JOURNAL OF SOLID STATE CHEMISTRY 29, 1–7 (1979)

Electron Spin Resonance of CrO_4^{3-} in Strontium Chloroapatite, $Sr_5(PO_4)_3Cl$

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Received July 3, 1978

The electron spin resonance of CrO_4^{3-} has been studied at 4.2°K in single crystals of $Sr_5(PO_4)_3Cl$. It is shown that strontium chloroapatite has the hexagonal $P6_3/m$ structure down to 4.2°K. No phase transition to the monoclinic $P2_1/b$ symmetry, observed in the $Ca_5(PO_4)_3Cl$ and $Ca_5(PO_4)_3OH$ analogs, has been found in $Sr_5(PO_4)_3Cl$. The principal values of g and A tensors are $g_x = 1.9348$, $g_y = 1.9430$, $g_z = 1.9822$, $A_x = 26.5 \times 10^{-4}\ \text{cm}^{-1}$, $A_y = 22.1 \times 10^{-4}\ \text{cm}^{-1}$, and $A_z = 6.7 \times 10^{-4}\ \text{cm}^{-1}$. The principal axes of g and A are found to be rotated by 8.6° relative to each other about the common y axis which is parallel to the crystallographic c axis. The ground state of the d^1 electron is d_{z^2} with considerable admixture of the higher-level d orbitals. The difference in the orientation of the x and z principal axes of the g and A tensors is due to this admixture. Crystal field parameters are extracted assuming a distortion of the oxygen tetrahedron which leaves only xz mirror plane (C_s) symmetry. An angular dependence of the linewidth is observed which is attributed to a distribution of distortions within the crystal.

Introduction

This electron spin resonance study of CrO_4^{3-} in strontium chloroapatite $Sr_5(PO_4)_3Cl$ was undertaken as part of our ongoing research program to characterize the structural properties of apatites. Strontium is known to substitute for calcium in calcium hydroxide phosphate, $Ca_5(PO_4)_3OH$, the major inorganic component of bone and teeth. It has been suggested that partial replacement of calcium by strontium in the apatite structure inhibits the formation of dental caries (*1*). There is substantial evidence that substitutional ions affect the physical properties of "biological apatite" through the local atomic changes they introduce in the crystal. Therefore, it is important to understand the structural differences between strontium and calcium apatites on an atomic scale.

The existence of a monoclinic $P2_1/b$ phase in synthetic calcium chloroapatite has been demonstrated (*2*) by measurements at 4.2°K of the ESR spectra of CrO_4^{3-} substituted in small quantities for the phosphate in single crystal $Ca_5(PO_4)_3Cl$. Measurement of the angular dependence of the ESR spectra of chromium in the pentavalent state was thus shown to be an extremely sensitive probe for detecting small structural differences.

Experimental

Single crystals of $Sr_5(PO_4, CrO_4)_3Cl$ were flux grown in a manner similar to that used to prepare $Ca_5(PO_4, CrO_4)_3Cl$ (*2*). The crystals were in the shape of needlelike irregular hexagonal prisms of light green color. A single crystal of $Sr_5(PO_4)_3Cl$ with about 0.5 mole% CrO_4^{3-} content was examined

0022-4596/79/070001-07$02.00/0

Printed in Great Britain

and oriented by X-ray diffraction, which confirmed the formation of $Sr_5(PO_4, CrO_4)_3Cl$ in a hexagonal phase at room temperature. Electron spin resonance spectra were obtained as described previously (*3*). No ESR was observed at room temperature or at liquid N_2 temperature, but sharp absorption lines were detected at 4.2°K.

Results and Preliminary Analysis

The electron resonance spectra of the unpaired *d* electron on CrO_4^{3-} substituted into $Sr_5(PO_4)_3Cl$ show three angular dependent resonance lines plus weaker hyperfine lines (Fig. 1). The X-ray structure determination of $Sr_5(PO_4)_3Cl$ has not been carried out, but $Sr_5(PO_4)_3OH$ (*4*) has been found to be isomorphous with hexagonal $Ca_5(PO_4)_3OH$, having $P6_3/m$ symmetry. Assuming this symmetry for the $Sr_5(PO_4)_3Cl$, there are six crystallographically equivalent PO_4^{3-} tetrahedra in two sets of three on mirror planes at $z = \frac{1}{4}$ and $\frac{3}{4}(6(h)$ in $P6_3/m)$. These tetrahedra occur in pairs that are related by inversion and cannot be distinguished by ESR. Thus in $P6_3/m$ there are three magnetically nonequivalent ions, geometrically identical, but differing by the orientations of their electric axes with respect to the unique crystal directions.

