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Electron Spin Resonance of CrO_4^{3-} in Chloroapatite $Ca_5(PO_4)_3Cl$*

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Electron spin resonance spectra measured in CrO_4^{3-}-doped chloroapatite ($Ca_5(PO_4)_3Cl$) single crystals at liquid helium temperatures indicate the presence of three magnetically inequivalent chromate(V) tetrahedra in agreement with structural results obtained by X-ray diffraction methods that showed $Ca_5(PO_4)_3Cl$ to be monoclinic ($P2_1/b$) below 200°C. A detailed analysis of the electron spin resonance spectra and the appropriate Spin-Hamiltonian parameters determined is presented. The ground state of the unpaired d^1 electron is shown to be d_{z^2}. The electronic structures of CrO_4^{3-} in $Ca_5(PO_4)_3Cl$ and in the related compound with spodiosite structure, Ca_2PO_4Cl are compared.

Introduction

Chloroapatite, $Ca_5(PO_4)_3Cl$, is structurally very similar to hexagonal hydroxyapatite, $Ca_5(PO_4)_3OH$, the mineral component of bone and teeth. Since large crystals of $Ca_5(PO_4)_3OH$ have not been grown successfully as yet, whereas relatively large crystals of $Ca_5(PO_4)_3Cl$ are easily available, we undertook the spectral study of CrO_4^{3-}-doped chloroapatite to establish the use of spectroscopic methods of investigating structural changes in apatite-like crystals, so that these methods can be applied to the study of doped hydroxyapatite crystals. Such studies should be useful in following structural changes in this biologically important material.

It has been established that synthetic chloroapatite, $Ca_5(PO_4)_3Cl$, is monoclinic ($P2_1/b$) at room temperature (*1*). At about 200°C this monoclinic phase changes to the hexagonal phase ($P6_3/m$) (*2*). It appears that the position of the chloride ions determines the symmetry. In hexagonal apatites there are six equivalent PO_4^{3-} tetrahedra. Detailed structural investigation of $Ca_5(PO_4)_3Cl$ single crystals by X-ray diffraction (*3*) shows that there are three crystallographically distinct phosphate tetrahedra in the monoclinic chloroapatite. All PO_4^{3-} tetrahedra are significantly distorted, and the distortions are slightly different in the three sets. These structural results are supported by fluorescence studies made on $Ca_5(PO_4)_3Cl$ doped with MnO_4^{3-} (*4*); three lines of about equal intensity and separated by 5 cm^{-1} are observed near 8600 cm^{-1}. The small value of splitting indicates that the three crystallographically inequivalent tetrahedra are not very different from each other. A preliminary low-temperature optical spectrum obtained on $Ca_5(PO_4,CrO_4)_3Cl$ single crystals similarly indicates the presence of three sets of phosphorus positions (*5*). Investigation of the electron spin resonance of CrO_4^{3-}-doped $Ca_5(PO_4)_3Cl$ was undertaken to confirm these results and to obtain more detailed information on the nature of the distortion.

Recently the electron spin resonance spectra of the related compound with spodiosite structure, Ca_2PO_4Cl doped with CrO_4^{3-}, have been studied in this laboratory (*6*). In Ca_2PO_4Cl, the phosphate tetrahedra are distorted from ideal T_d symmetry (*7*); however, the distortions are different than those in the apatites. In spodiosites, two tetrahedral angles are open, and four angles are closed a number of degrees, while in apatites three angles are open and three are closed. A detailed analysis of the ESR spectra of $Ca_2(PO_4,CrO_4)Cl$ showed that the ground state for the single d electron is a d_{z^2} orbital. One objective of the present study was to ascertain the influence of the different distortion in the apatite upon the electronic ground state in the CrO_4^{3-} ion.

