

## Electron Spin Resonance of $\text{CrO}_4^{3-}$ in Barium Chloroapatite, $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$

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An electron spin resonance study of Cr(V) substitutional for P in  $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$  shows that barium chloroapatite remains hexagonal down to 4.2°K. The  $g$  and hyperfine ( $^{53}\text{Cr}$ ) principal values observed are:  $g_x = 1.9222$ ,  $g_y = 1.9317$ ,  $g_z = 1.9737$ ,  $A_x = 26.2 \times 10^{-4} \text{ cm}^{-1}$ ,  $A_y = 22.3 \times 10^{-4} \text{ cm}^{-1}$ , and  $A_z = 6.5 \times 10^{-4} \text{ cm}^{-1}$ . The  $\text{CrO}_4^{3-}$  ion is distorted from tetrahedral symmetry with only a mirror plane remaining. The ground state doublet shows the smallest splitting yet observed in an apatite,  $\epsilon \sim 60 \text{ cm}^{-1}$ , with the  $d_{z^2}$  state lowest.

### Introduction

It is well established that "biological" apatite is impure  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  and many physical properties of bone and teeth are determined by the presence of ions substitutionally replacing various sites in the apatite crystals (1, 2). The structures of several apatites have been investigated by X-ray diffraction (3-9). However, these studies cannot determine the local distortion produced by impurities. In order to study local effects we have undertaken an electron spin resonance study of  $\text{CrO}_4^{3-}$  substituted for  $\text{PO}_4^{3-}$  in various  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  analogs. We have shown in previous studies (10-12) that the ESR of the single  $d$  electron on Cr(V) is a sensitive probe of structural changes and local distortions that result when  $\text{Cl}^-$  or  $\text{F}^-$  replaces  $\text{OH}^-$  and  $\text{Sr}^{2+}$  replaces  $\text{Ca}^{2+}$ .

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### Experimental

Single crystals of  $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$  with a small concentration of Cr were grown from the melt using excess  $\text{BaCl}_2$  as flux. The light green, irregularly shaped crystals were identified by X-ray diffraction as  $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$  in the hexagonal phase.

Details of the electron spin resonance measurements have been described elsewhere (11). No ESR signal was observed at room or liquid  $\text{N}_2$  temperatures, but sharp (4-5 G wide) signals with weak  $^{53}\text{Cr}$  hyperfine lines were detected at 4.2°K.

### Results and Discussion

The angular dependence of the ESR spectrum of Cr(V) in  $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$  is shown in Fig. 1 for rotation of the magnetic field about the  $a$ ,  $a^*$ , and  $c$  crystallographic axes. ( $a^*$  is perpendicular to  $a$  and  $c$ .) In hexagonal apatites ( $P6_3/m$ ) all six  $\text{PO}_4^{3-}$  tetrahedra are crystallographically equivalent (3). However, magnetically, they form three sets

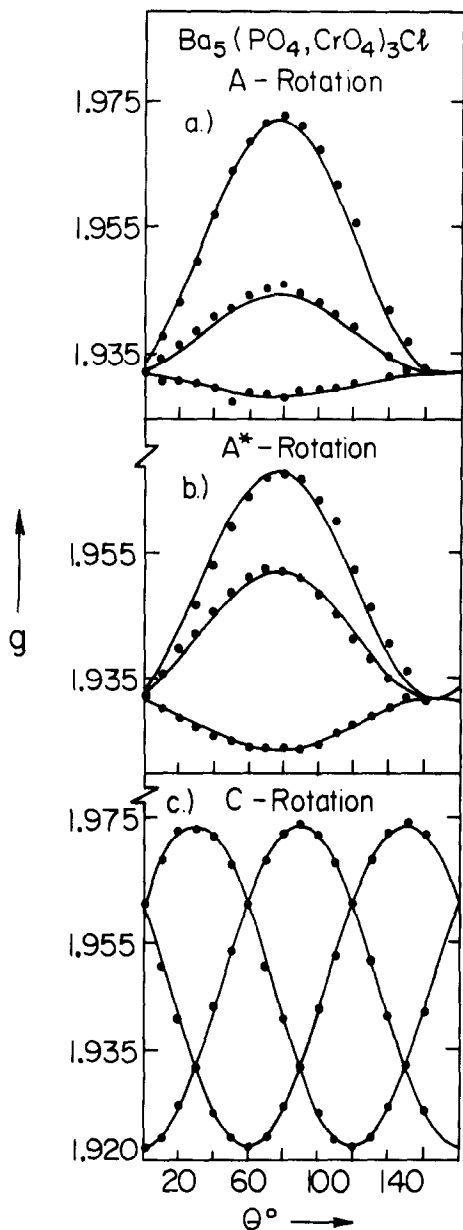


FIG. 1.  $g$  value of the ESR absorption of  $\text{Ba}_5(\text{PO}_4, \text{CrO}_4)_3\text{Cl}$  vs the angle between a crystallographic axis and the magnetic field. (a) Rotation about  $a$  axis,  $H$  parallel to  $a^*$  at  $\theta = 79^\circ$ . (b) Rotation about  $a^*$  axis,  $H$  parallel to  $a$  at  $\theta = 76^\circ$ . (c) Rotation about  $c$  axis,  $H$  parallel to  $a$  at  $\theta = 80^\circ$ . (●) Experimental values; (—) four-parameter fit as described in the text.