In $Ca_5(PO_4, CrO_4)_3Cl$ the helium temperature ESR spectra were observed (*2*) to be split into six lines which indicated a phase transition from hexagonal $P6_3/m$ to monoclinic $P2_1/b$ with six magnetically nonequivalent chromium sites. Subsequent X-ray studies by Mackie *et al.* (*5*) have shown that the monoclinic phase in $Ca_5(PO_4)_3Cl$ is stable up to room temperature. Our failure to observe any splitting in $Sr_5(PO_4, CrO_4)_3Cl$ indicates that the hexagonal-to-monoclinic phase transition does not occur down to 4.2°K.

Figure 2 shows the observed angular variations of the three lines as the magnetic field is rotated about the *a*, a^*, and *c* crystal axes. (a^* is the axis perpendicular to *a* and *c*.) The observed resonance field *H* has been converted to a *g* value using the relation $g = h\nu/\beta_e H$, where *h* is Planck's constant, β_e is the Bohr magneton, and ν is the microwave frequency. We have fit these data to a *g* tensor

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

where *l*, *m*, and *n* are the direction cosines of the magnetic field with respect to the principal axes of the *g* tensor. We find that g_x and g_z lie in the aa^* mirror plane with g_y along the *c* axis and g_z is rotated an angle α away from the a^* axis for P_I [which is the phosphorus site at $x, y, \frac{1}{4}$ of $6(h)$ in $P6_3/m$]

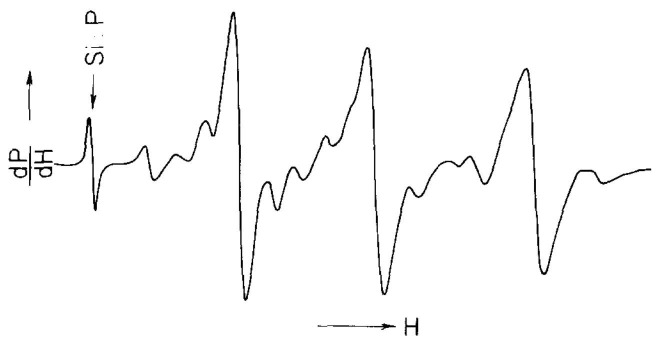

FIG. 1. First derivative of the electron spin resonance spectra for $Sr_5(PO_4, CrO_4)_3Cl$ for H lying in the plane aa^*.