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Experimental

Single crystals of $Ca_5(PO_4,CrO_4)_3Cl$ with small concentrations of Cr were grown from the melt using excess $CaCl_2$ as flux. A typical composition used for growth of a 0.5% CrO_4^{3-} content was: 2.995 mole $Ca_3(PO_4)_2$, 0.005 mole Cr_2O_3, 0.015 mole $CaCO_3$, and 5 mole of $CaCl_2$. The starting materials were thoroughly mixed and fired overnight in tightly covered platinum crucibles at 1280°C in air, and cooled at 3°C/hr to 1060°C. At 1060°C the crystals were quenched, as the incongruently melting compound, Ca_2PO_4Cl, forms at temperatures below 1040°C. Light green crystals of $Ca_5(PO_4,CrO_4)_3Cl$ were obtained this way. Most of the larger crystals were cracked or strained as a result of quenching. X-Ray diffraction patterns confirmed the formation of $Ca_5(PO_4,CrO_4)_3Cl$.

Electron Resonance Spectra

Electron spin resonance spectra were measured on a Varian ESR Spectrometer Model 4500. The klystron frequency was ~9300 MHz. A single crystal of $Ca_5(PO_4,CrO_4)_3Cl$ with about 0.5% Cr content produced no ESR signal at room temperature, but a very broad signal at about $g \cong 2$ was detected at liquid N_2 temperature. The width of this line did not change noticeably when crystals with smaller concentrations of Cr were checked. The liquid nitrogen spectrum was too broad (approximately 300 G) for a meaningful analysis. At liquid helium temperatures, the broad line split into three relatively sharp signals as shown by Fig. 1. A single crystal of $Ca_5(PO_4,CrO_4)_3Cl$ was oriented by X-ray diffraction techniques, and rotational ESR spectra were recorded at liquid helium temperature about three orthogonal crystallographic axes *a*, *a** (direction perpendicular to *ac* in the hexagonal cell), and *b* (hexagonal *c*). The magnetic field was perpendicular to the axis of rotation. Absorption lines were observed at 15° intervals as the crystal was rotated through 180°. No hyperfine lines were detected.

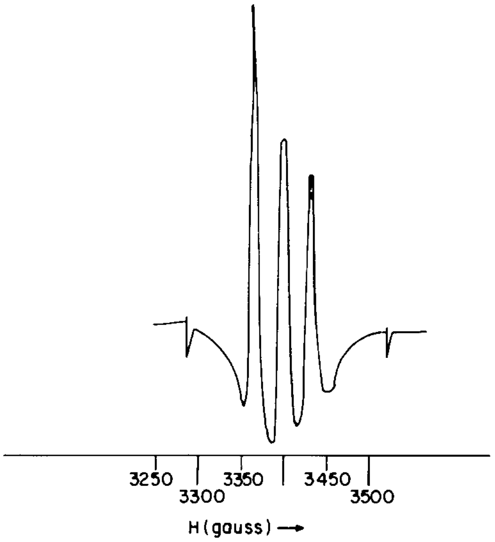

FIG. 1. The first derivative of the dispersion curve of the electron spin resonance at liquid He temperatures for $Ca_5(PO_4,CrO_4)_3Cl$. Rotation about *c* crystallographic direction. (The two small peaks are calibration marks.)

Results

Chloroapatite $Ca_5(PO_4)_3Cl$ appeared to be isomorphous with hexagonal hydroxyapatite $Ca_5(PO_4)_3OH$ and fluoroapatite $Ca_5(PO_4)_3F$. X-Ray diffraction and optical studies on synthetic crystals of chloroapatite have shown that the true symmetry at temperatures below 200°C is monoclinic $P\ 2_1/b$. The monoclinic unit cell arises by the doubling of the hexagonal *a* axis, due to the position of chloride ions, which changes the mirror plane of $P\ 6_3/m$ into the glide plane of $P\ 2_1/b$. The hexagonal *c* axis remains the unique axis. In $P\ 2_1/b$ the twelve P atoms lie on three crystallographically inequivalent sets of the fourfold position (*e*). The three crystallographically distinct PO_4^{3-} tetrahedra are considerably distorted and also differ significantly among themselves as shown in Table I (*3*). Thus in CrO_4^{3-}-doped $Ca_5(PO_4)_3Cl$, there will be at least three kinds of paramagnetic ion in the lattice. The CrO_4^{3-} ion with one unpaired electron has electronic spin $S = \frac{1}{2}$, so that the paramagnetic resonance spectrum for

