

In the case of heavy saturation,

$$T_1 \gamma^2 H_1^2 g(\nu_1) \hbar^2 (\Delta \nu_1)^2 / \bar{H}_0^2 \gg 1, \quad I_{z \text{ st}} = \hbar \Delta \nu_1 (H_{ss}^0)_{\text{st}} / H_0^2,$$

and the absorption line observed will be given by the relation

$$P(\nu_2, H_2) = \hbar \nu_2 \gamma^2 H_2^2 I_{z \text{ st}} \times \frac{1}{2} g(\nu_2) (1 - \Delta \nu_2 / \Delta \nu_1). \quad (4)$$

As seen from Eq. (4), for a Gaussian absorption line $g(\nu_2)$, the position of the line maximum will be accounted for by the expression

$$\Delta \nu_2 / \Delta \nu_1 = \frac{1}{2} - \left(\frac{1}{4} + \langle (\Delta \nu)^2 \rangle / (\Delta \nu_1)^2 \right)^{1/2}.$$

Here $\langle (\Delta \nu)^2 \rangle$ is the second moment of the absorption line in the absence of saturation. This result shows agreement with experimental data both in displacement and in the order of magnitude.

For the case of $H_1 \sim H_{\text{loc}}$ the distribution function of the spin system is³

$$\rho = c \exp \left(- \frac{\hbar \Delta \nu_1 I_z + (\mu H_1 / 2I)(I^1 + I^{-1}) + H_{ss}^0}{kT^*} \right).$$

³ A. G. Redfield, Phys. Rev. **98**, 1797 (1955).

For a stationary case the T^* value will be

$$\frac{1}{T^*} = \frac{1}{T_0} \left(1 + \frac{\nu_0 \Delta \nu_1}{(\Delta \nu_1)^2 + \gamma^2 H_1^2 / 4\pi^2 + H_0^2 / \hbar^2} \right).$$

It may be seen that in passing to a system of coordinates rotating together with H_1 , the rf field H_2 will induce transitions between Hamiltonian levels $\hbar \Delta \nu_1 I_z + (H_1 / 2I)(I^1 + I^{-1}) + H_{ss}^0 = H$, the energies of which differ by $\hbar(\nu_2 - \nu_1)$. Thus, by analogy with equations for ordinary resonance (see Van Vleck⁴), we may write for the absorbed energy of field H_2 :

$$P(\nu_2, H_2) = \hbar \nu_2 \gamma^2 H_2^2 I_{z \text{ st}} (1 - \Delta \nu_2 / \Delta \nu_1) G(\nu_1 - \nu_2),$$

$$G(\nu_1 - \nu_2) = \int_{-\infty}^{+\infty} dt e^{2\pi i(\nu_1 - \nu_2)t} \text{Spur } I^1 e^{iHt} I^{-1} e^{-iHt} / \text{Spur } I^1 I^{-1}. \quad (5)$$

The position of the $G(\nu)$ line maximum is determined by the first moment of this line. Direct calculation gives $\int_{-\infty}^{+\infty} \nu G(\nu) d\nu = \Delta \nu_1$. The second and fourth moments of the $G(\nu)$ line are characteristic of its shape and may be calculated by the Van Vleck method.⁴

⁴ J. Van Vleck, Phys. Rev. **74**, 1168 (1948).

Electron Spin Resonance of a Center in Calcium Fluorophosphate

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A spin-resonance center whose concentration is sensitive to x irradiation has been observed in synthetic calcium fluorophosphate crystals. It shows an electron spin of 1/2 and hyperfine interaction with two equivalent F^{19} nuclei. Arguments are presented which lead to its identification as an O^- ion occupying an F^- site.

I. INTRODUCTION

CALCIUM halophosphate, $3[\text{Ca}_3(\text{PO}_4)_2] \cdot \text{CaX}_2$, where X represents Cl or F or a mixture of the two, occurs widely in nature as the mineral apatite. Synthetic microcrystals containing small additions of manganese and antimony¹ are the most common fluorescent lamp phosphors. Recently large single crystals have been successfully grown from the melt by the Kryopoulos technique.² Irradiation with far ultraviolet and x ray has been found to create optical absorption bands in the near ultraviolet, visible, and infrared spectral regions.³ The availability of these crystals and the possibility of producing color centers

have prompted us to investigate defects in the apatite structure using electron spin resonance. In the present paper we discuss a resonant center in calcium fluorophosphate which we believe to be O^- occupying a F^- site. Subsequently, we plan to report on centers involving impurities, such as manganese, which play a role in luminescent processes.

