

Electron Paramagnetic Resonance of Fe³⁺ in NaF^{†‡}

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The EPR absorption of x-irradiated NaF containing iron as an impurity has been investigated at controlled temperatures below 180°K. Three spectra have been distinguished: (i) the *F*-center spectrum, (ii) a spectrum isotropically centered near $g=2.002$ and with a partially resolved anisotropic structure, and (iii) the Fe²⁺ spectrum centered near $g=4.344$. The spectrum near $g=2.002$ is satisfactorily described in terms of a spin Hamiltonian pertaining to an ⁶S_{5/2} ion located at a lattice site with cubic symmetry and interacting with six equivalent nuclei of spin $\frac{1}{2}$ each. This spectrum is attributed to Fe³⁺ at a cation site. Computer analyses of the observed temperature dependence of the Fe³⁺ spectrum have indicated that the fine-structure constant decreases as the first power in T , and the line width increases as the square root of T , when T changes from 77 to 180°K. The results are consistent qualitatively with the existing theories of the *S*-state ion. Quantitatively, however, the computed T dependence of the fine-structure constant disagrees substantially with current theories.

I. INTRODUCTION

THE present work is concerned with electron-paramagnetic-resonance (EPR) absorption studies of iron-doped NaF at controlled temperatures below 180°K. The paramagnetic resonance of iron impurity in NaF has been investigated by Bleaney and Hayes,¹ and Hayes and Jones.² These authors have observed an EPR absorption due to Fe²⁺ only. The EPR absorption of Fe³⁺ (⁶S_{5/2}) has been observed in several iron-doped single crystals^{3,4} other than alkali halides. However, no successful observation of the EPR absorption of Fe³⁺ seems to have been made in alkali halides.

In the present work, experimental evidences will be presented, which indicate strongly that the ionic state of the iron impurity of NaF may be changed from Fe²⁺ into a singly ionized state (Fe⁺) and a triple ionized state (Fe³⁺) by means of x-irradiation of the iron-doped NaF. Both Fe⁺ and Fe³⁺ appear to be located substitutionally at cation sites and to interact with the crystal-line field as well as the six nearest-neighbor fluorine ions. In particular, the interaction of the Fe²⁺ ion with its environment is remarkably temperature-dependent. The spin Hamiltonian for the Fe³⁺ has been determined in such a way that it can account for the observed temperature dependence. The results are compared with the current theory of the fine-structure splitting of *S*-state ions.

Experimental procedures are described briefly in Sec. II. The experimental results and the spin Hamiltonian are presented in Sec. III. The temperature dependence

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¹ B. Bleaney and W. Hayes, Proc. Phys. Soc. (London) **70B**, 626 (1957).

² W. Hayes and D. A. Jones, Proc. Phys. Soc. (London) **71**, 503 (1958).

³ Studies of Fe³⁺ in AgCl are summarized by M. Satoh and C. P. Slichter, Phys. Rev. **144**, 259 (1966). All Fe³⁺ studies before 1958 are reported in Ref. 4, pp. 139 and 140.

⁴ S. A. Al'tshuler and B. M. Kozyrev, *Electron Paramagnetic Resonance* (Academic Press Inc., New York, 1964).

of the spin Hamiltonian is described in Sec. IV, and the results are discussed in Sec. V. Finally, a conclusion is drawn in Sec. VI.

II. EXPERIMENTALS

Single crystals of NaF were obtained from the Harshaw Chemical Company, Cleveland, Ohio. Mass-spectroscopic analysis⁵ of these crystals indicated that the crystal samples contained 8 parts per million (ppm) of iron, 3 ppm of manganese, but no detectable amount of chromium ($< \frac{1}{10}$ ppm). Samples of dimensions approximately 3 mm×3 mm×15 mm were cut from these crystals in such a way that the longest dimension of the samples is parallel to the [110] direction.

