $c = 0.7206(2)$  nm (Sudarsnan and Young 1974). The general structural features are the same as those of fluoroapatite and hydroxyapatite except for the position of the Cl atom, which is located at  $(0, 0, 1)$ , midway between the two Sr triangles on the mirror planes at  $z = \frac{1}{4}$  and  $z = \frac{3}{4}$ . A projection of the  $a, b$  plane of the chloroapatite structure of  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ , showing the hexagonal unit cell used for fluoroapatite and hydroxyapatite as reported by Mackie *et al* (1972), is shown in figure 1. The tetrahedra in the apatite structure are distorted along the  $C_3$  axis, possessing  $C_{3v}$  symmetry in first approximation, superimposed by a small orthorhombic symmetry component (Reinen *et al* 1986).

A Bruker model ER 200D-SRC X-band EPR spectrometer was used for recording data. The sample inside the high- $Q$  cavity could be cooled to 110 K with an  $\text{N}_2$ -gas-flow controller unit (Bruker variable-temperature unit type EPR TBL B-VT 2000) with a temperature stability of  $\pm 0.1$  K. The sample could be rotated about a vertical axis in a goniometer so that the magnetic field could be effectively rotated in the magnetic planes defined by the principal axes of the  $B_2^m$  tensor (described by the coefficients of the  $O_2^m$  tensor in the spin Hamiltonian as defined by Abragam and Bleaney (1970)). The 100 kHz modulation was used for recording the spectra.

## 3. EPR data and analysis

The  $\text{Mn}^{5+}$  ion ( $3d^2$  configuration) is characterized by the electron spin  $S = 1$  and the nuclear spin  $I = \frac{5}{2}$ . Thus, the allowed transitions described by  $\Delta M = \pm 1$ ,  $\Delta m = 0$ ; where  $M$  and  $m$  are the electronic and nuclear magnetic quantum numbers, respectively, give rise to sextets of hyperfine lines for each fine-structure transition. The number of fine-structure transitions depends on the values of the zero-field-splitting parameters  $D$  and  $E$ , and the orientation of the external magnetic field ( $B$ ) with respect to the magnetic axes  $Z, X, Y$  defined to be those orientations of  $B$  for which one obtains extrema of overall splitting of lines; these splittings successively decrease for  $B \parallel Z, X, Y$ . Figure 2 exhibits the



**Figure 1.** A projection of the  $a, b$  plane of the chloroapatite structure for  $Ca_5(PO_4)_3Cl$  (Mackie *et al* 1972), showing the relation between the monoclinic (dotted lines) unit cell and the hexagonal (continuous lines) unit cell used for SPC. The Ca ions are replaced by Sr ions in SPC. The six  $PO_4$  tetrahedra in the unit cell have been identified by connecting the P atom to the two O atoms not overlapping it belonging to the tetrahedron.

energy-level diagram for  $Mn^{5+}$  using the spin-Hamiltonian parameters (derived later in this section) for  $B \parallel Z, X, Y$ . Thus, two fine-structure transitions are expected for  $B \parallel Z$ , while only one for  $B \parallel X$  or  $B \parallel Y$ , as seen from the resonance condition.

Since there are two formula units, each containing three  $PO_4^{3-}$  units, in the hexagonal unit cell of SPC, one expects a superposition of six distinct EPR  $Mn^{5+}$  spectra for a general orientation of  $B$ . However, these reduce to three distinct sets, since three pairs of magnetically inequivalent ions exist in the unit cell, as revealed by EPR spectra. In figure 3 first-derivative EPR absorption spectra at 120 K for  $B \parallel Z_1, X_1, Y_1$  are exhibited where the subscript 1 indicates one of the three magnetically inequivalent ions in the unit cell. By orienting the crystal so that  $B$  could be rotated in various planes, it was found that  $X_1 \parallel X_2 \parallel X_3$ , and  $Z_1Y_1, Z_2Y_2$  and  $Z_3Y_3$  planes are parallel to each other such that the magnetic axes  $Z_1, Z_2, Z_3$  are oriented at  $60^\circ$  from each other as seen from figure 4, depicting the angular variation of EPR line positions observed for the orientations of  $B$  in the magnetic  $Z_1X_1, X_1Y_1$  and  $Z_1Y_1$  planes. Thus, the  $X_1(\parallel X_2 \parallel X_3)$  axis is parallel to the  $C$  axis of the SPC crystal since this is the threefold axis of symmetry in the  $ZY$  plane (figure 1). This is consistent with the orientation of  $Z_1(Y_1), Z_2(Y_2), Z_3(Y_3)$  axes, which are related to each other by a threefold rotation, lying in the  $ab$  plane (figure 1). (Here the subscripts 1, 2, 3 denote the various magnetically inequivalent ions in the unit cell.)