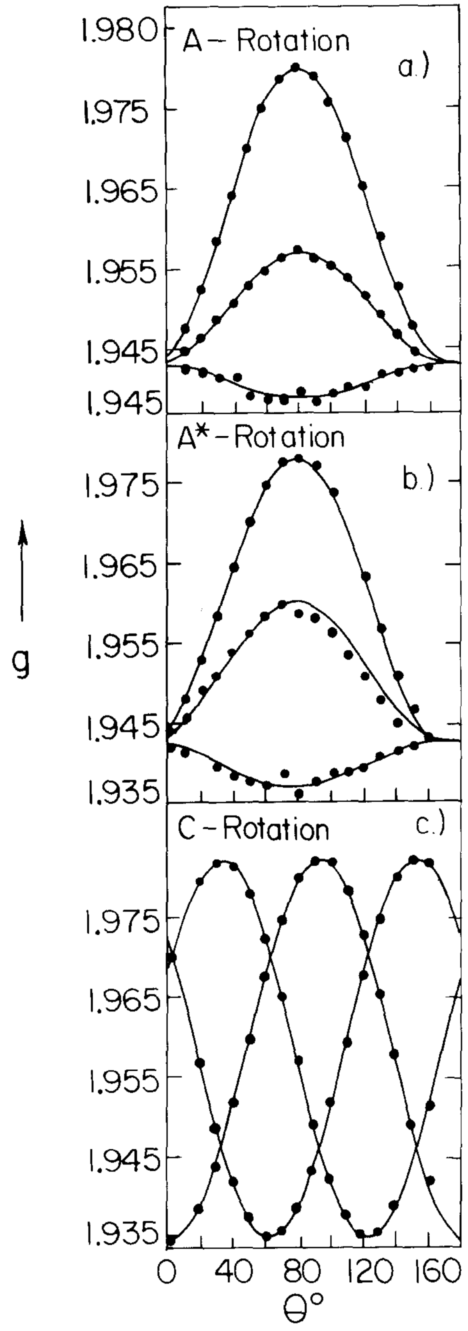

FIG. 2. g value of the ESR absorption of $Sr_5(PO_4, CrO_4)_3Cl$ vs the angle between a crystallographic axis and the magnetic field. (a) Rotation about a axis, H parallel to a^* at $\theta = 80°$. (b) Rotation about a^* axis, H parallel to a at $\theta = 79°$. (c) Rotation about c axis, H parallel to a at $\theta = 76°$. ●, Experimental values; ——, four-parameter fit as described in the text.

(*4*). For the other two P sites g_z is rotated by $\alpha + 60$ and $\alpha + 120$. The solid lines in Fig. 2 are obtained from Eq. (1) using the four parameters:

$$g_x = 1.9348 \pm 0.0003,$$
$$g_y = 1.9430 \pm 0.0003,$$
$$g_z = 1.9822 \pm 0.0003,$$
$$\alpha = 12.9 \pm 0.4°.$$

The maximum discrepancy between this four-parameter fit to all of the data and least-square fits to the individual lines is $\Delta g = \pm 0.0003$.

The hyperfine splitting was measured for the $m_I = \pm\frac{3}{2}$ transitions, and the data (Fig. 3) were fit to an expression (*6*) for gA similar to Eq. (1). The effects of a slight misalignment of the crystal are clearly visible in Fig. 3. The solid lines in Fig. 3 were calculated using the four parameters:

$$|A_x| = (26.5 \pm 0.5) \times 10^{-4}\ \text{cm}^{-1},$$
$$|A_y| = (22.1 \pm 0.5) \times 10^{-4}\ \text{cm}^{-1},$$
$$|A_z| = (6.7 \pm 0.5) \times 10^{-4}\ \text{cm}^{-1},$$
$$\phi = 8.6 \pm 2.0°,$$

where ϕ is the angle A_z makes with g_z. A_y lies along the c axis. For P_I, A_z makes an angle of 4° with the a axis. Figure 4 shows these angular relations and for comparison shows the location of the oxygens in the P_I tetrahedron in $Sr_5(PO_4)_3OH$.

The linewidth of the ESR has an angular dependence that closely follows the g variation. Measurement[1] of the linewidth is complicated by unresolved hyperfine lines near A_z, but the data are consistent with a linewidth of 1.9 ± 0.5 G when H is along the c axis (parallel with g_y) and 4.3 ± 0.5 G when H lies in the aa^* plane.

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[1] In order to measure the weak hyperfine lines, the data were taken at high power where the central line is partially saturated and thus comparable in size to the hyperfine lines.