of nonequivalent tetrahedra. Thus when  $\text{CrO}_4^{3-}$  is substituted for  $\text{PO}_4^{3-}$  the single  $d$  electron on the Cr(V) gives rise to three ESR signals, each accompanied by four weak hyperfine lines due to  $^{53}\text{Cr}$ . Transition to a lower symmetry monoclinic phase will split the ESR spectrum into six lines. Since only three resonances are observed in any orientation of the crystal, the  $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$  remains hexagonal down to 4.2°K and does not undergo the monoclinic phase transition observed for  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$  (10),  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  (13), and  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  (11).

We have fit the data in Fig. 1 to a  $g$  tensor,

$$g^2 = g_x^2 l^2 + g_y^2 m^2 + g_z^2 n^2, \quad (1)$$

where  $l$ ,  $m$ , and  $n$  are the direction cosines of the magnetic field with respect to the principal axes of the  $g$  tensor. The fit shows the  $\text{CrO}_4^{3-}$  tetrahedron is distorted so that the only element of symmetry left is a mirror plane perpendicular to the  $c$  axis. We find  $g_x = 1.9222$ ,  $g_y = 1.9317$ , and  $g_z = 1.9737$  with an estimated error of  $\pm 0.0005$ .  $g_y$  is parallel to the  $c$  axis and  $g_z$  is rotated an angle  $\theta_g = 10.5 \pm 1.0^\circ$  from the bisector of the angle between the two oxygens lying in the mirror plane. (This bisector is parallel with  $a^*$  for one of the three tetrahedra.)

The hyperfine splitting measured for the  $m_I = \pm \frac{3}{2}$  transitions shows a variation similar to the  $g$  splitting shown in Fig. 1. A fit to the hyperfine tensor (14) yields  $A_x = 26.2 \pm 0.5 \times 10^{-4} \text{ cm}^{-1}$ ,  $A_y = 22.3 \pm 0.5 \times 10^{-4} \text{ cm}^{-1}$ , and  $A_z = 6.5 \pm 1.0 \times 10^{-1} \text{ cm}^{-1}$  with  $A_y$  parallel to the  $c$  axis and  $A_z$  rotated  $\phi = 8.5 \pm 2.0^\circ$  from  $g_z$ . These fitting results are summarized in Table I where a comparison is made with the closely similar case of Cr(V) in  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$  (12).

The energy levels of the single  $d$  electron are split by the tetrahedral symmetry into a ground state doublet and a triplet separated by about  $10^4 \text{ cm}^{-1}$ . Distortion of the chromate tetrahedron by packing effects

TABLE I  
PRINCIPAL  $g$  AND  $A$  VALUES OF  $\text{CrO}_4^{3-}$  IN Ba AND Sr APATITE

	$\text{Ba}_5(\text{PO}_4)_3\text{Cl}$	$\text{Sr}_5(\text{PO}_4)_3\text{Cl}$
$g_x$	$1.9222 \pm 0.0005$	$1.9348 \pm 0.0003$
$g_y$	$1.9317 \pm 0.0005$	$1.9430 \pm 0.0003$
$g_z$	$1.9737 \pm 0.0005$	$1.9822 \pm 0.0003$
$\theta_g$	$10.5 \pm 1.0^\circ$	$12.9 \pm 0.4^\circ$
$A_x (\times 10^{-4} \text{ cm}^{-1})$	$26.2 \pm 0.5$	$26.5 \pm 0.5$
$A_y (\times 10^{-4} \text{ cm}^{-1})$	$22.3 \pm 0.5$	$22.1 \pm 0.5$
$A_z (\times 10^{-4} \text{ cm}^{-1})$	$6.5 \pm 1.0$	$6.7 \pm 0.5$
$\phi$	$8.5 \pm 2.0^\circ$	$8.6 \pm 2.0^\circ$

with neighboring ions in the apatite splits the doublet by an energy  $\varepsilon$  with either  $d_{z^2}$  or  $d_{xy}$  lying lower depending on the nature of the distortion; the anisotropic  $g$  values we observe with  $g_x, g_y < g_z$  are consistent with a  $d_{z^2}$  ground state. X-ray structure studies of various apatites have shown that the phosphate tetrahedra have a stretching distortion along a diagonal of the cube containing the tetrahedron of oxygens with the trigonal axis passing through a P–O bond in the mirror plane. However, a trigonal distortion cannot split the ground state doublet. So an additional small distortion having mirror symmetry is required. The similarity of the resonance parameters in Table I and in particular the correspondence  $g_x < g_y$  and  $A_y < A_x$  indicate the distortions have the same symmetry in both the Ba and Sr apatites.

