JOURNAL OF SOLID STATE CHEMISTRY 39, 148–153 (1981)

EPR Detection of Acetate Ions Trapping in *B*-Type Carbonated Fluorapatites

G. BACQUET* AND VO QUANG TRUONG

Laboratoire de Physique des Solides, Associé au CNRS, 118, Route de Narbonne, 31062 Toulouse Cédex, France

AND M. VIGNOLES AND G. BONEL

ERA 263, 38, Rue des 36 Ponts, 31400 Toulouse, France

Received December 30, 1980; in revised form March 12, 1981

Carbonated fluorapatites were prepared by precipitation, using calcium acetate. After irradiation and annealing at 150°C the *X*-band ESR spectrum of the $\dot{C}H_3$ radical was recorded. The spin Hamiltonian parameters were determined at RT, 110 K, and 16 K. From the thermal behavior of the spectrum it is deduced that different recombination processes of the defect are involved. This radical originates from the degradation of acetate ions trapped at anion sites of the tunnels.

Introduction

The apatites constitute a large family of isomorphous compounds the structural feature of which is that of the hydroxyapatite (*1*):

$$Ca_{10}(PO_4)_6(OH)_2.$$

They form a wide range of substitution solid solutions by partial or complete replacement of one kind of ion by another. Thus in *B*-type carbonated apatites (*B*-C*Ap*), phosphate ions can be replaced by carbonate ions. We have shown that there are two ways of substitution of these phosphate ions by carbonate ions (*2, 3*): on the one hand, fixation of the associated CO_3^{2-} + F^- (or CO_3^{2-} + OH^-) ions in the PO_4^{3-} sites, on the other hand, substitution of a PO_4^{3-} ion by a CO_3^{2-} ion and, simultaneously, when the apatite is prepared in a Na^+-free medium, the appearance of vacancies in a Ca^{2+} and a F^- (or OH^-) adjacent site. The consequence of this last mechanism is to partially empty the channels present in the lattice along the screw axis. These different methods of substitution, which define the structure of the *B*-C*Ap*, have been supported by previous studies (*3*), which have shown, especially, that the number of oxygen vacancies in *B*-type carbonated fluorapatites (*B*-CF*Ap*) reaches a maximum value before decreasing with increasing amount of carbonate. On the other hand, these compounds exhibit, between 70 and 480°C, a weight loss generally attributed to water. In order to check whether other species were present in the unheated samples, they were X-irradiated and then studied by ESR. The purpose of the present paper is to give the results obtained.

---

* Author to whom all correspondence should be addressed.

0022-4596/81/110148-06$02.00/0

1. Samples Preparation

The (B-CFAp) specimens were prepared at 90°C in two ways, following a method analogous to that described by Labarthe *et al.* (*4*): first, by dripping calcium acetate solution (250 ml, 0.04 M) into a phosphate solution (750 ml, 0.016 M) containing fluoride ions (0.06 M) and different concentrations of carbonate (from 0 to 0.48 M); second, by dripping phosphate solution (250 ml, 0.096 M) containing fluoride ions (0.06 M) and different concentrations of carbonate (from 0 to 0.96 M) into a calcium acetate solution (750 ml, 0.013 M). For the sake of simplification, we shall henceforth call the first "direct" B-CFAp and the second "reverse" B-CFAp.

2. Experimental

X-Band ESR spectra were recorded using an E-type Varian spectrometer, fitted with a variable temperature attachment. A modulation frequency of 25 kHz, with a peak-to-peak intensity $\leq 0.2 \times 10^{-4}$ T, was adopted for the major part of the measurements. To avoid saturation effects we have generally used an incident microwave power ≤ 5 mW. All the irradiations were carried out at RT with a CGR X-ray generator running at 50 kV and 10 mA.

Before being exposed to ionizing radiation, powdered samples of B-CFAp with different amounts of carbonate were either annealed in air at temperatures ranging between 190 and 300°C for 30 min or were left untreated. No signal due to paramagnetic species was observed at that time. Various series of experiments were then undertaken.

2.1. First Type of Experiments

The spectra recorded immediately after a 15-min irradiation (step A) contained several lines, the number and the behavior of which depended upon various parameters such as: carbonate content, heat treatment, and observation temperature. No attempt was made to determine the nature of the paramagnetic defects responsible for these lines.

The specimens were then heated in air at 150°C for 15 min (step B), the purpose of such an annealing being to eliminate the hole-trapped species (*5*): effectively some of the lines previously observed have disappeared. The most striking feature of the RT spectra then obtained with the major part of the B-CFAp samples is the presence[1]: of four narrow ($\Delta H \sim 0.6 \times 10^{-4}$ T) symmetrical lines of relative intensities 1:3:3:1 centered on $g = 2.00248 \pm 0.00006$ and separated by $A = (22.7 \pm 0.1) \times 10^{-4}$ T. These lines, which are characteristic of the coupling of the unpaired electron with three equivalent $I = \frac{1}{2}$ nuclear spins arise from a defect in a tumbling state, the maximum concentration of which does not exceed 400 ppm. Their intensity, which is much greater in "reverse" than in "direct" B-CFAp, increases with the amount of carbonate, reaches a maximum, and then decreases.