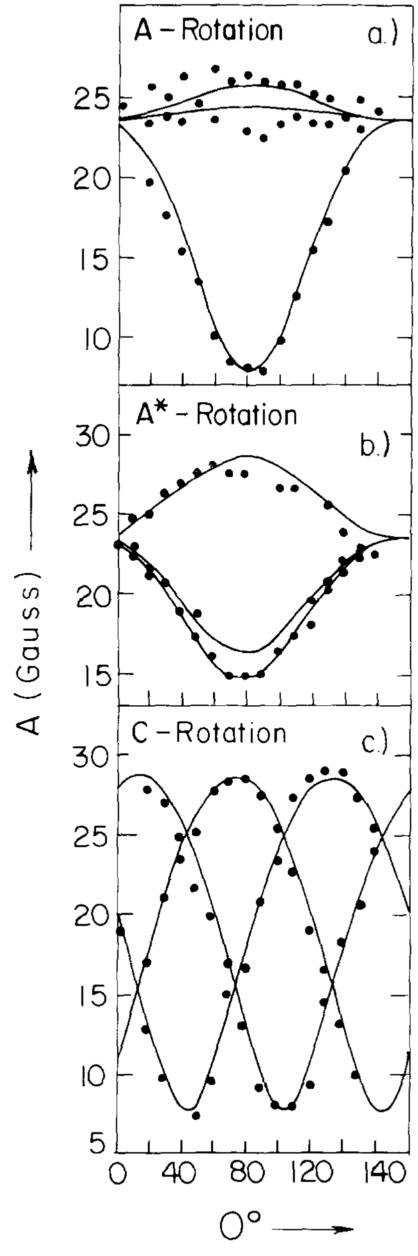

FIG. 3. Hyperfine constant (gauss) of ^{53}Cr in $Sr_5(PO_4, CrO_4)_3Cl$ vs the angle between a crystallographic axis and the magnetic field. (a) Rotation about *a* axis, *H* parallel to *a** at $\theta = 80°$. (b) Rotation about *a** axis, *H* parallel to *a* at $\theta = 79°$. (c) Rotation about *c* axis, *H* parallel to *a* at $\theta = 76°$. ●, Experimental values; ——, four-parameter fit as described in the text.

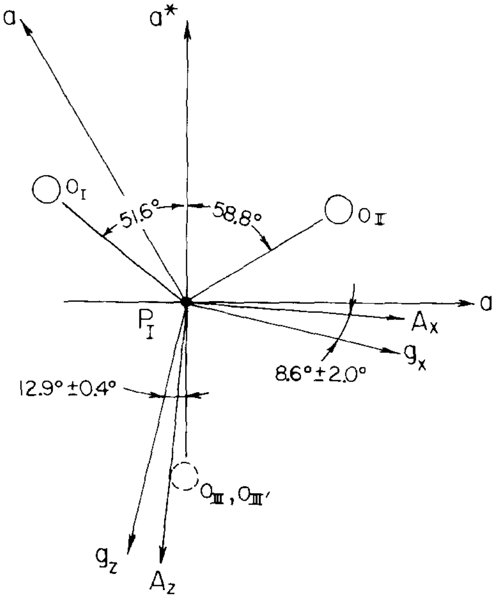

FIG. 4. Orientation of the *g* and *A* tensors in the *aa** plane of $Sr_5(PO_4)_3Cl$. g_y and A_y are perpendicular to the plane. The locations of the neighboring oxygens as determined by X rays for $Sr_5(PO_4)_3OH$ are shown for comparison.

Theory and Discussion

The energy levels of the single *d* electron on CrO_4^{3-} are split by the tetrahedral symmetry into a ground state doublet and a triplet separated by $\sim 10^4\,\mathrm{cm}^{-1}$. Distortion of the phosphate tetrahedron by packing effects with neighboring ions in the apatite splits the doublet by an energy ε 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 with significant distortion (*7*). If the distortion leaves any symmetry element, the principle axes of the *g* tensor must be oriented in a manner consistent with that symmetry. For a d_{z^2} wavefunction the $\hat{z}$ axis will point along the bisector of the angle between oxygens. For tetrahedral symmetry there are three possible orientations for $\hat{z}$. However, with distortion, the bisector which provides minimum overlap of d_{z^2} with the oxygen orbitals will be chosen. In the apatites the X-ray structure shows that to a first approximation the distortion of the PO_4^{3-} is trigonal; the angles between O_I and the other oxygens are larger than 109.5°, and the remaining three O–O angles are smaller. $\hat{z}$ will then bisect the largest of the angles less than 109.5°. For $Sr_5(PO_4)_3OH$ the X-ray data show (*4*) that $\hat{z}$ should bisect O_{III}–$O_{III'}$. Assuming the same is true for the chloroapatite, we see in Fig. 4 that g is rotated by 12.9° from $\hat{z}$ in the ab plane. Thus the only element of symmetry left in the CrO_4^{3-} tetrahedron in $Sr_5(PO_4)_3Cl$ is a mirror plane (C_s). In previous analyses (*2, 8*) of CrO_4^{3-} in Ca_2PO_4Cl and $Ca_5(PO_4)_3Cl$ high symmetry (D_{2d} or C_{2v}) was assumed for the tetrahedron which amounts to ignoring the rotation of g_z from $\hat{z}$.