It is noted that the three pairs of magnetically inequivalent ions together give the overall appearance of sixfold rotation pattern at high magnetic fields. However, for any one magnetically inequivalent pair of  $Mn^{5+}$  ions in the unit cell, the rotation pattern is, indeed, twofold, in accordance with the spin Hamiltonian given by (1) in the next section.

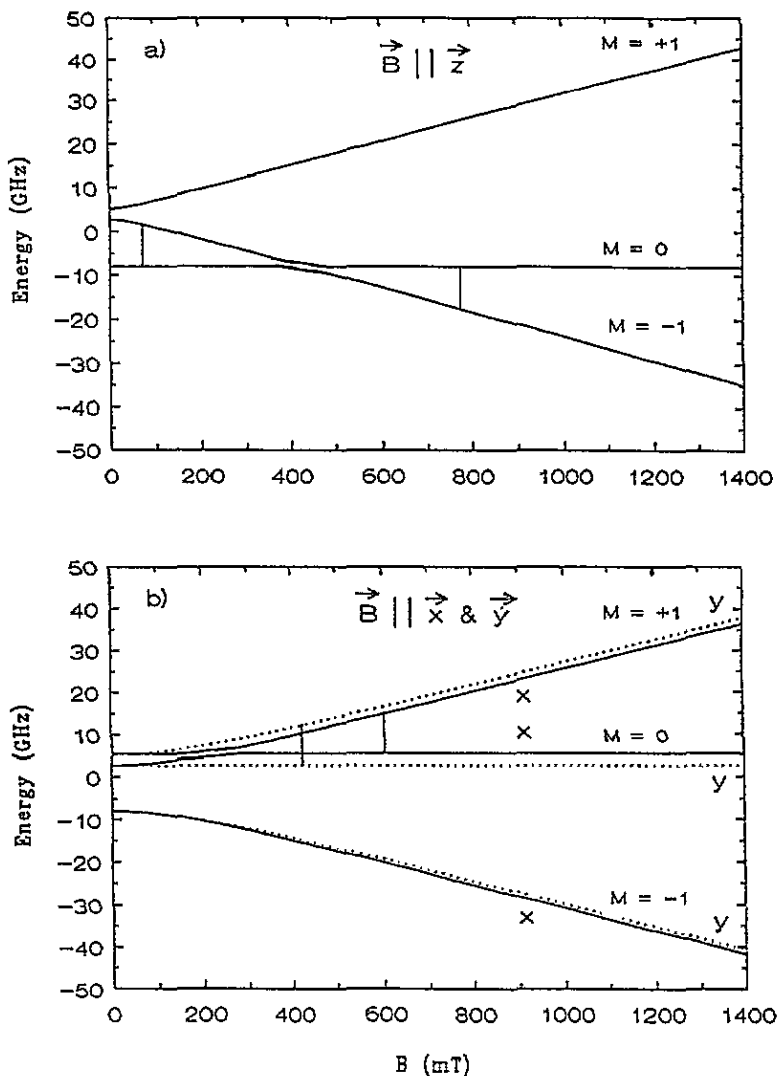


Figure 2. The variation of Mn<sup>5+</sup> energy levels for the orientation of the external magnetic field parallel to the magnetic (a) Z, (b) X and Y axes in an SPC single crystal. The same diagrams apply for the three magnetically inequivalent Mn<sup>5+</sup> pairs of ions in the unit cell characterized by the same values of the spin-Hamiltonian parameters, except for having different orientations of the X, Y, Z axes.