Lowering the observation temperature causes a broadening of the lines and a continuous decrease in their intensity. At 110 K, where the linewidth is $\Delta H = 2.6 \times 10^{-4}$ T, it is then possible to observe, at about 5.3×10^{-4} T on both sides of each of the outer main lines, one line of lower intensity (Fig. 1). Such lines are also present around the two inner lines but two of them are hidden by the strong central signal caused by an unknown defect. Inside each of the three quartets the intensities ratio remains equal to 1:3:3:1. At 10 K, the general shape of the spectrum is always the same but the spectral intensity is still lower and an extra line of strong intensity is now present at $g = 2.0287$.

---

[1] With one sample (see table II) these lines are also observed before annealing at 150°C, but their intensity is very weak.

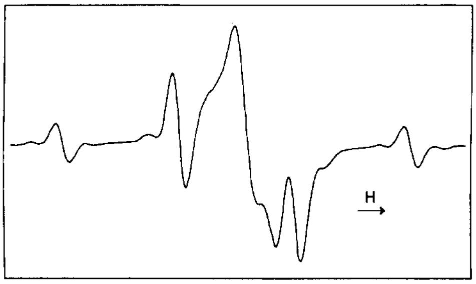

FIG. 1. *X*-Band spectrum of the methyl radical in a powdered sample of *B*-CF*Ap* X-irradiated at RT and subsequently warmed at 150°C. $T = 110$ K. The strong central line is due to an unidentified species.

Such a spectrum is due to radicals containing a methyl group (*6, 7*) and more precisely to the methyl radical $\dot{C}H_3$ as the 1 : 3 : 3 : 1 RT spectrum does not transform into a 1 : 1 : 1 : 2 : 1 : 1 : 1 : pattern below 30 K as expected for a $CH_3\text{-}\dot{C} =$ type radical when the frequency of tunneling rotation of the methyl group becomes comparable with the strength of the hyperfine interaction measured in frequency units (*8, 9*).

The methyl radical having an axial symmetry, the small satellite lines cannot be considered as reflecting a $\tilde{g}$-tensor anisotropy. In fact, they are due to $\Delta(M + m) = 2$ transitions ("flip–flip") and $\Delta(M + m) = 0$ transitions ("flip–flop"), which are partially allowed by the mixing of $m^{(k)} = \pm\frac{1}{2}$ states belonging to the same M under the action of operators like $S_z I_\pm^k$ (*10*) arising in the development of a spin Hamiltonian

$$\mathscr{H} = g\mu_B(\mathbf{H} \cdot \mathbf{S}_1) - g_1\mu_B \sum_{k=1}^{3} (\mathbf{H} \cdot \mathbf{I}_j^k) + \sum_{k=1}^{3} (\mathbf{S}_1 \cdot \tilde{A}'_{ij} \cdot \mathbf{I}_j^k), \quad (1)$$

where a small anisotropy (responsible of the line broadening) of the hyperfine coupling constant with the α protons is considered and with $S = I^k = \frac{1}{2}$.

TABLE I

SPIN HAMILTONIAN PARAMETERS FOR THE $\dot{C}H_3$ RADICAL IN *B*-CF*Ap*

T (K)	g	g_1[a]	$\langle A \rangle = \langle A' \rangle / g\mu_B$ (10^{-4} T)
110	2.0022 ± 0.0002	0.0033 ± 0.0001	23.0 ± 0.1
16	2.0024 ± 0.0002	0.0033 ± 0.0002	23.0 ± 0.2

[a] With the values of μ_B, μ_N, and g_N quoted in (*11*), one finds $g_1 = 0.00306$.

These transitions arise respectively for $h\nu = (g \pm g_1)\mu_B H_0$. The best fit was obtained with the constants listed in Table I, as we have found that the contributions of the off-diagonal terms $A'_{zx}S_zI_x$ and $A'_{zy}S_zI_y$ were much lower than the experimental uncertainty for all lines.

We shall specify here that such a paramagnetic center is thermally stable up to 200°C but it decays with a half-life of 10 min at 250°C (step C1). Figure 2 presents a plot of $1/I$ (where I is the intensity of the second line of the quartet) as a function of time. Such a linear variation is generally characteristic of a bimolecular recombination. Subsequent X irradiation for 15 min (step D1) followed by an annealing at 150°C for 15 min (step E1) restore the initial spectral intensity.