Ezzeh and McGarvey (*9*) have calculated the elements of the g and hyperfine tensors for a d^1 electron in a d_{z^2} ground state with xz mirror symmetry and we shall follow their treatment. However, in their calculation they have neglected terms of order $\eta_2{}^2$, where $\eta_2 = \xi/\varepsilon$ is the ratio of the spin–orbit coupling parameter to the crystal field splitting of the doublet. In the present case $\eta_2 \sim 0.4$ so we have extended the calculation to include all terms in η_2.

The crystal distortion admixes the d wavefunctions so with xz mirror symmetry the doublet states are taken to be

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

$$\psi_{xy} = ed_{xy} + fd_{yz}, \tag{3}$$

where $a \sim 1$, $e \sim 1$, and b, c, and $f \ll 1$. The y axis is constrained to be perpendicular to the xz mirror plane. There is no constraint on the orientation of $\hat{z}$ in the plane so we choose the orientation for which $c = 0$. Ezzeh and McGarvey (*9*) noted that for $BaSeO_4$ this orientation corresponds to the principal axes of the hyperfine tensor. We find this is also true for the present case, although there is no requirement that it be generally true. Using these coordinate axes we find the components of the g and A tensors to be

$$\begin{aligned} g_{xx} &= g_0 - 6f^2\eta_2 - 4b^2\eta_2^2 \\ &\quad - 6\eta_1\left[1 + \frac{2}{3^{1/2}}b(1+\eta_2)\right], \end{aligned} \tag{4}$$

$$\begin{aligned} g_y &= g_0 - (3f^2 + 4b^2)\eta_2^2 \\ &\quad - 6\eta_3\left[1 - \frac{2}{3^{1/2}}b(1+\eta_2)\right], \end{aligned} \tag{5}$$

$$g_{zz} = g_0 - 8b^2\eta_2 - 3f^2\eta_2^2, \tag{6}$$

$$g_{xz} = 2(3^{1/2})bf\eta_2(2-\eta_2), \tag{7}$$

$$\begin{aligned} A_{xx} &= -K - \frac{2P}{7}\left[1 - 2b^2 - \frac{3}{2}f^2\eta_2^2 + 21f^2\eta_2\right. \\ &\quad + 2(3^{1/2})b(1+\eta_2) + \frac{3}{2}\eta_3 + 21\eta_1 \\ &\quad \left.\times\left(1 + \frac{2b}{3^{1/2}}\right) + 15(3^{1/2})b\eta_1\eta_2\right], \end{aligned} \tag{8}$$

$$\begin{aligned} A_y &= -K - \frac{2P}{7}\left[1 - 2b^2 + \frac{3}{2}f^2\eta_2\right. \\ &\quad - 2(3^{1/2})b(1+\eta_2) + 21\eta_3\left(1 - \frac{2}{3^{1/2}}b\right) \\ &\quad \left.+ \frac{3}{2}\eta_1 - 15(3^{1/2})b\eta_1\eta_2\right], \end{aligned} \tag{9}$$

$$\begin{aligned} A_{zz} &= -K + \frac{4P}{7}[1 - 2b^2 - 2b^2\eta_2^2 \\ &\quad + \frac{3}{4}\eta_2 f^2 - 14b^2\eta_2 + \frac{3}{4}(\eta_3 + \eta_1)], \end{aligned} \tag{10}$$

$$A_{xz} = -\frac{3^{1/2}}{7}Pfn_2[1 - 14b - b\eta_s], \tag{11}$$

where

$$g_0 = 2.0023,$$

$$P = g_0 g_N \beta_e \beta_N \langle r^{-3}\rangle_{av},$$

$$\eta_1 = \xi/\Delta E_{yz},\ \eta_2 = \xi/\epsilon,\ \eta_3 = \xi/\Delta E_{xz},$$

K is the isotropic Fermi contact term, β_e and β_N are the Bohr and nuclear magnetons, and ξ is the spin–orbit coupling constant. We have required A and g to be symmetric. In the calculation of g we have kept terms of order b^2 or $b\eta_3$ and set $b\eta_3 = b\eta_1$ but have made no assumption about the size of η_2. In the hyperfine components where the experimental errors are larger, we have dropped terms of order $b\eta_3$ except where the numerical coefficient in front is large. Note that g_y and A_y are principal values of the tensors but g_{xx}, g_{zz}, A_{xx}, and A_{zz} are not unless g_{xz} or A_{xz} is zero. Experimentally it is a good approximation to take g_{xx} (or g_{zz}) to be the value of g when H is along the x (z) axis, which in the present case is the x (z) principal axis of A. g_{xz} is given by

$$\begin{aligned} g_{xz} &= \tfrac{1}{2}(g_z - g_x)\sin 2\phi \\ &= \tfrac{1}{2}(g_{zz} - g_{xx})\tan 2\phi, \qquad (12) \end{aligned}$$

where g_z and g_x are principal values and ϕ is the angle g_z is rotated from the z axis.