### 3.1. Spin Hamiltonian

The following spin Hamiltonian was used to describe the Mn<sup>5+</sup> ion in SPC taking into account the C<sub>3v</sub> site symmetry superimposed by a small orthorhombic symmetry component:

$$\mathcal{H} = \mu_B [g_{\parallel} B_z S_z + g_{\perp} (B_x S_x + B_y S_y)] + D [S_z^2 - \frac{1}{3} S(S+1)] + E (S_x^2 - S_y^2) + Q' [I_z^2 - \frac{1}{3} I(I+1)] + Q'' (I_x^2 - I_y^2) + A S_z I_z + B (S_x I_x + S_y I_y). \quad (1)$$

In (1),  $\mu_B$  is the Bohr magneton,  $g_{\parallel}$ ,  $g_{\perp}$ ,  $D$ ,  $E$  are the fine structure parameters and  $Q'$ ,  $Q''$ ,  $A$ ,  $B$  are the hyperfine-structure parameters. The parameter  $E$  appears in (1) due to the

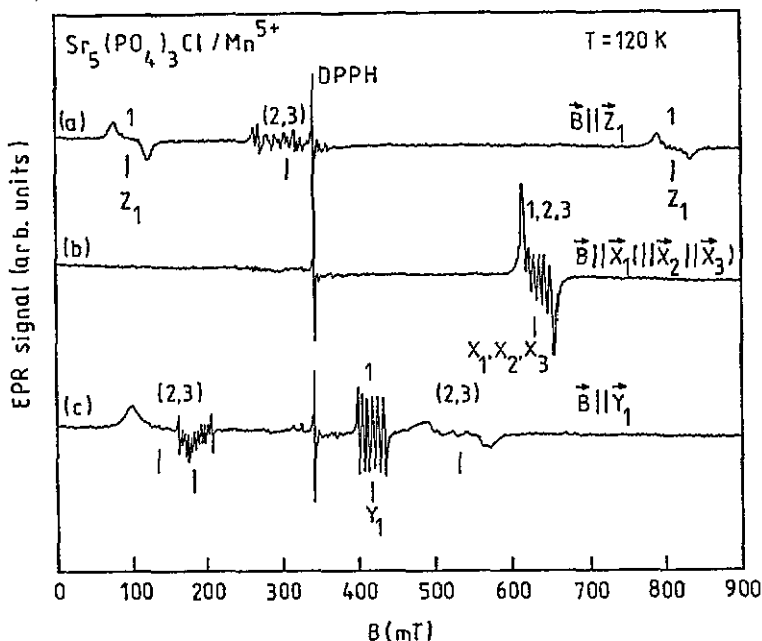
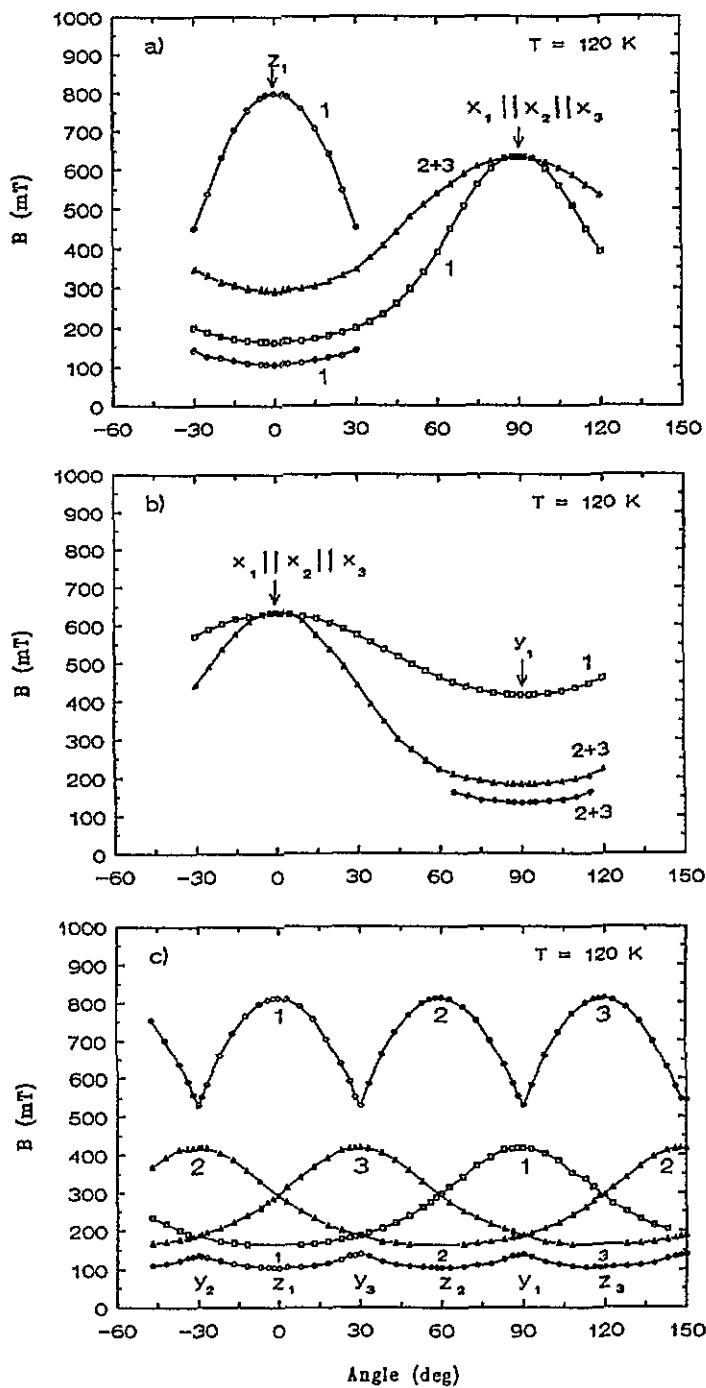


