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EPR of Mn^{+2} in Calcium Fluorophosphate. I. The Ca(II) Site

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There are two different calcium sites in calcium fluorophosphate, called Ca(I) and Ca(II). Manganese ions have been found at the Ca(I) site by several investigators using EPR techniques. We report the observation of manganese at the Ca(II) site. The EPR spectrum of these ions, i.e., of Mn(II), has been fit with a spin Hamiltonian which includes crystalline D and E terms, an isotropic hyperfine term, and an axial superhyperfine term expressing its coupling to a nearby fluorine ion. The symmetry properties of the spectrum and the superhyperfine coupling to fluorine are the basis for the identification with Mn(II). The dependence of the concentrations of Mn(I) and Mn(II) upon the manganese concentration in the melt has been measured and is consistent with current speculations about the substitution of manganese into calcium fluorophosphate.

INTRODUCTION

Calcium fluorophosphate, FAP, is a crystal found in nature and prepared synthetically. It has a very stable structure capable of many major chemical modifications as well as the incorporation of small amounts of a wide number of impurities. Wyckoff[1] lists the dimensions of its unit cell, the position of the individual ions, and many of the modified forms prepared synthetically or found to occur naturally. When doped with antimony and manganese and modified by a partial substitution of chlorine for fluorine, FAP serves as the phosphor found in most fluorescent lamps. In a recent paper, Ryan *et al.*[2] have discussed the optical properties of FAP crystals containing manganese. EPR measurements have been made on FAP by several workers[3–6] to determine the details of the manganese site. FAP has hexagonal space group $P6_3/m(C_{6h}^2)$ with two molecules of $Ca_5(PO_4)_3F$ per unit cell. It was expected that manganese would be found in the lattice substituted for calcium at both of its inequivalent sites (one called Ca(I) with C_3 symmetry and the other called Ca(II) with C_{1h} symmetry), and that these ions should be easily identified by the symmetry of their spin-resonance signals. Prior to this work manganese has been detected and identified at the Ca(I) site[3–6] and other manganese resonances have been found[4] which are of lower symmetry and not clearly identified with any specific site, but no resonance due to manganese at the Ca(II) site has been identified.

Most of the early measurements were performed with powders or natural crystals which give poorly resolved spin-resonance spectra. We have access to synthetic FAP crystals which were developed for use in lasers and are, therefore, of unusually high perfection. Because of the high resolution possible with these crystals, we have been able to detect the EPR spectra due to manganese at four different sites in FAP. Two of the sites have low symmetry and involve manganese associated with other defects. They will be discussed in a later paper. The two reported in this paper are the Ca(I) and Ca(II) sites. The purpose of this paper is to present the arguments supporting the identification of the Ca(II) site, the parameters found for its spin Hamiltonian, and data showing the unusual dependence of the concentrations of manganese at the Ca(I) and Ca(II) sites on the crystal-growth parameters.

CRYSTAL GROWTH

A discussion of the growth of our FAP crystals can be found elsewhere[7]; the techniques which are responsible for their high quality are growth from the melt using oriented seeds, precise control of temperature and temperature gradients to minimize strain, and slow growth and slow cooling after growth. It was found that variations in the stoichiometry of the melt were reflected by variations in the composition of the crystals. In particular, crystals grown from a stoichiometric melt were found to be fluorine deficient and to have a large optical absorption band at 2500 Å. Prener *et al.*[8] have observed this band and have partially identified the defect center causing it as some combination of oxygen ions substituted for fluorine ions and fluorine ion vacancies. When doped with manganese such crystals were found to contain four different kinds of manganese centers. On the other hand, crystals grown from melts containing a large excess of CaF_2 were found to be more nearly stoichiometric and contained fewer oxygen-vacancy defects. When doped with manganese, they contained mostly the Mn(I) and Mn(II) centers discussed in this paper.