The samples were then irradiated by x rays from a molybdenum target tube operated at 50 kV and 20 mA for about 90 h at room temperature.

The (EPR) spectra of these samples before and after the irradiation were investigated near 77 and 4.2°K. The EPR spectrometer used for these studies is a Varian model V4500 X-band spectrometer with 100 kc/sec and audio frequency magnetic-field modulation. A multipurpose liquid-helium cryostat designed by the present authors⁶ has been employed for parts of the present work.

The angular dependence of the spectra is investigated by rotating the samples about the [110] axis which is held perpendicular to the dc and microwave magnetic fields. The angle (θ) of rotation is measured from the [100] direction of the samples to the direction of the dc magnetic field, which remains on the (110) plane.

III. EXPERIMENTAL RESULTS AND SPIN HAMILTONIAN

The samples have yielded weak EPR spectra of the 3 ppm of manganese impurity before the x-irradiation, but no trace of the EPR absorption of the 8 ppm of iron⁷ impurity. The lack of the resonance of the iron impurity is not unexpected, since the iron enters the

⁵ Spectroscopic analysis was performed by the Harshaw Chemical Company.

⁶ R. A. Andrews and Y. W. Kim, Rev. Sci. Instr. **37**, 411 (1966).

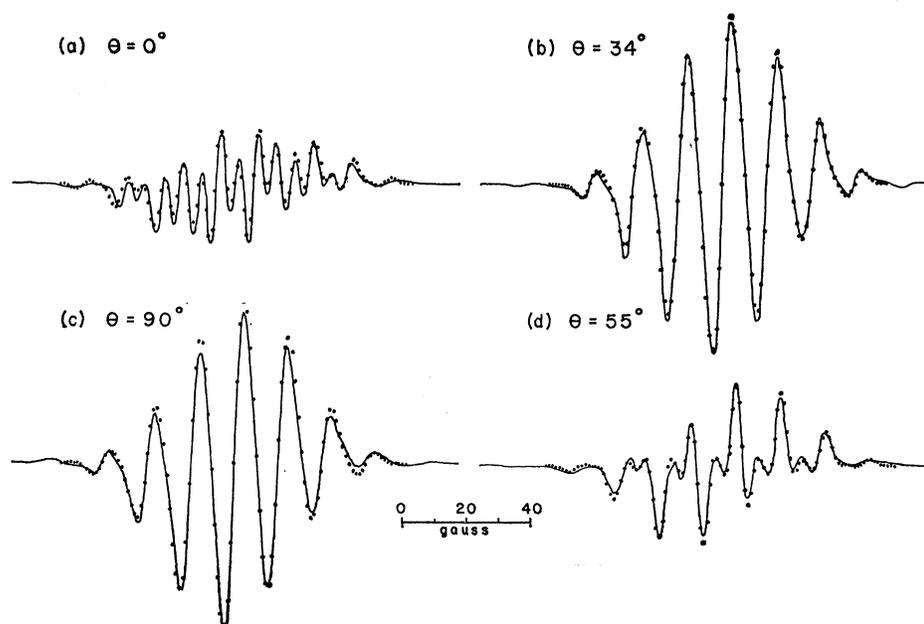


FIG. 1. The observed EPR spectra (solid lines) and the theoretical fit (dots) of Fe^{3+} in NaF at 77°K for $\theta=0^\circ$, 34° , 55° , and 90° .

lattice of NaF as a divalent ion⁷ (Fe^{2+}) and the EPR resonance of Fe^{2+} is very sensitive to the lattice defects,⁸ making the width of the resonance so broad as to be practically unnoticeable.

The x irradiation has been found to reduce the intensity of the manganese resonance to practically nil, and to induce three EPR spectra which are easily distinguishable at different temperatures.