II. RESULTS

Synthetic single crystals of calcium fluorophosphate were examined in a spin-resonance spectrometer which has been described previously.⁴ A spectrum observed in most crystals is shown in Fig. 1. For the applied magnetic field H parallel to the hexagonal (c) axis the spec-

¹ H. G. Jenkins, A. H. McKeag, and P. W. Ranby, J. Electrochem. Soc. **96**, 1 (1949).

² P. D. Johnson, J. Electrochem. Soc. **108**, 159 (1961).

³ P. D. Johnson, J. Appl. Phys. **32**, 127 (1961).

⁴ G. W. Ludwig and H. H. Woodbury, Phys. Rev. **113**, 1014 (1959); H. H. Woodbury and G. W. Ludwig, *ibid.* **117**, 102 (1960).

trum is clearly resolved into three components of relative intensity 1:2:1. As the magnetic field is rotated toward a direction perpendicular to the c axis, the pattern moves and the separation between the components decreases. For H in the plane perpendicular to the c axis the spectrum is isotropic and shows no resolved structure.

Three lines of relative intensity 1:2:1 are to be expected if the resonant center involves two equivalent nuclei having spin 1/2. To decide whether this explanation is the correct one the spectrum was investigated by the electron-nuclear double resonance (ENDOR) technique developed by Feher.⁵ One of the two sets of ENDOR transitions which were detected is shown in Fig. 2. Analysis of this set indicates that the structure in Fig. 1 indeed represents hyperfine interaction with nuclei of spin 1/2. Moreover, the nuclear g factor determined from these transitions identifies the two equivalent nuclei as F^{19} . The second set of ENDOR transitions corresponds to hyperfine interaction, too weak to be resolved in Fig. 1, with P^{31} , as shown by the nuclear g factor.

The spin resonance and the F^{19} ENDOR transitions can be described in terms of the following spin Hamiltonian:

$$\mathcal{H} = \beta[g_{11}S_zH_z + g_{\perp}(S_xH_x + S_yH_y)] + \sum_{i=1,2} [-\gamma_F\beta_N\mathbf{H}\cdot\mathbf{I}_i + A_F S_z I_{iz} + B_F(S_x I_{ix} + S_y I_{iy})]. \quad (1)$$

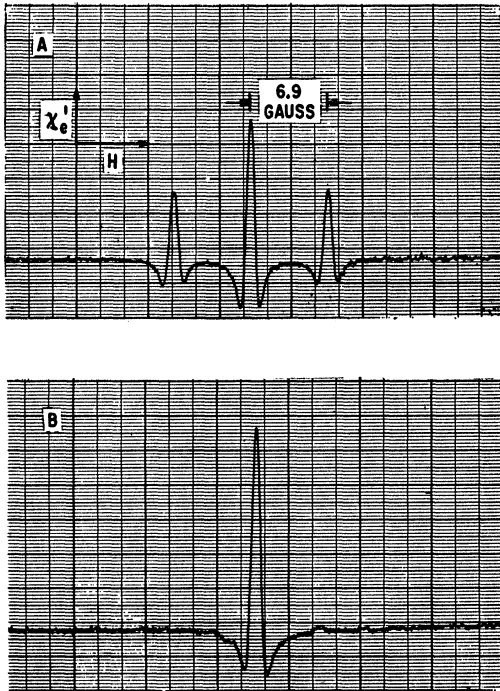


FIG. 1. Spin resonance spectrum of a center in calcium fluorophosphate with the spectrometer tuned to dispersion (A) $H\parallel c$; (B) $H\perp c$. The pattern is centered about different values of field in (A) and (B).

⁵ G. Feher, Phys. Rev. 114, 1219 (1959).