The seven unknown parameters (η_1, η_2, η_3, K, P, b, and f) can be obtained from Eqs. (2)–(10) and (12) by iteration. In order to obtain a fit it was necessary for all three A components to have the same sign. In order to obtain a negative P (since $g_N < 0$ for ^{53}Cr) we took $A_{zz} > 0$. The results of the fit are given in Table I. The errors in the table are derived from the change in the fit when the input data are varied by their quoted errors. Most of the error comes from uncertainty in the components of A and in particular in the difference $A_y - A_x$.

The parameters in Table I clearly show the importance of assuming C_s symmetry. f would have been zero if C_{2v} symmetry had been assumed. The large value of η_2 indicates small splitting of the ground state doublet due to the distortion of the tetrahedron. This does not imply that the distortion is small. X-ray studies of PO_4^{3-} in various apatite structures show a basically trigonal distortion. But in C_{3v} the ground state doublet is not split although the triplet is. Thus the doublet splitting only reflects the additional distortion from C_{3v}.

TABLE I

CRYSTAL FIELD PARAMETERS FOR CrO_4^{3-} IN $Sr_5(PO_4)_3Cl$

P (10^{-4} cm^{-1})	-19.6 ± 0.6
K (10^{-4} cm^{-1})	-17.6 ± 0.3
η_1	0.008 ± 0.001
η_2	$0.4^{+0.3}_{-0.1}$
η_3	0.0104 ± 0.0010
b	0.08 ± 0.02
f	$0.036^{+0.007}_{-0.00}$

The trigonal distortion does show up in the value of $\eta_3 - \eta_1$, which is much larger than one would expect if the triplet splitting were simply due to the distortion producing η_2. Optical absorption data are not available for comparison with our values of η_1 and η_3. Optical data by Banks *et al.* (*10*) on CrO_4^{3-} in $Ca_5(PO_4)_3Cl$ show an absorption peak at 9100 cm^{-1} which can be associated with η_1 and a series of peaks extending up to 20,000 cm^{-1}. If the optical spectrum of Sr–apatite is similar, one of these peaks should correspond to η_3. However, identification is not straightforward since a molecular orbital calculation (*9*) of the effects of *d–p* hybridization shows that the corrections to η_1 and η_3 are different. We have not attempted a MO calculation since the angular dependent line broadening, the small g_N, and low abundance of ^{53}Cr make the errors in our starting parameters too large to obtain meaningful results. Assuming $\Delta E_{yz} =$ 9100 cm^{-1} our fit yields $\xi = 73$ cm^{-1} for the spin orbit parameter and $\varepsilon = 180$ cm^{-1} for the doublet splitting which indicates the distortion of the CrO_4^{3-} tetrahedra in $Sr_5(PO_4)_3Cl$ is smaller than in $Ca_5(PO_4)_3Cl$ where $\varepsilon = 350$ cm^{-1}. (*2*)

The parameter

$$\begin{aligned} \chi &= \frac{4\pi}{S}\left(\psi\middle|\sum_i \delta(r_i)S_{zi}\middle|\psi\right) \\ &= -\tfrac{3}{2}(hca_0^3/g_0 g_N \beta_e \beta_N)K \qquad (13) \end{aligned}$$

defined by Abragam *et al.* (*11*) which characterizes the density of the unpaired spin at the nucleus is easily calculated from K. We find $\chi = -2.62 \pm 0.06$ a.u. It has been found that χ is nearly constant for a given configuration of similar ligands (*12, 13*). Thus our results seem to be in disagreement with those of Banks *et al.* (*8*), who found $K = -10.3 \times 10^{-4}$ cm^{-1}, $P = -31.0 \times 10^{-4}$ cm^{-1}, and $\chi = -1.54$ a.u. for CrO_4^{3-} in Ca_2PO_4Cl. Their analysis, however, was based on incomplete data and a fit for $Az > 0$ may be possible. On the other hand our value for P is much lower than the value of $P = -29.5 \times 10^{-4}$ cm^{-1} or $P = -34.6 \times 10^{-4}$ cm^{-1} obtained for Cr^{+1} and Cr^{2+}, respectively, from Freeman and Watson's (*14*) unrestricted Hartree–Foch calculations of $\langle r^{-3} \rangle_{av}$.