Near 77°K , only two of them are observable. One represents the well-known F -center resonance.⁹ The intensity of this F -center resonance, however, can be reduced substantially by optically bleaching the x-irradiated samples with F light ($340\text{ m}\mu$). After the optical bleaching, then, the other of the two spectra is better identified. This second spectrum is centered approximately at $g=2.002$, and exhibits a partially resolved anisotropic structure. The solid curves of Fig. 1 illustrate four spectra recorded at $\theta=0^\circ$, 34° , 55° , and 90° . $\theta=0^\circ$, 55° , and 90° correspond to $[100]$, $[111]$, and $[110]$, respectively. The best resolution is obtained for $\theta=34^\circ$ and 90° , while poorer resolutions are noticed for $\theta=0^\circ$ and 55° . For the orientations of best resolution, the spectrum consists of seven lines, which are approximately equally spaced (13.7 G apart). The intensity ratio of the seven lines is approximately $1:6:15:20:15:6:1$.

Near 4.2°K , the second spectrum is not observable, and the F -center resonance has already been reduced by the optical bleach. Instead, a third spectrum with a partially resolved anisotropic structure is noticed. This one is centered near $g=4.344$. The anisotropy of this

spectrum is different from that of the second spectrum, and has been found to be satisfactorily described in terms of the spin Hamiltonian that Bleaney and Hayes¹ previously assigned to Fe^{3+} located at a cation site in NaF . In the remaining part of this paper, therefore, only the second anisotropic spectrum will be dealt with.

As preliminary clues to the determination of the proper spin Hamiltonian for describing the spectrum, two points of observation have been used: First, the intensity ratio of the seven lines mentioned in the preceding is very close to that which would be expected from six equivalent nuclei of spin $I=\frac{1}{2}$, each interacting with the paramagnetic ion responsible for the spectrum. In the present case, Na^{23} and F^{19} are both 100% naturally occurring isotopes with nuclear spins of $\frac{3}{2}$ and $\frac{1}{2}$, respectively. This suggests that the paramagnetic ion be situated on a cation site with cubic symmetry and interact with six equivalent nearest-neighbor fluorine ions. Secondly, if the resolved spectrum is due solely to the hyperfine interaction, the resolution should be best for $\theta=55^\circ$, when the anisotropic part of the hyperfine interaction vanishes and leaves only seven lines.¹⁰ However, this is not the case (see Fig. 1). Instead, the observed angular dependence of the resolution appears to be more similar to what would be expected from unresolved fine structure splitting of an ion in the ${}^6S_{5/2}$ state.¹¹ Thus, the spin Hamiltonian for the spectrum is taken to be

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + \sum_{n=1}^6 \mathbf{S}\cdot\mathbf{A}_n\cdot\mathbf{I}_n + F(a). \quad (1)$$

¹⁰ This is the case for cubic symmetry when $\mathbf{H}\parallel[111]$; then $(3\cos^2\theta_n - 1) = 0$ for $n=1, \dots, 6$.

¹¹ W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960), pp. 114-117.

⁷ W. Hayes, J. Appl. Phys., Suppl. 33, 329 (1962).

⁸ D. H. McMahon, Phys. Rev. 134, A128 (1964).

⁹ The F -center resonance in NaF is an isotropic line at $g=2.001$ with a partially resolved structure: 19 lines with 37.7 G separation. See: W. C. Holton and H. Blum, Phys. Rev. 125, 89 (1962).

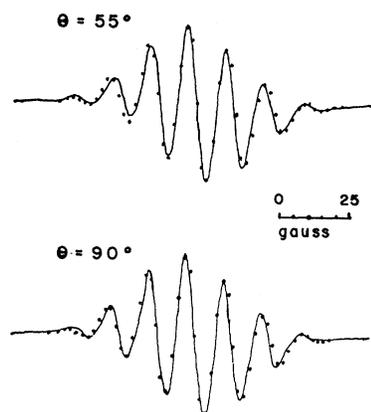


FIG. 2. The observed EPR spectra (solid lines) and the theoretical fit (dots) of Fe^{3+} in NaF near 180°K for $\theta = 90^\circ$ and $\theta = 55^\circ$.