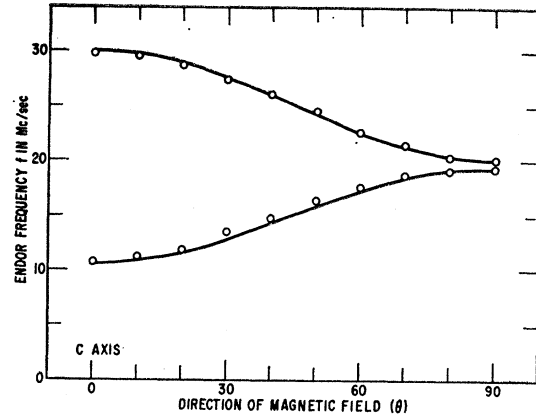


FIG. 2. The angular dependence of the ENDOR transitions of F^{19} . The solid lines represent Eq. (4) using the values for parameters given in (5).

Here g_{11} and g_{\perp} are the g factors along and at right angles to the c axis, while γ_F , A_F , and B_F are the nuclear g factor and hyperfine interaction parameters, respectively, of the F^{19} nuclei. Assuming $|\beta\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{H}| \gg |\gamma_F\beta_N\mathbf{H}\cdot\mathbf{I}_i| \gg |A_F S_z I_{iz} + B_F(S_x I_{ix} + S_y I_{iy})|$, the energy levels appropriate to (1) are given approximately by⁶

$$W_{M,m} = g\beta HM + m\{\gamma\beta_N H - M[(g_{11}/g)A_F \cos^2\theta + (g_{\perp}/g)B_F \sin^2\theta]\}, \quad (2)$$

where $g = (g_{11}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta)^{1/2}$, m is the sum of the quantum numbers m_i of the two fluorine nuclei and θ is the angle between H and the c axis. The M to $M-1$ spin resonance transition is described by

$$h\nu = g\beta H - m[(g_{11}/g)A_F \cos^2\theta + (g_{\perp}/g)B_F \sin^2\theta]. \quad (3)$$

This transition is split into three components corresponding to the three possible values of $m = \sum_{i=1,2} m_i$ for $I=1/2$. The selection rule for ENDOR transitions is $\Delta M = \Delta m_i = 0$ (for $i \neq j$); $\Delta m_j = \pm 1$. The frequency f of such transitions is

$$hf = |\gamma_F\beta_N H - M[(g_{11}/g)A_F \cos^2\theta + (g_{\perp}/g)B_F \sin^2\theta]|. \quad (4)$$

From our measurements, we find

$$\begin{aligned} S &= 1/2, \\ g_{11} &= 2.0012, \quad A_F = \pm 6.5 \times 10^{-4} \text{ cm}^{-1}, \\ g_{\perp} &= 2.0516, \quad B_F = \pm 0.3 \times 10^{-4} \text{ cm}^{-1}. \end{aligned} \quad (5)$$

The hyperfine interaction with neighboring P^{31} nuclei has not been fully investigated. It is slightly anisotropic, and has a strength of about $0.3 \times 10^{-4} \text{ cm}^{-1}$.

As-grown crystals typically contain on the order of 10^{16} resonant centers/cm³. The concentration has been increased to $\sim 3 \times 10^{17}$ /cm³ by irradiation of the crystals with 40-keV x rays.

⁶ See the Appendix and Eq. (7) of H. H. Woodbury and G. W. Ludwig, Phys. Rev. 124, 1083 (1961).

III. DISCUSSION

Any model for the resonant center should be consistent with the following experimental information:

(a) The spectrum is isotropic about the c axis, implying that the c axis is a threefold or higher axis of symmetry of the center. (b) Two F^{19} nuclei, whose axis is the c axis, are involved in the center. (c) g_1 is considerably larger than the free electron value, while g_{11} is slightly less. (d) The hyperfine interaction with F^{19} is relatively weak. (e) The hyperfine interaction parameter A_F is much larger than the parameter B_F . (f) The resonant center is not one of the centers for which optical absorption has been previously reported³; the optically absorbing centers can be bleached under conditions which leave the spin-resonance absorption unaffected.

Since the crystals contain no intentionally added impurities, it is tempting to identify the center as a lattice defect. The apatite structure is well known to tolerate substantial departures from perfect stoichiometry. The conditions of crystal growth favor CaF_2 deficiency and oxygen excess. We will consider four possibilities, as follows: (1) The center is a hole trapped by a pair of F^- ions, i.e., it is a F_2^- molecule, an analog of the V center found in alkali halides.⁷ (2) The center is a F^- vacancy which has trapped an electron, an analog of the F center. (3) The center is a Ca^{2+} vacancy which has trapped a hole. (4) The center is an O^- ion occupying a F^- site.