TABLE I

ANGLES AND DISTANCES IN THE PHOSPHATE TETRAHEDRA IN $CA_5(PO_4)_3Cl$

PO_4 Tetrahedra	*A*	*B*	*C*
O_I–P–O_{II} (°)	111.30	111.22	111.22
O_I–P–O_{III} (°)	111.28	111.85	111.50
O_I–P–O_{IV} (°)	112.23	111.97	112.16
O_{II}–P–O_{III} (°)	107.72	107.29	107.59
O_{II}–P–O_{IV} (°)	106.24	106.56	106.19
O_{III}–P–O_{IV} (°)	107.82	107.69	107.92
P–O_I (Å)	1.530	1.532	1.530
P–O_{II} (Å)	1.544	1.544	1.545
P–O_{III} (Å)	1.531	1.534	1.536
P–O_{IV} (Å)	1.538	1.533	1.533

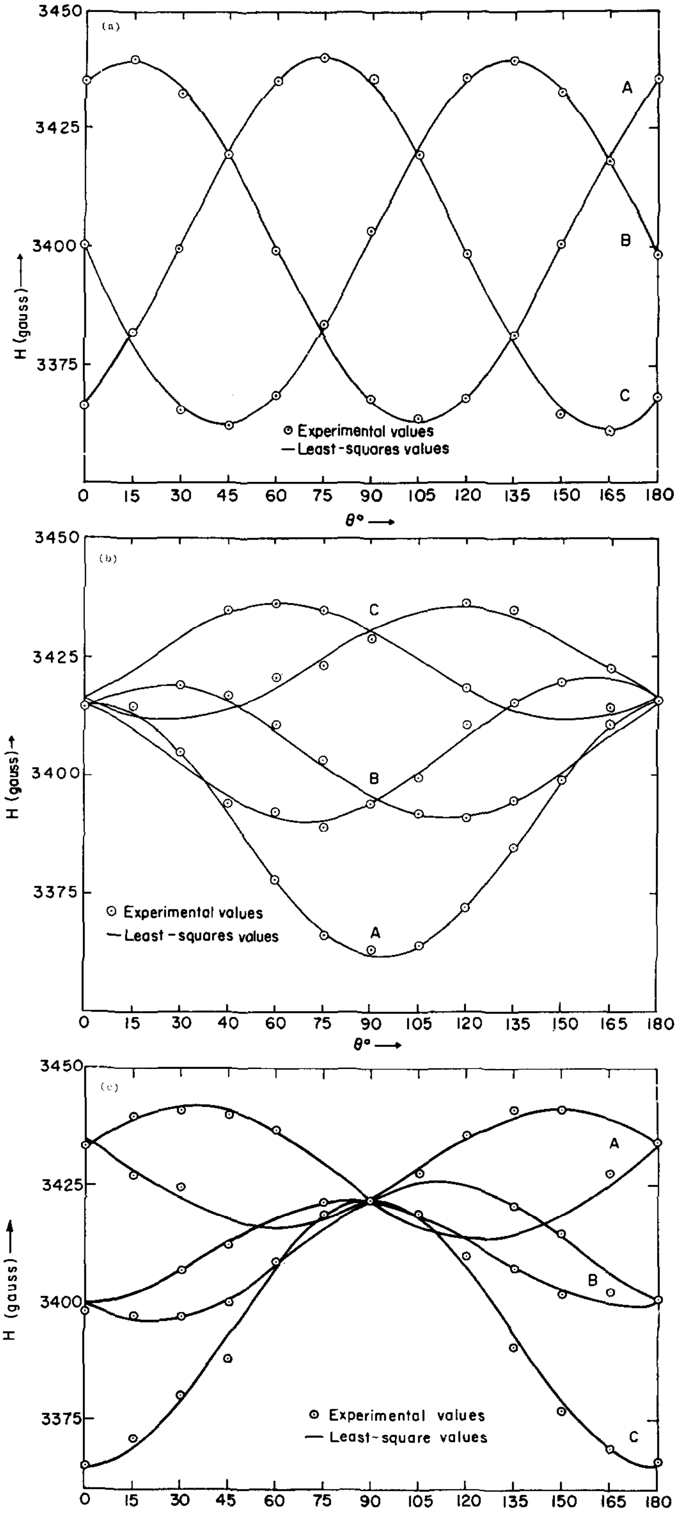

FIG. 2. Magnetic field *H* (G) at center of peak vs. θ the angle between the crystallographic axis and the magnetic field (a) Rotation about *c* axis, *H* parallel to *a* at $\theta = 0°$. (b) Rotation about *a* axis, *H* parallel to *c* at $\theta = 0°$. (c) Rotation abou a^* axis, *H* parallel to *a* at $\theta = 0°$. The small difference in the maximum values of curves B and C indicates a small misalignmen of the rotational axis.