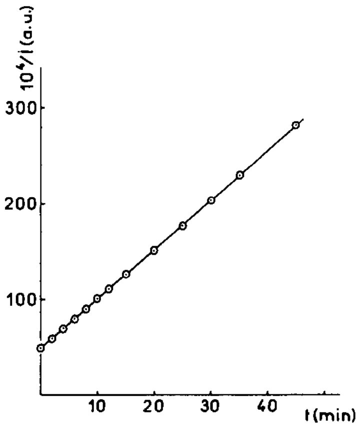

FIG. 2. Decay of the spectral intensity under annealing *in situ* at 250°C. Plot of $1/I$ as a function of time.

2.2. *Second Type of Experiments*

The sample which gave the strongest

signal was divided in three equal parts which were first respectively X-irradiated for 10, 20, and 30 min (step A) without a previous thermal treatment. Once their respective spectrum was recorded they were submitted to the following treatment: (1) annealing at 160°C for 15 min (step B); (2) a first irradiation for 15 min; (3) a second irradiation for the same time (both 2 and 3 correspond to step C2).

Table II gives the intensity of each spectrum (sum of the intensities of each individual line in the quadruplet) recorded using the same experimental conditions after each step of the 1-2-3 sequence.

2.3. *Complementary Experiments*

As hydrogen is not an intrinsic constituent of *B*-CF*Ap*, methyl radicals must result from the degradation of an impurity under the combined action of X rays and subsequent warming at 150°C.

We saw, in a previous section, that our samples were prepared by precipitation at 90°C using calcium acetate and that the quantity of defects is greater in "reverse" apatites than in "direct" apatites. "Reverse" apatites were prepared in a medium rich in acetate ions and "direct" apatites in a medium lacking in acetate ions. Consequently it is likely that traces (≤400 ppm) of acetate ions are present in the samples as the four-line spectrum was not observed in *B*-CF*Ap* prepared using calcium nitrate instead of calcium acetate.

TABLE II

INTENSITY OF SPECTRA RECORDED AFTER EACH STEP OF THE PROCESS DESCRIBED IN THE TEXT[a]

After	Spectral intensity (au)		
Initial irradiation	13	21	30
160°C annealing	282	215	210
First reirradiation	116	90	95
Second reirradiation	66	65	67

[a] Section 2.2.

In order to determine the location of these ions, either at the surface of the crystallites or inside the apatitic lattice, we have undertaken the experiments which will be described in the following.

First, calcium acetate was submitted to the usual treatment (X rays and subsequent annealing at 150°C): the signal was not seen. This is not too surprising, as the Kolbe reaction (*12*):

$$CH_3COO^- + h^+ \text{ (positive hole)} \rightarrow \dot{C}H_3 + CO_2$$

and

$$2\dot{C}H_3 \rightarrow C_2H_6$$

is expected.

Then, we have treated a *B*-CF*Ap* prepared without the use of calcium acetate in a boiling suspension of this acetate during 24 hr. After separation by filtration, washing and drying at 70°C, the obtained powder submitted to X rays and to a subsequent annealing at 150°C did not exhibit the four-line spectrum. On the other hand, this spectrum is not observed in fluorated apatites prepared in acetate medium not containing carbonate ions.

3. Discussion

The above results may be summarized as follows:

(i) Acetate ions are trapped into the apatitic lattice;

(ii) It is necessary to irradiate (step A) and then to anneal the samples at 150°C (step B) to observe the four-line spectrum;

(iii) This resonance disappears under warming at 250°C (step C1) but the electron traps are not destroyed;

(iv) Once the maximal spectral intensity is obtained, the effect of extra exposure to ionizing radiations (step C2) is to lower the spectral intensity.

Our observations involve the existence of different recombination processes, the nature of which is not clear at all as we shall see in the following.

The conditions of creation of $\dot{C}H_3$ in *B*-CF*Ap* and its thermal stability up to 200°C are already surprising, as the methyl radicals observed in other compounds were created and observed at liquid nitrogen temperature (*13–15*) or liquid helium temperature (*16*) and it was found that they diffused and reacted rapidly above 77 K to give C_2H_6.

It has been suggested (*15*) that in γ-irradiated crystals of sodium acetate · $3D_2O$ the $\dot{C}H_3$ radicals might be formed at 77 K by thermal decomposition of CH_3CO_2 radicals produced by the ionization of the parent $CH_3CO_2^-$.