Consideration of possibility (1), that the center is a V center, shows that it is consistent with (a), (b), (c), and (e). However, in a V center the unpaired spin occupies an orbital which is a linear combination of s and p orbitals localized about two halide nuclei.⁷ Thus, the hyperfine interaction parameter A_F is large, typically being of order $600 \times 10^{-4} \text{ cm}^{-1}$, and is insensitive to the interatomic distance. Since we find an A_F which is 2 factors of 10 smaller, we discard the possibility that the center is a V center.

Possibility (2) is that the center is an F center. However, in an F center one would expect the higher electronic states to give rise to a small negative g shift,⁸ which is inconsistent with (c).

Possibility (3) is inconsistent with (b). This type of center may, however, be responsible for some of the optical absorption bands.

We favor the fourth possibility, that the center is an O^- ion substituting for F^- . This model is consistent with (a) and (b). We will now show that it is also consistent with the other experimental information.

The energy level scheme for O^- at an F^- site is given in Fig. 3. As shown there, the $\sigma_+(s)$ level is lowest. Moreover, the $\pi_+(p_x, p_y)$ levels are lower than the $\sigma(p_z)$ level as seen from consideration of the electrostatic field

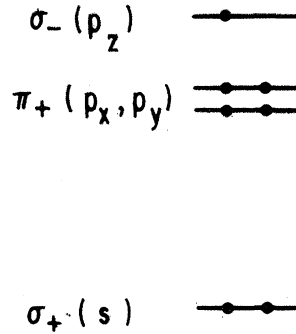


FIG. 3. Schematic representation of the energy levels of O^- occupying a F^- site in calcium fluorophosphate.

of the nearest neighbors, which are three Ca^{2+} ions lying in a plane perpendicular to the z axis. In second-order perturbation theory the shift of the components of g from the free electron value is given by⁹

$$\Delta g_{ij} = -\lambda \sum_{n \neq 0} \langle 0 | L_i | n \rangle \langle n | L_j | 0 \rangle / (E_n - E_0). \quad (6)$$

Here λ is the spin-orbit coupling parameter and the L_i are components of the angular momentum operator. Because of symmetry the matrix elements of L_z between the ground state and the other states in Fig. 3 vanish. Contributions to Δg_{11} from higher states and from higher order terms in $\lambda / (E_n - E_0)$ are small and negative, in agreement with observation. On the other hand, L_x and L_y do connect the ground state with other states in Fig. 3. We find

$$\Delta g_1 \approx -\lambda / (E_1 - E_0). \quad (7)$$

Taking $\lambda \sim +100 \text{ cm}^{-1}$ for the $2p$ states of O^- , one obtains agreement between (7) and the experimental $\Delta g_1 = 0.05$ if E_1 lies roughly 0.3 eV below E_0 , which seems reasonable.

The hyperfine interaction parameters A_F and B_F are related to the contact and the dipolar interactions by

$$A_F = \beta g \beta_N \gamma_F \left[\frac{8\pi}{3} |\psi(\mathbf{r}_F)|^2 + \frac{4}{5} \left\langle \frac{1}{r^3} \right\rangle_F \right], \quad (8)$$

$$B_F = \beta g \beta_N \gamma_F \left[\frac{8\pi}{3} |\psi(\mathbf{r}_F)|^2 - \frac{2}{5} \left\langle \frac{1}{r^3} \right\rangle_F \right].$$

Here $\psi(\mathbf{r}_F)$ denotes the wave function of the unpaired electron evaluated at the nucleus of one of the two neighboring F^- ions, and $\langle r^{-3} \rangle_F$ is the average of $|\mathbf{r} - \mathbf{r}_F|^{-3}$ over the p component of the wave function about that nucleus. We see that the very small value of B_F relative to A_F results from the approximate cancellation of the two types of contributions. From this it is evident that A_F is approximately equal to three times the contact term alone.

To evaluate the hyperfine parameters, we require

⁷ See, for example, T. G. Castner and W. Kanzig, *J. Phys. Chem. Solids* **3**, 178 (1957).

⁸ See B. S. Gourary and F. J. Adrian, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 127.