TABLE II

Principal g Values of the Three Tetrahedra in $Ca_5(PO_4,CrO_4)_3Cl$[a]

	g_x	g_y	g_z
A	1.933	1.946	1.979
B	1.934	1.942	1.980
C	1.932	1.946	1.979

[a] The error is ±0.002 in each.

three crystallographically distinct chromate ions will show three to six lines (in the absence of hyperfine structure) depending on orientation as shown by Fig. 1.

In Fig. 2a–c are plotted the resonant magnetic fields for the peaks of the spectrum as a function of the angle of rotation. Because the tetrahedra lie on mirror planes at $z \cong 1/2$ and $z \cong 3/4$, rotation about the b axis shows only three peaks; clearly, each of the peaks A, B, and C correspond to one of the three distinct chromate tetrahedra. The observed splitting of peaks when the crystal is rotated about a and a^* axes occurs because the magnetic field makes different angles with the electric axes of symmetry-related tetrahedra. The spectra can be fitted to the Spin-Hamiltonian:

$$H = g_x \beta_e H_x S_x + g_y \beta_e H_y S_y + g_z \beta_e H_z S_z.$$

The data given in Fig. 2(a–c) have been fitted by a least-squares program to the above equation. The principal g values are given in Table II.

Discussion and Theory

It is seen from the principal g values of the chromate tetrahedra in chloroapatite, that no axial symmetry of the electric axis exists; the g values are highly anisotropic. Furthermore, the three sets of principal g values corresponding to the three different CrO_4^{3-} are the same, within experimental error.

This indicates that the chromate tetrahedra are different only in the orientation of the electric axes as far as ESR measurements can detect. Possibly, the geometrical differences among the three, indicated by the X-ray analysis, might have been shown by ESR if the g values were determined with greater accuracy.

To correlate species A, B, and C of the data with tetrahedra a, b, and c, we assumed that since all three chromate tetrahedra have nearly identical geometries and magnetically they differ primarily in the orientation of the principal g tensors, the angle between g_z of A, B, and C and a unique direction chosen in each of the three tetrahedra (for example the P–O_I bond direction) should be the same when proper correlation is effected.

A computer program was used to calculate the direction cosines of the principal g tensors with respect to the three crystallographic axes, a, a^* and b for species A, B, and C (*8*). The direction cosine of bond direction P–O_I in tetrahedra a, b, c with respect to the axes a, a^* and b were calculated from X-ray data. From the above results, the angles between g_z and P–O_I for all possible combinations of species A, B, and C and tetrahedra a, b, and c were calculated. Similarly angles between g_x and P–O_I as well as g_y and P–O_I were determined. Three different numerically consistent correlated sets were found. Two were eliminated by considerations of the geometry of the tetrahedra and the most likely orientations of the electric axes expected. In this way, species A was identified with tetrahedron a, B with b, and C with c.

Table III gives the orientations of the principal g tensors in the three tetrahedra with respect to axes a, a^*, and b.

Figure 3 shows the orientation of g_x, g_y, and g_z in tetrahedron a. For later considerations, it is important to notice that the principal axes approximate those expected for a distorted tetrahedron of C_{2v} symmetry. For this coordinate system the d^1 configuration will have either the d_{z^2} or d_{xy} orbital as the ground state. The nature of the ground state was established as follows. If we approximate the orientation of the g tensor to axial symmetry, then $g_\parallel \cong 1.98$ and $g_\perp \cong 1.94$. Assuming pure d orbitals and using first- and second-order perturbation

TABLE III

Orientation of the Principal g Values in $Ca_5(PO_4,CrO_4)_3Cl$

Line	g	Angle to a	Angle to a^*	Angle to c
A	x	29	77	116
	y	66	81	26
	z	105	16	93
B	x	127	49	117
	y	110	73	27
	z	44	46	88
C	x	77	27	113
	y	82	69	23
	z	165	75	88