We have fit the resonance parameters to crystal-field equations (12) assuming an arbitrary distortion with  $xz$  mirror plane symmetry. The results of the fit are compared in Table II to a similar fit for  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ . In Table II  $\xi$  is the spin-orbit coupling constant,  $\Delta E_{yz}$  and  $\Delta E_{xz}$  are energy differences between the ground state and upper triplet states;  $b$  and  $f$  are parameters giving the amount of admixture of the  $d_{x^2-y^2}$  state into the  $d_{z^2}$  ground state and of the  $d_{yz}$  state into  $d_{xy}$ , respectively,  $P = 2.0023 g_n \beta_n \beta_e \langle r^{-3} \rangle_{av}$ ,  $K$

TABLE II  
CRYSTAL-FIELD PARAMETERS OF  $\text{CrO}_4^{3-}$  IN Ba AND Sr APATITE

	$\text{Ba}_5(\text{PO}_4)_3\text{Cl}$	$\text{Sr}_5(\text{PO}_4)_3\text{Cl}$
$\xi/\Delta E_{yz}$	$0.0071 \pm 0.0008$	$0.008 \pm 0.001$
$\xi/\Delta E_{xz}$	$0.0089 \pm 0.0008$	$0.0104 \pm 0.0010$
$\xi/\varepsilon$	$1.21 \pm 0.15$	$0.4 \pm 0.3$
$b$	$0.042 \pm 0.007$	$0.08 \pm 0.02$
$f$	$0.055 \pm 0.010$	$0.036 \pm 0.007$
		$-0.000$
$P (\times 10^{-4} \text{ cm}^{-1})$	$-19.5 \pm 1.0$	$-19.6 \pm 0.6$
$K (\times 10^{-4} \text{ cm}^{-1})$	$-17.5 \pm 0.5$	$-17.6 \pm 0.3$
$\chi$ (a.u.)	$-2.61 \pm 0.07$	$-2.62 \pm 0.06$

is the isotropic hyperfine contact term, and  $\chi$  characterizes the density of unpaired spin at the nucleus (15). The errors in Table II are derived from the change in the fit when the input data are individually varied by their quoted errors.

The crystal-field parameters for the two apatites agree within experimental error except for  $\xi/\varepsilon$ ,  $b$ , and  $f$ . These parameters are determined by the magnitude of the small distortion of the  $\text{CrO}_4^{3-}$  tetrahedron from trigonal symmetry. The value of  $\xi$  is not well known. However, assuming  $\xi$  is the same for  $\text{CrO}_4^{3-}$  in all the apatites and using  $\Delta E_{yz} = 9100 \text{ cm}^{-1}$  obtained from optical absorption (16) in  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$  we estimate  $\xi \approx 73 \text{ cm}^{-1}$ . Then  $\varepsilon \sim 60 \text{ cm}^{-1}$  in  $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ ,  $\varepsilon \sim 180 \text{ cm}^{-1}$  in  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$ , and  $\varepsilon \sim 350 \text{ cm}^{-1}$  in  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ . Thus the distortion of the tetrahedron from trigonal symmetry in  $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$  is by far the smallest for any apatite studied to date, although we have observed smaller distortions of  $\text{CrO}_4^{3-}$  in other hosts (17). There appears to be a regular decrease in the distortion as the size of the divalent ion increases from  $\sim 0.99 \text{ \AA}$  for  $\text{Ca}^{2+}$  to  $\sim 1.13 \text{ \AA}$  for  $\text{Sr}^{2+}$  and  $\sim 1.35 \text{ \AA}$  for  $\text{Ba}^{2+}$ . We are in the process of verifying this trend in the analog apatites of Pb ( $\sim 1.20 \text{ \AA}$ ) and Cd ( $\sim 0.97 \text{ \AA}$ ).

In  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$  we observed an angular dependence of the line width due to a distribution in the size of the doublet splitting. In the  $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$  we observe a much smaller angular dependence with  $\Delta H$  varying from 4.0 to 5.5 G. The crystal-field equations for the parameters in Table II predict that unlike the Sr apatite the doublet splitting parameters make a comparable contribution to all three principal axes so little angular dependence is expected. This does not imply that the distribution of splittings is absent in  $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$ . In fact the linewidth is comparable to the maximum linewidth in  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$  (4.3 G). Thus it appears that the linewidth in  $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$  is likewise determined by a roughly 5% spread in the doublet splitting.

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