Figure 3.  $Mn^{2+}$  EPR spectra in SPC single crystal (9.6 GHz) at 120 K for the orientation of the external magnetic field parallel to (a) the  $Z_1$  axis (the lines indicated as 2, 3 belong to the magnetically inequivalent ions 2, 3), (b)  $X_1 \parallel X_2 \parallel X_3$  axes and (c) the  $Y_1$  axis (the lines indicated as 2, 3 belong to the magnetically inequivalent ions 2, 3). The subscripts refer to the three magnetically inequivalent ions. The numbers indicate the magnetic ion to which a particular line belongs. When two numbers are placed in brackets, this represents the overlap of lines due to the corresponding two ions, and when two numbers are put next to each other without brackets, this indicates coincidence of the lines belonging to the ions. For further clarification, see figure 2 giving the energy-level diagram for  $B \parallel X, Y, Z$ , and figure 4 giving the angular variation of lines for the three pairs of ions.

presence of the lower-symmetry component. The values of  $Q'$ ,  $Q''$  cannot be determined from allowed hyperfine line positions since the separations of energy levels participating in resonance do not depend on them.  $D = 3B_2^0$  and  $E = B_2^2$ , where  $B_2^m$  are the coefficients of  $O_2^m$ , the spin operators as defined by Abragam and Bleaney (1970). It is noted that for spin  $S = 1$  the spin Hamiltonian cannot contain terms  $O_l^m$ , where  $l > 2$ , and of course  $|m| \leq l$ .