When a crystal containing manganese was to be grown, MnO was added to the melt and an equal amount of CaO was left out. A segregation coefficient for manganese of about 0.2 was found at all concentrations. The upper limit to the manganese concentration in the melt was about 10%, for poor crystals grow with higher concentrations due to the co-precipitation of a second high-manganese phase. At about this same concentration the EPR measurements became useless because the resonance line had broadened too much because of interactions between the manganese ions. A lower limit on the manganese concentration of about 10 ppm was set by EPR signal-to-noise considerations and by the size of available samples. Many measurements

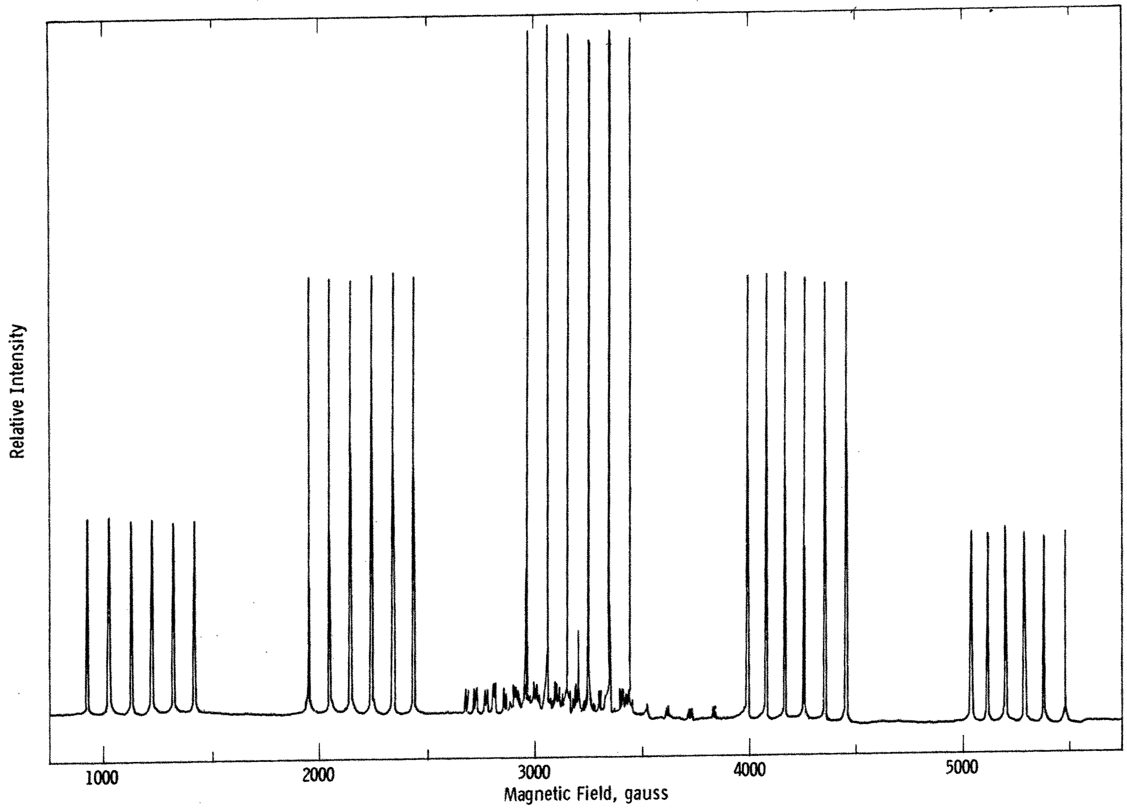

FIG. 1. EPR spectrum with H parallel to the c axis.

were made on samples containing about 0.01% manganese, for in these samples the signal-to-noise ratio was high enough to allow a search for minor fractions of the manganese which might occupy unusual sites while the lines of the major fraction of the manganese were not broadened enough to obscure the minor lines.

EPR MEASUREMENTS

EPR measurements were made at about 9 GHz and 77°K, with a few investigations carried out at 2 and 300°K. The EPR apparatus is conventional except for the sample holder, which is in the form of a rotating table. The sample is glued to the table which is mounted inside the cavity and arranged so that a combined rotation of the table on a horizontal axis and the magnet on a vertical axis will align the magnetic field along any direction in the crystal. It was sometimes necessary to achieve an accuracy of alignment of ±0.2 deg to resolve certain resonance lines.