The first term of Eq. (1) describes the Zeeman interaction of the electron spin ($S = \frac{5}{2}$) with the magnetic field H , where the spectroscopic splitting factor $g = 2.002$, and β is the electronic Bohr magneton. The second term of Eq. (1) denotes the summation of the hyperfine interaction tensor \mathbf{A}_n of the n th fluorine nucleus of spin $I_n (= \frac{1}{2})$ over the six nearest-neighbor fluorine nuclei.

Since the paramagnetic ion is on a cubic lattice site, each of the hyperfine tensors is axially symmetric and the hyperfine term can be written as follows¹²:

$$\sum_n I_{nz} S_{z'} [\delta + \gamma (3 \cos^2 \theta_n - 1)], \quad (2)$$

where the subscript z' refers to the direction of the external field along which \mathbf{S} and \mathbf{I}_n are quantized,¹² and θ_n is the angle between the direction of the magnetic field and the axis joining the n th fluorine nucleus to the paramagnetic ion. The two Greek letters δ and γ represent the isotropic and anisotropic (hyperfine) coupling constants respectively.

The third term of Eq. (1) is the fine structure term for the ${}^6S_{5/2}$ ion in a cubic crystalline field. It has the following form¹¹:

$$F(a) = \left(\frac{1}{6}\right)a[S_x^4 + S_y^4 + S_z^4 - \left(\frac{1}{3}\right)S(S+1)(3S^2 + 3S - 1)], \quad (3)$$

where the suffices x , y , and z refer to the crystalline axes, and a is the fine-structure constant. The fine structure term depends only on the electron-spin operators, and splits transitions between the electron spin levels as follows¹¹:

$$M_s = \pm \frac{1}{2} \rightarrow \mp \frac{1}{2}: H = H_0, \quad (4)$$

$$M_s = \pm \frac{3}{2} \rightarrow \pm \frac{1}{2}: H = H_0 \pm \left(\frac{5}{2}\right)p(a/g\beta), \quad (5)$$

$$M_s = \pm \frac{5}{2} \rightarrow \pm \frac{3}{2}: H = H_0 \pm 2p(a/g\beta), \quad (6)$$

where $H_0 = h\nu/g\beta$, ν being the fixed microwave resonance frequency, and $p = \left(\frac{1}{3}\right)(l^2m^2 + m^2n^2 + n^2l^2)$ with l ,

¹² H. Seidel and H. C. Wolf, Phys. Status Solidi 11, 3 (1965).

TABLE I. Spin-Hamiltonian parameters for the observed resonance due to Fe^{3+} in NaF at 77°K .

$g = 2.002 \pm 0.0008$	
$a = 2.29 \pm 0.05$	10^{-4} cm^{-1} (2.45 G)
$\delta = 12.8 \pm 0.03$	10^{-4} cm^{-1} (13.7 G)
$\gamma = 1.7 \pm 0.1$	10^{-4} cm^{-1} (1.8 G)
$W = 4.69 \text{ G}$	

m , n the direction cosines of \mathbf{H} referred to the cubic axes of the crystal. The transitions given by Eqs. (4), (5), and (6) have an intensity ratio of 9:8:5 respectively.¹³