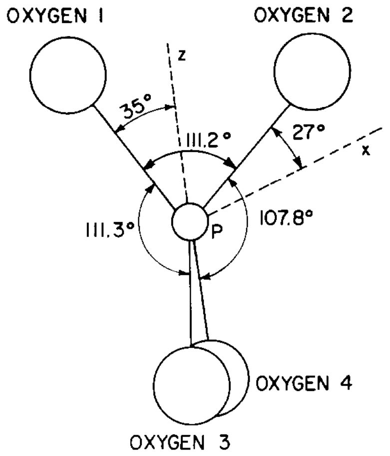

FIG. 3. Orientation of the principal g tensors in CrO_4^{3-} tetrahedra a in $Ca_5(PO_4,CrO_4)_3Cl$. 01, 02, and P define the plane of paper; g_z is also in this plane; g_x is below the plane of paper ~13°; g_y makes about 77° to plane of paper.

theory, the Spin-Hamiltonian parameters for a d_{xy} ground state are

$$g_\parallel = 2.0023 - \frac{8\lambda}{\Delta E_{(x^2-y^2)}}$$

and

$$g_\perp = 2.0023 - \frac{2\lambda}{\Delta E_{(xz,yz)}},$$

while for a d_{z^2} state the parameters are

$$g_\parallel = 2.0023,$$

$$g_\perp = 2.0023 - \frac{6\lambda}{\Delta E_{(xz,yz)}}.$$

Accordingly for a d_{xy} ground state, $g_\parallel < g_\perp$ unless $\Delta E_{xz,yz}$ is much smaller than $\Delta E_{x^2-y^2}$. For a d_{z^2} ground state $g_\parallel > g_\perp$; however $g_\parallel$ must be close to 2.0023. Considering the schematic energy level diagram of d orbitals for the two ground states shown in Fig. 4a and b. $\Delta E_{x^2-y^2}$ can not possibly be four times greater than $\Delta E_{xz,yz}$. If we consider d_{z^2} as the ground state, we must explain the large deviation of $g_\parallel$ from 2.0023. This difference may be attributed to the observed distortion from axial symmetry.

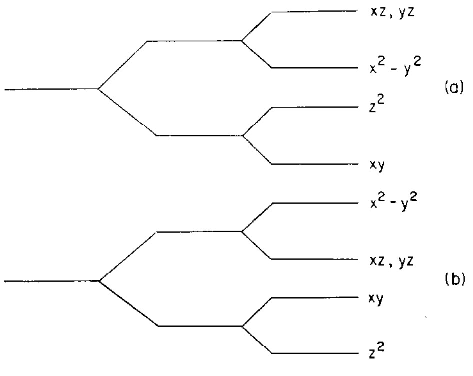

FIG. 4. Schematic energy level diagram for the ground state of d orbitals in distorted T_d symmetry (a) d_{xy}, (b) d_{z^2}.

Similar results were obtained in our analysis of the ESR of CrO_4^{3-} in Ca_2PO_4Cl (*6*). In this system $g_\parallel = 1.9936$, $g_\perp = 1.9498$, and only the hyperfine terms indicated a slight deviation from axial symmetry. It was shown (*9*) that by approximating C_{2v} symmetry for the tetrahedra, both d_{z^2} and $d_{x^2}\_d_{y^2}$ orbitals must be represented as

$$\psi_{z^2} = ad_{z^2} + bd_{x^2-y^2},$$

$$\psi_{x^2-y^2} = ad_{x^2-y^2} - bd_{z^2}.$$

Assuming pure d orbitals and using first- and second-order perturbation theory, the following Spin-Hamiltonian parameters were obtained:

$$g_z = 2.0023 - \frac{8b^2\lambda}{\Delta E_{xy}};$$

$$g_x = 2.0023 - \frac{2\lambda(\sqrt{3}a + b)^2}{\Delta E_{yz}};$$

$$g_y = 2.0023 - \frac{2\lambda(\sqrt{3}a - b)^2}{\Delta E_{xz}}.$$

Solution of these equations with additional ones for hyperfine interactions provides the values $b^2 = 0.0053$, $\lambda/\Delta E_{xy} = 0.21$, $\lambda/\Delta E_{xz} = 0.00959$ and $\lambda/\Delta E_{yz} = 0.0081$. The magnitude of b indicates the small extent of mixing of the $d_{x^2-y^2}$ into the d_{z^2} ground states and accounts for the small deviation of $g_\parallel$ from 2.0023.