Figure 1 shows a typical spectrum of a sample con-

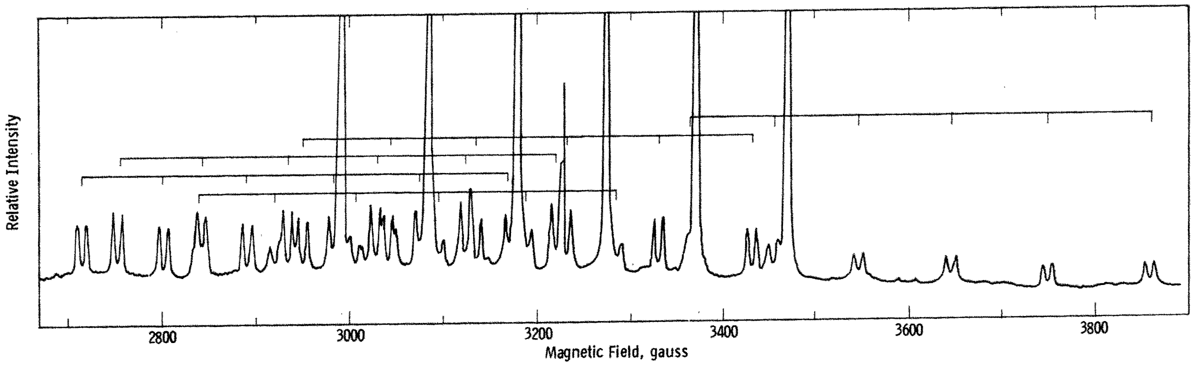

FIG. 2. Enlarged view of Fig. 1 showing the Mn(II) spectrum.

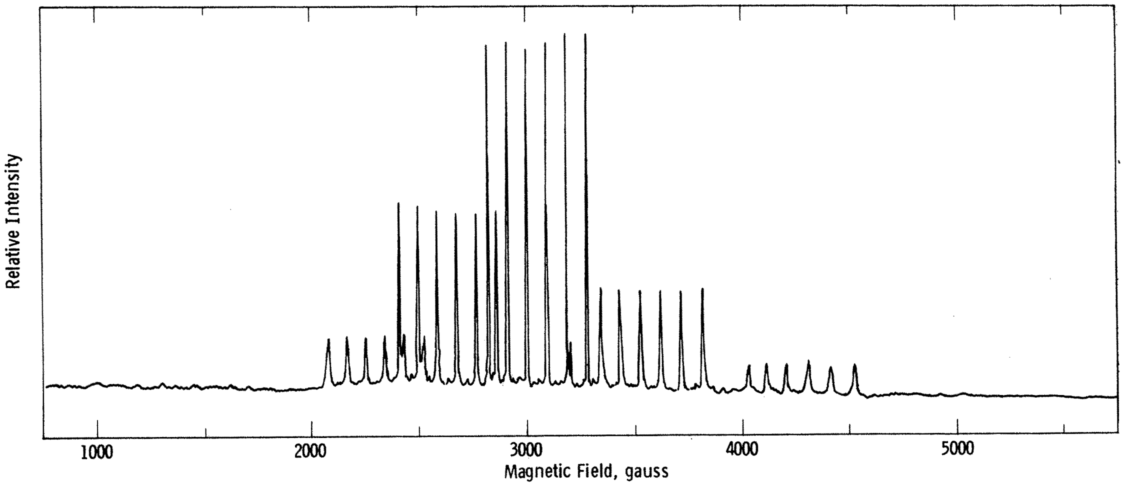

FIG. 3. EPR spectrum with H perpendicular to the c axis.

taining 0.02% manganese measured at 77°K when $\theta=0°$, i.e., when the magnetic field is parallel to the threefold c axis of the crystal. As is usual for Mn^{+2} ions, the major lines can be described as five groups of six lines. This spectrum has been observed before in powders[3] and in crystals[4–6] and has been identified as due to manganese at Ca(I) sites. It will hereafter be called the Mn(I) spectrum and Mn(I) site. In addition to these strong lines, one can see a much weaker spectrum, shown in an enlarged view in Fig. 2, which can also be organized into five groups of six lines. An interesting feature of this spectrum is that each line has been split into two by a mechanism we ascribe to superhyperfine coupling to a neighboring fluorine ion. Figure 3 shows the spectrum observed for the sample when $\theta=90°$, i.e., when the magnetic field is rotated perpendicular to the crystal c axis. The positions of the major lines, due to Mn(I), are independent of ϕ, the orientation of the field in the plane perpendicular to the c direction, while the weaker spectrum, which can barely be seen in Fig. 3, splits into three sets each of which depends strongly upon ϕ. Rotating the magnetic field out of the c plane gives no further splitting of the Mn(I) or the weaker spectrum while under these condi-