Using the spin Hamiltonian given in Eq. (1), theoretical spectra were calculated with the aid of an IBM 7074 computer (W.S.U. Computing & Data Processing Center, Detroit, Michigan). The first step in this calculation is to determine the magnetic energy-level structure of \mathcal{H} . The Zeeman term yields six equally spaced electron spin levels and each of them is split into the nuclear hyperfine structure determined by the hyperfine term. *In general*, there are 64 hyperfine levels, each corresponding to one of the $(2I_n + 1)^6$ possible orientations of the six nuclear spins, each $I_n = \frac{1}{2}$. Finally, the fine-structure term splits each of these into five levels. From this structure, then, the energy separation, ΔE_i , of all the allowed transitions is determined along with the magnetic field value $H_i = \Delta E_i/g\beta$, at which the transition will take place. Knowing all possible values of H_i it is then possible to construct a theoretical spectrum. Using the magnetic field H as the abscissa, the derivative of a Gaussian line,¹⁴ which has a width W between the points of maximum slope, is placed at all values of H_i . Each of these Gaussian lines is weighted by the appropriate intensity factor. The individual Gaussian derivative curves are then superimposed and added together at 0.5-G intervals to obtain the over-all composite spectrum. The interval of summation (0.5 G) is chosen to obtain the maximum resolution in the computed spectrum. The structure and anisotropy of the computed spectrum naturally depends on the values of the parameters (δ , γ , a , and W). These parameters are varied over wide ranges, so that the resulting computed spectra fit well the observed spectra. Two facts are especially helpful in determining the best fit: (1) for $\theta = 55^\circ$ the anisotropic hyperfine interaction vanishes and has no effect on the spectrum, and (2) for $\theta \approx 30^\circ$ the fine-structure splitting vanishes¹⁵ ($p = 0$) and a has no effect on the spectrum.

The results of this computer fit for the observed spectra at 77°K are illustrated in Fig. 1, where the

¹³ L. M. Matarrese and C. Kikuchi, J. Phys. Chem. Solids 1, 117 (1956).

¹⁴ Gaussian-shaped lines were used in this calculation, since there is probably some broadening due to the hyperfine interaction with next-nearest-neighbor nuclei. Also, the individual lines making up the composite spectra are probably broadened by thermal vibrations as will be shown later on in this paper.

¹⁵ Experimentally, the spectra reaches a maximum amplitude for θ near 34° even though the fine structure disappears near 30° . This is probably due to the anisotropic hyperfine interaction which is decreasing at this point and vanishes when $\theta = 55^\circ$.

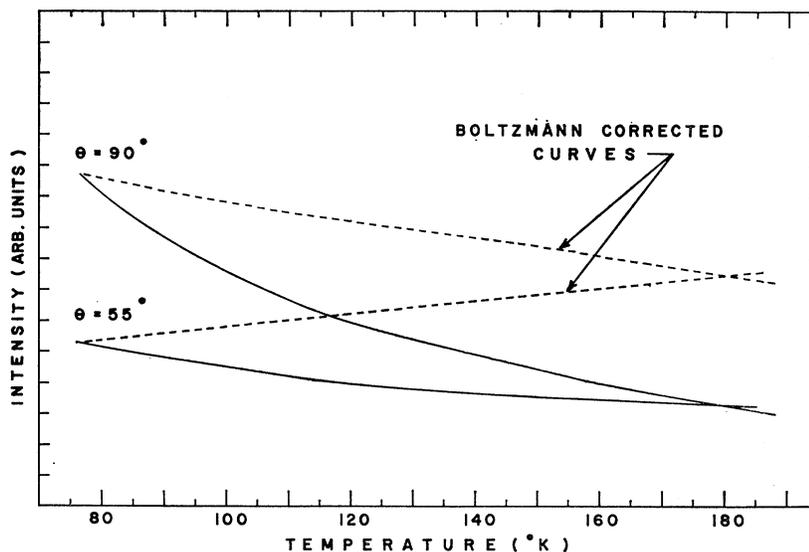


FIG. 3. The observed temperature dependence of the EPR spectral amplitude for $\theta=90^\circ$ and $\theta=55^\circ$ (solid curves). The dashed curves represent the experimental curves corrected for the Boltzmann temperature dependence.

spectra for four values of θ (0° , 34° , 55° , and 90°) are compared. The solid lines are the observed spectra and the dots represent the computed spectra. The values of the spin-Hamiltonian parameters which gave this fit are given in Table I. The agreement between the observed spectra and the calculated spectra is remarkably satisfactory and justifies the reasoning that led to the choice of the electronic state of the paramagnetic ion (${}^6S_{5/2}$) in a cubic site and its spin Hamiltonian.