Such a process is likely to account for steps A and B, but it seems difficult to explain why the spectral intensity decreases under the effect of X rays (step C2). Nevertheless, this difficulty could be overcome assuming that ionizing radiation would create an unknown paramagnetic species, labeled X, reacting very efficiently with $\dot{C}H_3$, the obtained diamagnetic entity having a bonding energy sufficiently weak to be broken under the action of a 150°C annealing. It is then worthwhile to say that this last sequence can also explain the steps A and B:

Step A

$$CH_3CO_2^- + h\nu \rightarrow \dot{C}H_3 + CO_2,$$
$$X + h\nu \rightarrow \dot{X},$$
$$\dot{C}H_3 + \dot{X} \rightarrow CH_3X.$$

This first type of recombination would explain why the Kolbe reaction does not occur.

Step B

$$CH_3X \rightarrow \dot{C}H_3 + \dot{X},$$

and

$$\dot{X} \rightarrow X.$$

As we have observed a weak $\dot{C}H_3$ spectrum in one sample after step A, we think that this last sequence is probably the right one.

The major difficulty is now the explanation of the step C1 as the decay of the spectral intensity under warming at 250°C seems to be characteristic of a bimolecular recombination. As an example, let us suppose that the $\dot{C}H_3$ can migrate at 250°C (this is not the case for $T \leq 200$°C!) and recombine together leading to C_2H_6. It seems first surprising that gaseous ethane, which would then be the product of this second type of recombination, stays trapped into the lattice at 250°C. If this were the case, what could be the effects of a subsequent irradiation (step D1) which does not permit us to observe the $\dot{C}H_3$ spectrum? One could imagine, for instance, the following sequence:

$$C_2H_6 \rightarrow 2\dot{C}H_3,$$
$$X \rightarrow \dot{X},$$
$$\dot{C}H_3 + \dot{X} \rightarrow CH_3X.$$

This would mean that the reactivity between $\dot{X}$ and $\dot{C}H_3$ is much greater than that between the two neighbor $\dot{C}H_3$ (they cannot migrate at RT).

But if the effect of the annealing at 150°C is always the same, i.e.,

$$CH_3X \rightarrow \dot{C}H_3 + \dot{X}$$

and

$$\dot{X} \rightarrow X$$

why the neighbor $\dot{C}H_3$ would not recombine together (the $\dot{C}H_3$ spectrum is now observed with the same intensity as before the step C1)?

In fact, the only certainties we have are the existence of at least two recombination processs involving the presence of different unknown entities and that the usual pathway of a Kolbe reaction does not take place.

On the basis of all our experiments, we

shall say in conclusion that acetate ions are trapped into the *B*-CF*Ap* lattice during the sample preparation and more specially at the monovalent anion sites of the channels, where the free space is important. This is confirmed by the fact that the spectrum intensity depends on the amount of carbonate ions introduced in the *B*-CF*Ap* lattice: the number of acetate ions detected is a function of the number of vacancies present in and near the tunnels. This result can be compared to that obtained in the case of the F^+ (*3*) and constitutes a confirmation of the formula we have proposed for the *B*-CF*Ap* structure.

References

1. M. I. Kay, R. A. Young, and A. S. Posner, *Nature* **204,** 1050 (1964).
2. G. Bonel, J. C. Labarthe, and C. Vignoles, *C.R. Coll. Int. CNRS* **230,** 117 (1973).
3. G. Bacquet, Vo Quang Truong, G. Bonel, and M. Vignoles, *J. Solid State Chem.* **33,** 189 (1980).
4. J. C. Labarthe, G. Bonel, and G. Montel, *Ann. Chim.* **8,** 289 (1973).
5. H. W. Den Hartog and H. Benning, *Phys. Status Solidi A* **43,** 633 (1977).
6. P. W. Atkins and M. C. R. Symmons, "The Structure of Inorganic Radicals." Elsevier, Amsterdam (1967).
7. C. Heller, *J. Chem. Phys.* **36,** 175 (1962).
8. J. H. Freed, *J. Chem. Phys.* **43,** 1710 (1965).
9. S. Clough and F. Poldy, *Phys. Lett. A* **24,** 545 (1967).
10. A. Abragam and B. Bleaney, "RPE des Ions de Transition." Presses Univ. France, Paris (1971).
11. B. Rånby and J. F. Rabek, "ESR Spectroscopy in Polymer Research." Springer-Verlag, Berlin (1977).
12. B. Kraeutler and A. J. Bard, *J. Amer. Chem. Soc.* **99,** 7729 (1977); L. Eberson, *in* "Organic Electrochemistry" (M. M. Baizer, Ed.). Dekker, New York (1973).
13. J. E. Bennet and B. Mile, *Trans. Faraday Soc.* **67,** 1587 (1971).
14. T. Cole, H. O. Pritchard, N. R. Davidson, and H. M. McConnell, *Mol. Phys.* **1,** 406 (1958).
15. J. Janecka, H. M. Vyas, and M. Fujimoto, *J. Chem. Phys.* **54,** 3229 (1971).
16. C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, *Phys. Rev.* **112,** 1169 (1958).