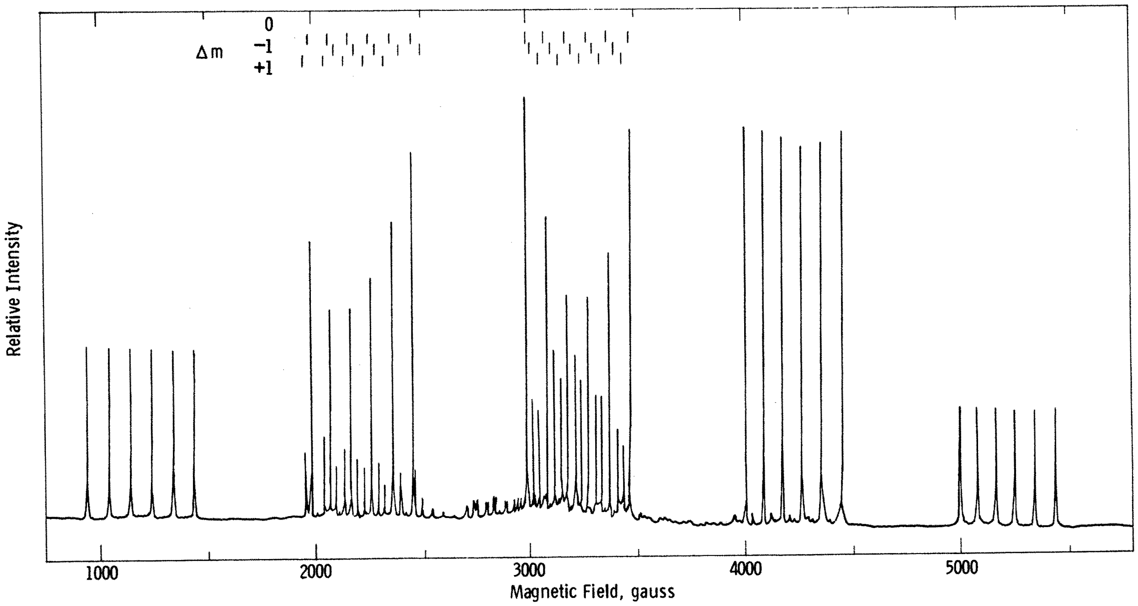

FIG. 4. EPR spectrum with a 5° angle between H and the c axis.

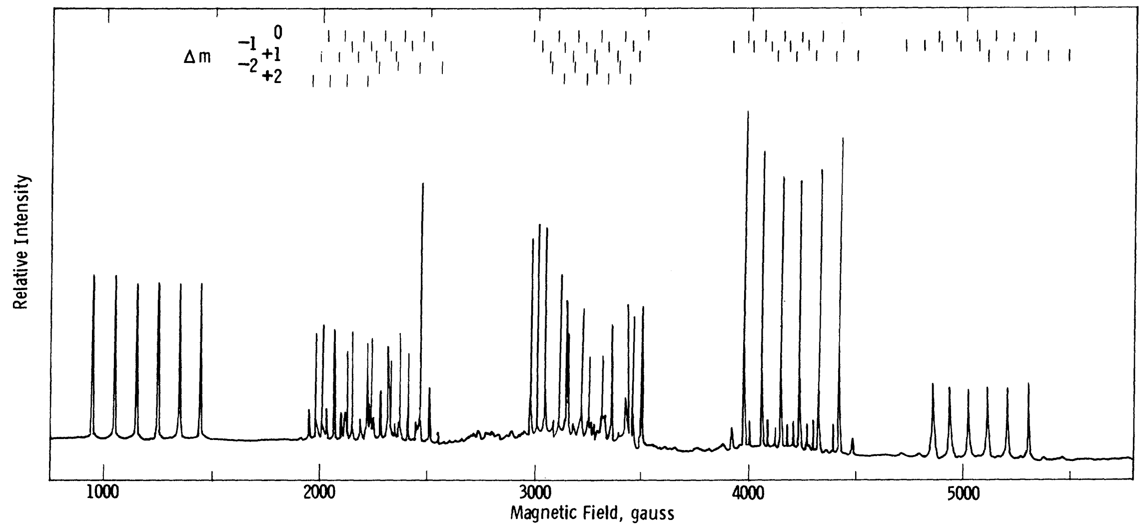

FIG. 5. EPR spectrum with a 10° angle between H and the c axis.