IV. TEMPERATURE EFFECTS

As the temperature of the samples is raised from 77 to 180°K ,¹⁶ the features of the spectra for different angles change quite rapidly and significantly. For example, near 180°K , the spectra for all values of θ tend to show only a seven-line pattern as is observed for $\theta=90^\circ$ at 77°K , and there is an accompanying decrease of the spectral amplitude. The solid curves of Fig. 2 illustrate the spectra for $\theta=55^\circ$ and $\theta=90^\circ$ near 180°K , and the solid curves of Fig. 3 show the observed temperature dependence of the amplitude of the two spectra in Fig. 2.

A comparison of the spectrum for $\theta=55^\circ$ of Fig. 2, for example, with the corresponding spectrum in Fig. 1 would indicate easily the interesting effect of the temperature change. The structural change of the spectra at 180°K indicates that the spin-Hamiltonian parameters are changing and that the temperature effect is not solely due to the Boltzmann temperature dependence of the spin level population. Another evidence in support of this view is given by the observed temperature dependence of the spectral amplitude. The portion of the amplitude change due to the Boltzmann temperature dependence (of the spin level populations) can be

¹⁶ At higher temperatures, the spectral intensity at $\theta=0^\circ$ becomes quite small and weak signals due to unidentifiable impurities make a detailed analysis of this spectrum difficult.

readily removed by means of a correction factor. When the correction is made, the solid curves in Fig. 3 should behave like the two dashed curves. If the amplitude change were due solely to the Boltzmann temperature dependence, the dashed curves would have to be horizontal. The fact that they are not indicates that the spin-Hamiltonian parameters and/or W are changing, as the temperature is varied.

A major consideration in the computer analysis of the temperature dependence of these spectra is, therefore, that the computed spectra show only the basic seven-line pattern near 180°K and that the anisotropy of the computed spectra corresponds to the observed anisotropy. Otherwise, theoretical spectra for the higher temperatures were calculated in the same way as described previously for the 77°K spectra by adjusting the values of a , γ , and W . All the computed spectra were normalized so that the area under the absorption curve remained constant for changes in W .

The computation results have indicated that the observed change in the structure and amplitude of the spectra for different temperatures is primarily due to the temperature dependence of a and W , and slightly due to γ , while g and δ appear to remain constant within experimental errors. The results of the computation are illustrated by the dots in Fig. 2. The agreement is satisfactory. Figure 4 illustrates the computed temperature dependence of a , W , and γ , which has been found to be satisfactory to account for the observed temperature dependence of the spectra. Three points of significance should be noticed: First, a decreases practically linearly as T increases. Second, W is found to be proportional to the square root of T . Third, γ tends to decrease as T increases, but the large error in the computational difficulty makes it doubtful whether the change of γ is significant, as compared with the change of a and W .