### 3.2. Evaluation of spin-Hamiltonian parameters (SHPs)

The least-squares-fitting (LSF) method described for the electron-nuclear spin-coupled system by Misra (1983) for  $Mn^{2+}$  was used to evaluate the SHPs, the only difference being that here the centres of hyperfine sextets, rather than their weighted centres calculated so as to reflect the absence of hyperfine interactions, were used to evaluate first the fine-structure parameters, to be used in a subsequent simultaneous fitting of *all* hyperfine line positions to evaluate all SHPs, including the hyperfine parameters  $A$ ,  $B$ . The LSF method yields the correct relative signs of SHPs. The absolute sign of the fine-structure parameter  $D$  was assumed to be positive in accordance with Reinen *et al* (1986), and that deduced for  $Mn^{5+}$  in  $Ca_2PO_4Cl$  by Lachwa and Reinen (1989). The absolute signs for  $A$ ,  $B$  were assumed to be negative, each in accordance with that determined from hyperfine-interaction



**Figure 4.** The angular variation of the EPR line positions as observed at 120 K for the orientation of the external magnetic field in (a) the  $Z_1X_1$  magnetic plane (which also contains  $X_2 \parallel X_3$  axes, parallel to the  $X_1$  axis); (c)  $Z_1Y_1$  magnetic plane (parallel to  $Z_2Y_2$  and  $Z_3Y_3$  planes) and (b)  $X_1Y_1$  plane. The numbers next to the lines indicate the magnetically inequivalent ions to which they belong.

data (Steudel 1976). Thus, the signs of all the parameters as listed in table 1 should be considered absolute.

All the line positions observed for several orientations of  $B$  in the  $ZX$ ,  $XY$ ,  $ZY$  planes were simultaneously fitted. The complex spin-Hamiltonian matrix was diagonalized on a digital computer to evaluate its eigenvalues and (complex) eigenvectors required in the LSF procedure to calculate the first and second derivatives of the differences in the eigenvalues of the pairs of levels participating in resonance. (For more details see Misra (1983).) It is seen from table 1 that while the  $g$  values remain the same, the magnitudes of the parameters  $D$ ,  $E$  increase with decreasing temperature. The parameter  $E$  is found to have opposite sign to that of  $D$ , while its magnitude is about 10% that of  $D$ , indicating only a small orthorhombic distortion of the  $(PO_4)^{3-}$  tetrahedra, which possess  $C_3$  symmetry when undistorted.

The fitting is rather good as judged by the small values of the mean deviation per line of the calculated energy separation of levels participating in resonance (in frequency units) from the klystron frequency, as seen from table 1. It is noted that the three magnetically inequivalent ions are physically equivalent to each other in that their spectra are observed to be exactly the same except for different orientations of their magnetic axes. Thus, the SHPs are the same for the three magnetically inequivalent ions 1, 2, 3.

The values of the zero-field splitting parameters  $D$  and  $E$  for  $Mn^{5+}$  in SPC with apatite structure can be compared with those in SPC reported by Lachwa and Reinen (1989) and by Reinen *et al* (1986), which are also listed in table 1. These values have about the same magnitudes as those presently estimated, which, in turn, are about the same as in the apatite  $Ba_5(PO_4)_3Cl$  reported by Lachwa and Reinen (1989), being in gigahertz  $(D, E) = (13.2, 1.5)$ ,  $(13.8, 1.5)$  and  $(14.1, 1.8)$  at 298, 130, and 4 K, respectively. Apart from a precise determination of the values of SHPs from single-crystal data made presently, an important difference lies in the opposite signs of  $D$  and  $E$  as determined presently from single-crystal data compared to the same signs of  $D$  and  $E$  reported previously determined from powder data; the latter enable only the determination of the value of  $E^2$ , thus not enabling the determination of the absolute sign of  $E$ . Further, the previous studies did not consider anisotropic  $g$  and  $A$  tensors, unlike the present study where anisotropy is found in these tensors at all temperatures beyond experimental error (see table 1).