tions the spectra of manganese at sites of no symmetry are found to split further, as expected, into six equivalent sets of lines. These symmetry properties of the weak spectrum are sufficient to show that the manganese ions responsible for it are at sites which have reflection symmetry in the c plane. The superhyperfine splitting and the way it depends upon the orientation of the magnetic field, discussed below, shows that each of these manganese ions is near one fluorine ion and that the line connecting the two is in the c plane. These prescriptions are all consistent with Mn^{2+} ions substituted for Ca^{+2} ions at the Ca(II) site and no other feasible model has been found which fits the facts. We, therefore, identify the weak spectrum with manganese at this site and call it the Mn(II) spectrum and Mn(II) site.

In our experiments the Mn(I) spectrum was always much stronger than the Mn(II) spectrum and tended to obscure it. In addition, many other resonance lines were observed due mainly to two kinds of forbidden transitions of Mn(I) ions. It became clear that to map the Mn(II) spectrum and determine its parameters, it would be necessary first to fully map the Mn(I) spectrum and identify the forbidden lines that were being observed. The strongest of these were observed close to the allowed lines and correspond to transitions in which the manganese nucleus as well as its electrons change their spin quantum numbers, i.e., $\Delta M=\pm 1$, $\Delta m\neq 0$. Examples of these transitions are shown in Figs. 4 and 5. The spectra were observed under conditions identical to those of Figs. 1–3 except that $\theta=5°$ and $10°$, respectively. The positions of the observed transitions are indicated in the upper part of the figures and Δm given. Their energies are in agreement with those evaluated for Mn(I) by Burley,[5] who used a normal Hamiltonian and perturbation calculations but found it necessary to carry the calculations to a very high order because of the large size of the parameters A and D. The intensities of the forbidden transitions are zero for $\theta=0°$ and $90°$ but become very large at intermediate angles. For θ between 15° and 75° the forbidden transitions are so strong and there are so many of them that individual ones cannot be followed but only recognized as one of the lines of approximately equal strength that are in the group corresponding to a certain electronic transition. Fortunately, these lines can always be distinguished from Mn(II) lines owing to their lack of dependence upon ϕ.

The second kind of forbidden transition observed is an electron-spin transition where $\Delta M\neq\pm 1$. These transitions do not occur close to allowed transitions but are found mostly at low magnetic fields. To help identify them, computer calculations were performed[9] of the expected position and intensity of all 15 lines in the spin-resonance spectrum corresponding to all of the allowed and forbidden transitions of this kind. A spin Hamiltonian was used containing an isotropic g term and a D term expressing the crystal-field strength, but with the hyperfine parameter set equal to zero to make the calculations tractable. The results of the calculations, a plot of the resonant fields versus angle θ, is shown in Fig. 6. To give a good fit of the allowed transitions, the parameters were chosen to be $D/g\beta=-506$ G and $g=2.000$. These numbers are in good agreement with the values previously found[3,4] for Mn(I)·in FAP. The calculations for the various forbidden transitions can now be used to predict the approximate position of the center of the groups of from six to 36 hyperfine lines corresponding to each forbidden electronic transition and to predict the strengths of the groups. The calculations show that the $\Delta M=\pm 2$ transitions should have zero intensity at

$\theta=0°$ and 90°, but reach 10% of the intensity of the allowed lines at intermediate angles. These transitions were not clearly identified because strong hyperfine forbidden transitions developed at intermediate angles which broadened or split the spectrum into an unidentifiable composite. The $\Delta M=\pm3$ transitions also should approach zero intensity at $\theta=0°$ but in contrast reach a maximum intensity at 90° where the hyperfine forbidden transitions are weak. They were observed at 90° and found to be very close to their calculated positions. Their intensity, in agreement with the calculations, was about 1% of the most intense allowed line. The $\Delta M=\pm4$ and ±5 spectra were too weak to be observed.