A similar analysis of the Spin-Hamiltonian parameters of CrO_4^{3-} in apatite can be made with the additional approximation that $\Delta E_{yz} = \Delta E_{xz}$. This gives the values

$$b^2 = 0.009 \pm 0.001,$$

$$\lambda/\Delta E_{xz} = 0.32 \pm 0.02,$$

$$\lambda/\Delta E_{xy} = 0.011 \pm 0.001.$$

Results for the two systems are seen to be consistent. The larger value of $\lambda/\Delta E_{xy}$ for apatite is in agreement with the experimental observation that while sharp ESR spectra were detected at liquid N_2 temperatures in $Ca_2(PO_4,CrO_4)Cl$, liquid helium temperatures were required for the detection of ESR in apatite. Using 10 000 cm^{-1} for ΔE_{xz} obtained from optical data (*10*), $\lambda \sim 110$ cm^{-1} and $\Delta E_{xy} \sim 350$ cm^{-1} for apatite, and ~500 cm^{-1} for spodiosite. Comparison of b^2 values for the two systems shows a greater distortion from axial symmetry of the CrO_4^{3-} tetrahedra in apatite.

TABLE IV

DIMENSIONS OF CrO_4^{3-} TETRAHEDRON IN $Ca_5(CrO_4)_3OH$

Cr–O(1)	1.640 Å	O(1)–Cr–O(2)	115.0 (°)
Cr–O(2)	1.653 Å	2[O(1)–Cr–O(3)]	113.6
2[Cr–O(3)]	1.686 Å	2[O(2)–Cr–O(3)]	103.6
		O(3)–Cr–O(3)	106.4

It appears that the effective distortion of CrO_4^{3-} from tetrahedral symmetry in apatite lowers the magnitude of ΔE_{xy} and increases the distortion from axial symmetry, as compared to spodiosite. This allows for a greater mixing of $d_{x^2-y^2}$ orbitals into the d_{z^2} ground state, which accounts for the large deviation of $g_{\parallel}$ from 2.0023.

Finally a d_{z^2} ground state is not incompatible with the orientation of the electric axis as shown in Fig. 4. Actually the CrO_4^{3-} ion is probably more distorted than the PO_4^{3-} in chloroapatite. Such additional increase in the distortion of chromate tetrahedron is suggested by the dimensions of CrO_4^{3-} in $Ca_5(CrO_4)_3OH$ as given in Table IV (*11*). Assuming similar dimensions of the chromate tetrahedra in $Ca_5(CrO_4)_3Cl$, it appears that the electric axis is twisted by about 12° from the center line bisecting the plane between 0(1) and 0(2). It is notable, that the angle between 0(1) and 0(2) has increased from 111° for phosphate to a 115° for chromate, apparently providing a lower energy state for the single electron. A comparable increase of distortion from phosphate to chromate was observed in Ca_2XO_4Cl ($X = P$, Cr) and was attributed to electronic ordering similar to a Jahn-Teller type effect.

Preliminary electron spin resonance studies on $Ca_5(PO_4,CrO_4)_3F$ at liquid helium temperatures indicate the presence of more than one phosphorus site. This suggests that hexagonal ($P6_3/m$) $Ca_5(PO_4)_3F$ undergoes a phase transition somewhere below room temperature analogous to that found in chloroapatite at 200°C. Recently evidence has been presented that such a phase transition occurs at about 140°K (*12*). As the low-temperature ESR spectra of $Ca_5(PO_4,CrO_4)_3F$ are considerably different from the spectra of $Ca_5(PO_4,CrO_4)_3Cl$, the established monoclinic structure of chloroapatite cannot be assumed for the low-temperature phase of fluoroapatite. The low-temperature ESR spectra cannot be interpreted until we determine the structure of the low-temperature phase of $Ca_5(PO_4)_3F$. Work is now in progress to do this by low-temperature X-ray diffraction techniques.

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