### 3.3. Linewidths

The peak-to-peak linewidth of the first-derivative line shape for each of the six hyperfine-structure lines was found to be dependent on temperature. On average, for  $B \parallel X$ , it was 3.5 mT at 120 K, 3.7 mT at 190 K and 4.0 mT at 296 K; for  $B \parallel Y$  it was 2.6 mT at both 120 and 190 K, increasing to 3.5 mT at 296 K; and for  $B \parallel Z$  it was 4.5 mT at both 120 and 190 K, increasing to 4.8 mT at 296 K. The increase in the linewidth with increasing temperature indicates enhanced vibrations of  $(MnO_4)^{3-}$  tetrahedra, while its anisotropy indicates strain effects, which increase with increasing temperature. The  $Mn^{5+}$  EPR linewidths depend in an extremely complex manner upon interaction of the  $Mn^{5+}$  ions with the lattice and other spins present in the lattice (Abragam and Bleaney 1970). They may also depend indirectly upon superhyperfine interaction. Further analysis is well beyond the scope of this paper.

## 4. Concluding remarks

The following are the main findings of the present report.



Table 1. Values of the spin-Hamiltonian parameters at various temperatures.  $g$ ,  $g_{\parallel}$  and  $g_{\perp}$  are dimensionless, while the other parameters are in gigahertz.  $n$  represents the number of lines simultaneously fitted to evaluate the parameters. MDL (GHz) is the mean deviation per line (as a percentage) of the calculated energy differences of the hyperfine levels participating in resonance from the klystron frequency.

	296 K <sup>a</sup>	190 K <sup>a</sup>	120 K <sup>a</sup>	298 K	130 K	4 K
$g$	—	—	—	1.97 <sup>b,c</sup>	1.97 <sup>b,c</sup>	1.97 <sup>b,c</sup>
$g_{\parallel}$	1.9658 ± 0.0005	1.9625 ± 0.005	1.9608 ± 0.0005	—	—	—
$g_{\perp}$	1.9774 ± 0.0005	1.9785 ± 0.0005	1.9768 ± 0.0005	—	—	—
$D$	11.79 ± 0.005	12.41 ± 0.005	12.77 ± 0.005	10.8 <sup>b</sup> , 12.0 <sup>c</sup>	12.9 <sup>b</sup> , 13.2 <sup>c</sup>	13.2 <sup>b</sup> , 13.2 <sup>c</sup>
$E$	-1.305 ± 0.005	-1.498 ± 0.005	-1.599 ± 0.005	1.2 <sup>b</sup> , 1.4 <sup>c</sup>	1.5 <sup>b</sup> , 1.8 <sup>c</sup>	1.8 <sup>b</sup> , 1.8 <sup>c</sup>
$A$	0.203 ± 0.001	0.196 ± 0.001	0.197 ± 0.001	0.21 <sup>c</sup>	—	—
$B$	0.201 ± 0.001	0.201 ± 0.001	0.200 ± 0.001	—	—	—
MDL(%)	0.63	0.68	0.70	—	—	—
$n$	144	132	126	—	—	—

<sup>a</sup> Present work.

<sup>b</sup> Lachwa and Reinen (1989).

<sup>c</sup> Reinen *et al* (1986).

(i) Three pairs of magnetically inequivalent, but physically equivalent,  $Mn^{5+}$  ions exist in the unit cell of SPC.

(ii) The values of all the SHPs have been rigorously evaluated at 296, 190 and 120 K from a simultaneous fitting of all the EPR line positions observed for several orientations of  $B$  in the various magnetic planes.

(iii) The absolute sign of the parameter  $E$  has been determined to be opposite to that of  $D$ . The small magnitude of  $E$  relative to  $D$  indicates that the  $(MnO_4)^{3-}$  tetrahedra are only slightly distorted. This, in turn, implies that the site symmetry of  $Mn^{5+}$  ions is predominantly  $C_{3v}$  with a small admixture of an orthorhombic symmetry component.

(iv) Both the  $g$  and  $A$  tensors are found to be slightly anisotropic at all temperatures.

(v) The linewidths increase with increasing temperature indicating enhanced vibrations of  $(MnO_4)^{3-}$  tetrahedra and strain effects at higher temperatures.

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