PARAMETERS OF Mn(II)

Mapping of the three sets of Mn(II) lines was done where the Mn(I) forbidden lines were not so strong as to obscure the Mn(II) lines, i.e., for $|\theta|<15°$ and $|\theta-90°|<15°$, and in addition where the Mn(II) lines themselves had not developed strong forbidden lines, i.e., for $|\phi|\leq15°$ and $|\phi-90°|\leq15°$. The spectra have been fit with the spin Hamiltonian

$$\mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}+D[S_z^2-\tfrac{1}{3}S(S+1)]+E(S_x^2-S_y^2)$$
$$+A\mathbf{I}\cdot\mathbf{S}+a_F\mathbf{I}(F)\cdot\mathbf{S}+b_F[3I_z(F)S_z-\mathbf{I}(F)\cdot\mathbf{S}],$$

where D and E express the axial and rhombic components of the crystal field, A, the strength of the hyperfine coupling to the manganese nucleus, and a_F and b_F, the strength of the superhyperfine coupling to the neighboring fluorine nucleus. The values found for these parameters at 77°K are $g=2.000$, $D/g\beta=-504$ G, $E/g\beta=-114$ G, $A/g\beta=-96$ G, $a_{F/g\beta}=\pm13$ G, and $b_{F/g\beta}=\pm3$ G. The signs of D and E have been determined by comparing the EPR spectra obtained at 2°K and at 77°K. At 77°K the six electronic states are about equally occupied and the intensities of the transitions between them are in the ratio 5:8:9:9:8:5. At 2°K, however, the states of lower energy are preferentially occupied, causing an altered intensity ratio from which the sign of D and E can be determined. The sign of a_F and b_F are not known. The three sets of Mn(II) lines observed are all fit by this Hamiltonian but have three different sets of coordinate axes oriented with respect to each other and the crystalline axes in the following way: All of the X axes are common with the crystal c axis. The three Z axes are in the c plane, rotated 120 deg with respect to each other, and according to x-ray-diffraction measurements parallel with the crystalline "a" direction within ±2 deg.

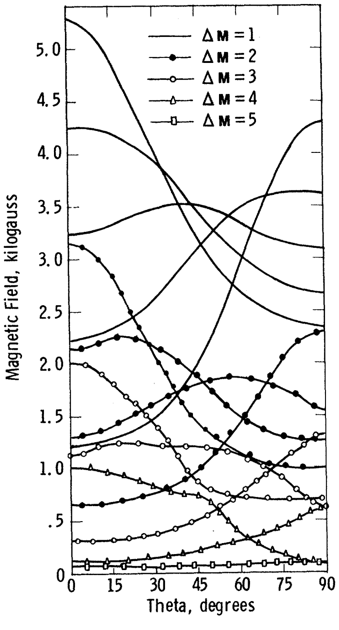

FIG. 6. Calculated EPR spectrum versus angle. Hyperfine interactions have been ignored. Allowed ($\Delta M=1$) and forbidden ($\Delta M\neq1$) transitions are shown.

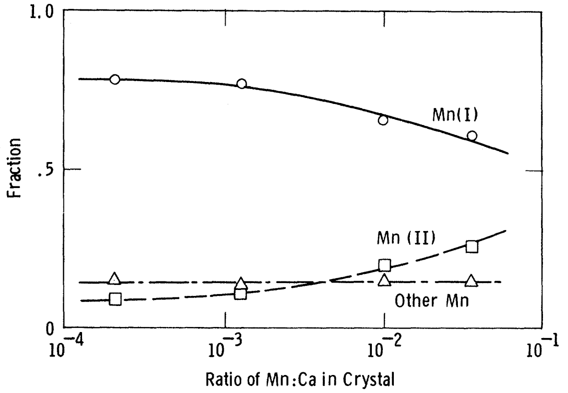

FIG. 7. Fraction of manganese found in different sites as a function of total magnanese concentration.