⁹ See, for example, Sec. 8 of W. Low, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Suppl. 2.

some knowledge of $\psi(\mathbf{r})$ in the vicinity of the F^- nuclei. Clearly the simple O^- ion orbital is inadequate as we can note from the fact that in the region of a neighboring F^- ion it falls off exponentially instead of having the proper "atomic"-like oscillatory behavior. An approximate $\psi(\mathbf{r})$ which is more appropriate for our purpose is obtained by orthogonalizing the free O^- orbital $\varphi_0(\mathbf{r})$ to the occupied states of the F^- ion,⁸ i.e.,

$$\psi(\mathbf{r}) = \varphi_0(\mathbf{r}) - \sum_{\mu} \sum_{i=1,2} \langle \varphi_0 | \chi_{\mu}^i \rangle \chi_{\mu}^i(\mathbf{r}), \quad (9)$$

where $\chi_{\mu}^i(\mathbf{r})$ is an F^- atomic orbital associated with the i th nucleus, and $\langle \varphi_0 | \chi_{\mu}^i \rangle$ is the overlap integral between the indicated functions.

In this approximation the hyperfine parameter A_F is given by

$$A_F = \beta g \beta_N \gamma_N \{ (8\pi/3) |\chi_{2s}(0)|^2 |\langle \varphi_0 | \chi_{2s} \rangle|^2 + \frac{4}{5} \langle \chi_{2p} | (r^{-3}) | \chi_{2p} \rangle |\langle \varphi_0 | \chi_{2p} \rangle|^2 \}, \quad (10)$$

where the two terms represent the contact and dipolar contributions of the F^- ions weighted by the square of the appropriate overlap integrals. (The contribution of the χ_{1s} to (10) is neglected because of the much smaller overlap integral associated with it.) A corresponding expression holds, of course, for the parameter B_F .

In evaluating A_F as given by Eq. (10), Hartree-Fock functions for the $2p$ O^- orbitals¹⁰ and for the $2s$ and $2p$ F^- orbitals¹¹ were used. The separation of the O^- and F^- ions was taken to be the same as the F^- — F^- interatomic distance in the perfect crystal. The calculated value of A_F is $24 \times 10^{-4} \text{ cm}^{-1}$. Though this is nearly four times the experimental value, we feel that the agreement is satisfactory considering the approximate nature of the $\psi(\mathbf{r})$ used, the sensitivity of A_F to the tails of the atomic functions involved, and the uncertainty in the O^- — F^- separation distance.¹² By way

of comparison the V center model leads to a result about 100 times too large.⁷

The parameter B_F is even more difficult to calculate accurately, as its small value is due to the near cancellation of the two different type contributions. Thus, an inaccuracy in either term yields a relatively large error in B_F . Using the free ion values of $|\chi_{2s}(0)|^2$ and $\langle r^{-3} \rangle_F$,¹³ and the experimental ratio $A_F:B_F$, we find $|\langle \varphi_0 | \chi_{2p} \rangle|^2 \approx 20 |\langle \varphi_0 | \chi_{2s} \rangle|^2$. In comparison, the calculated ratio of overlap integrals is about 17. Thus, the model yields approximately the proper ratio of contact to dipolar terms.

No optical absorption which can be associated with the resonance center has been detected between 1 to 6 eV. It is possible to estimate the energy at which optical absorption might occur for this center by comparison with the electron transfer process between F^- and Ca^{++} . The latter process requires at least the fundamental absorption energy of calcium fluorophosphate which is 8 eV.² The transfer from O^- to Ca^{++} should require 1–2 eV less, because the electron affinity of oxygen is smaller than that of fluorine by about that amount, as indicated by the Hartree-Fock calculations.^{10,11} Thus, absorption due to the O^- center is expected to be in the region above 6 eV, where it may be masked by absorption due to other defects in our crystals.²

In summary, the proposed model, that the center is an O^- ion at an F^- site, is consistent with the information obtained in the spin resonance experiments and with the chemical and optical properties of synthetic apatite crystals.

ACKNOWLEDGMENTS

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¹⁰ D. R. Hartree, W. Hartree, and B. Swirles, Phil. Trans. Roy. Soc. London **A239**, 229 (1939).

¹¹ C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1957).

¹² A comparison of the free-ion wave functions indicates that the ionic "radius" of O^- is about 10% larger than that of F^- . This

would suggest that the separation between the two ions is somewhat larger than we have used. An increase in the interatomic distance would, of course, result in a reduction of the calculated value of overlap integrals and hence in A_F and B_F .

¹³ R. Sternheimer, Phys. Rev. **84**, 244 (1953).