We attribute the angular dependence of the ESR line width to small variations in the size of the distortion of the tetrahedra from C_{3v} symmetry, possibly due to random strains. Substituting the values for b, f, and η_2 from Table I into the terms involving these parameters in Eqs. (4)–(6):

$$-\Delta g_{xx} = 6f^2\eta_2 + 4b^2\eta_2^2 = 0.027,$$

$$-\Delta g_y = 3f^2\eta_2^2 + 4b^2\eta_2^2 = 0.011,$$

$$-\Delta g_{zz} = 8b^2\eta_2 + 3f^2\eta_2^2 = 0.027.$$

We assume each Δg changes by $\pm s\Delta g$ due to random changes in η_2, b, and f. This shows up as a line broadening

$$\Delta H_s = (2s\Delta g)H/g,$$

where $H \simeq 3200$ G is the applied field. Then if ΔH_0 is the intrinsic linewidth, the total angular dependent width is

$$\Delta H = \Delta H_0 + 2s\Delta gH/g.$$

We can then fit the observed widths of 4.3 G in the xz plane and 1.9 G along the c (y) axis with $s = 4.5\%$ and $\Delta H_0 = 0.4$ G. Although a ±4.5% distribution seems large it must be remembered this is not the total distortion but the additional distortion from trigonal symmetry.

Acknowledgments

This research received support from the Busch Memorial Fund and the Research Council, Rutgers University, New Brunswick, New Jersey. Helium gas supplied by the Office of Naval Research.

References

1. M. E. J. CURZON, B. L. ADKINS, B. G. BIBBY, AND F. L. LOSEE, *J. Dent. Res.* **49**, 526 (1970).

2. E. BANKS, M. GREENBLATT, AND B. R. MCGARVEY, *J. Solid State Chem.* **3**, 308 (1971).

3. M. GREENBLATT AND J. H. PIFER, *J. Chem. Phys.* **66**, 559 (1977).

4. K. SUDARSANAN AND R. A. YOUNG, *Acta Crystallogr. Sect. B* **28**, 3668 (1972).

5. P. E. MACKIE, J. C. ELLIOTT, AND R. A. YOUNG, *Acta Crystallogr. Sect. B* **28**, 1840 (1972).

6. A. ABRAGAM AND B. BLEANEY, "Electron Paramagnetic Resonance of Transition Ions," p. 170, Oxford Univ. Press (Clarendon), London/New York (1970).

7. B. R. MCGARVEY, "Electron Spin Resonance of Metal Complexes," Plenum, New York (1969).

8. E. BANKS, M. GREENBLATT, AND B. R. MCGARVEY, *J. Chem. Phys.* **47**, 3772 (1967).

9. C. EZZEH AND B. R. MCGARVEY, *J. Chem. Phys.* **61**, 2675 (1974).

10. E. BANKS, M. GREENBLATT, AND S. HOLT, unpublished; C. ROSENBLUM AND S. L. HOLT, *in* "Transition Metal Chemistry" (R. Carlin, Ed.), Vol. 7, pp. 108–110, Dekker, New York, 1972.

11. A. ABRAGAM, J. HOROWITZ, AND M. H. L. PRYCE, *Proc. Roy. Soc. Ser. A* **230**, 169 (1955).

12. S. GESCHWIND, *J. Appl. Phys.* **36**, 920 (1965).

13. B. R. MCGARVEY, *J. Phys. Chem.* **71**, 51 (1967).

14. A. J. FREEMAN AND R. E. WATSON, *in* "Magnetism" (G. T. Rado and H. Suhl, Eds.), Vol. IIA, p. 167, Academic Press, New York (1965).