Several comments should be made about the parameters and the spin Hamiltonian. (1) Fourth-order crystal-field terms V_4^0, $V_4^{\pm2}$, and $V_4^{\pm4}$ should be included in the Hamiltonian for completeness. They will contribute to the energy and alter the splittings of the levels, but the small size of their contribution found for Mn(I) (about 10 G) and the limited precision of the measurements for Mn(II) have led us to conclude that their effect would also be small for Mn(II) and that the five fourth-order parameters should be ignored. (2) The manganese hyperfine term in the spin Hamiltonian is isotropic; however, the observed splitting is not but shows a variation of about 4 G between the three principle directions. This is due in part to an interaction between the crystal field and hyperfine terms of the Hamiltonian which shows up in third-order perturbation calculations as angle-dependent terms in the hyperfine splitting. There also appears to be a real anisotropy in A which is so small that we have not evaluated it. (3) The superhyperfine splitting has axial symmetry. According to our model for Mn(II) the axis should be identified with the line connecting Mn(II) and the nearest fluorine ion. We have labeled the axis of the splitting the Z axis; the line connecting Mn(II) and the nearest fluorine ion is within a few degrees of the crystal a axis. X-ray measurements have been made to investigate the relative orientation of these axes and confirm that within the experimental error of $\pm 10°$ these axes are the same. (4) Symmetry does not demand that the Y and Z axes of the superhyperfine and crystal-field parameters are related and yet the data can be fit by the spin Hamiltonian for which these axes are common. This implies that the dominant contributor to the crystal field is the fluorine ion, the source of the superhyperfine splitting. (5) The resonance spectra found by Ohkubo and Mizuno[4] and tentatively identified as due to Mn(II) is entirely different from this one, and so must be due to manganese at another site.

RELATIVE CONCENTRATIONS OF Mn(I) AND Mn(II)

A series of crystals were grown from melts containing an excess of CaF_2 under conditions that were identical except for variations in the concentration of manganese in the melt. The over-all manganese concentration of one crystal was established by chemical means and the relative amounts of Mn(I) and Mn(II) in this crystal and all of the others was determined by estimating the total areas under their EPR spectra. Figure 7 shows the fraction of manganese found to be in each site versus the total manganese content of the crystal. Unavoidable variations in the growth procedures and difficulties associated with the measurement of the EPR spectra cause a 10% scatter in the points. An unusual effect is apparent. At low manganese concentrations few of the Mn^{+2} ions are at Ca(II) sites, while at high concentrations about one-quarter of them are. These results are in complete agreement with conjectures of Parodi[10] based upon his magnetic susceptibility measurements and early EPR measurements.

We propose the following explanation for this phenomenon: The manganese ion is about 20% smaller than the calcium ion and so substitutes for it with some difficulty producing the low segregation coefficient which is observed. Assume that the Ca(II) site is too large to be readily occupied by manganese. As manganese ions are introduced into FAP they enter primarily the Ca(I) site and cause a steady shrinkage of the lattice (which has in fact been observed[10]). Among other things, this shrinkage reduces the size of the Ca(II) site until at high-enough manganese concentrations the Ca(II) site also becomes available for substitution by manganese. If this hypothesis is correct, one might expect to observe a more localized phenomenon whereby the Ca(II) sites occupied by manganese are spatially correlated with Mn(I); for instance, in an extreme example, that many Mn(II) are nearest neighbors to Mn(I). This possibility was investigated in two ways. First, a search was made for Mn(II) ions whose spectrum was perturbed by their proximity to a Mn(I). None was seen. Second, evidence was sought for the existence of antiferromagnetically coupled pairs of manganese ions such as have been found in other crystals.[11] None was found. We conclude that the Mn(I) and Mn(II) ions are substantially randomly distributed in the FAP crystal.

CONCLUSIONS

Manganese ions have been detected in FAP by EPR techniques at several different sites, two of which are isolated from other defects. One of these is the previously identified Mn(I) site and the other the newly observed Mn(II) site. The identification of the Mn(II) site is based upon its reflection symmetry and the details of its electric and magnetic interactions with the nearby fluorine ion. The preponderance of manganese is found at Mn(I) sites in crystals containing little manganese. This is why Mn(II) was not detected earlier. At higher manganese concentrations, the fractions in Mn(I) and Mn(II) sites become comparable and it appears that a limit may be reached where manganese is divided evenly between the two sites.

ACKNOWLEDGMENTS

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