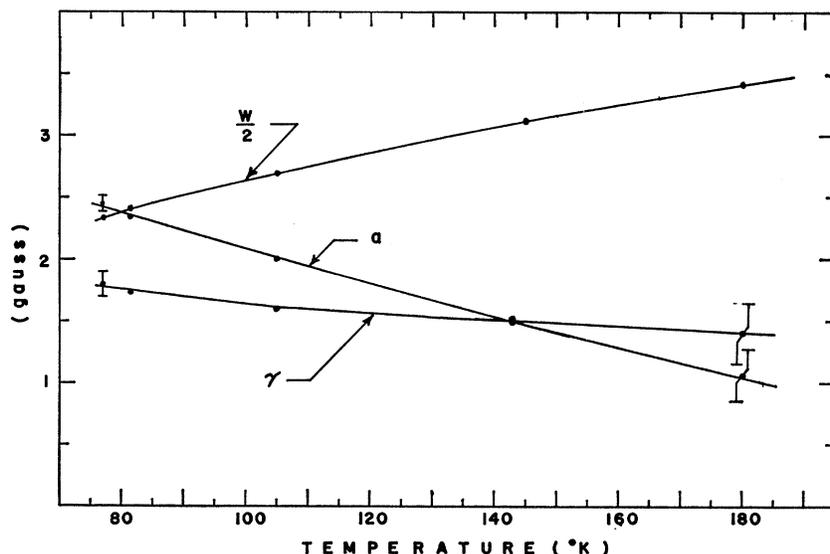


FIG. 4. The temperature dependence of a , γ , and W found by fitting the experimental data at several temperatures. g and δ are found to be constant within experimental error.

V. DISCUSSION

The results of the analyses in the preceding show that the choice of the electronic state (${}^6S_{5/2}$) of the paramagnetic ion, its location at a cation site surrounded by a cubic field, and the accompanying spin-Hamiltonian Eq. (1) is very satisfactory in accounting for the anisotropy of the spectra as well as for the temperature dependence of the spectra.

Each of the three metallic impurities (iron, manganese, and chromium) of the NaF samples investigated in the present work can exist in the ${}^6S_{5/2}$ electronic state: Fe^{3+} , Mn^{2+} , and Cr^{3+} . Of the three possibilities, Fe^{3+} is most favorable. The following reasons may be cited. *First*, Mn^{2+} has a nuclear spin of $\frac{5}{2}$ and a large nuclear magnetic moment, which would lead to a large hyperfine splitting of the spectra and would contribute to the spin Hamiltonian in Eq. (1) an additional term representing the hyperfine interaction of the electronic spin with the nuclear spin of Mn^{2+} . This additional term would then lead to a hyperfine splitting (~ 90 G) of the spectra, which is not the case in the present work.

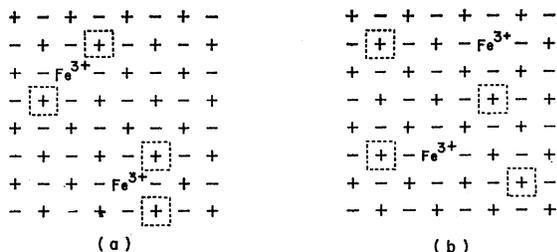


FIG. 5. (a) Associated charge compensating cation vacancies in next-nearest-neighbor positions forming a "complex." (b) Charge compensating vacancies away from the Fe^{3+} ion. The Fe^{3+} ions are left in a site with cubic symmetry and the vacancies are free to migrate at sufficiently high temperatures depending on the activation energy.

Furthermore, the x irradiation has reduced the resonance of Mn^{2+} practically to nil (see Sec. III). *Secondly*, the concentration of the chromium impurity is too small (less than 0.1 ppm), to be responsible for the spectra, since the observed spectra corresponds to a concentration of at least 1 ppm of impurity. *Thirdly*, the parameter for Cr^{3+} in NaF reported by Hayes and Jones² are not the same as the parameters determined in the present work.

The ionic radius of Fe^{3+} ion is relatively small (0.6 Å)¹⁷ and the interatomic spacing of the NaF lattice is 2.31 Å. This might lead one to speculate that the Fe^{3+} should be located in an interstitial position as it is in AgCl^3 . The conclusion in the present work that it is not in an interstitial position is probably attributable to the stability¹⁸ of the complex $(\text{FeF}_6)^{3-}$. This complex puts the iron in a lattice site with cubic symmetry.

To preserve local electrical neutrality in the lattice, each Fe^{3+} should produce two cation vacancies. These vacancies will cause departures from cubic symmetry at the Fe^{3+} site [see Fig. 5(a)], if they are close to the Fe^{3+} site forming a complex. This would introduce additional noncubic terms into the spin Hamiltonian, Eq. (1). Since the resonance can be fit by only cubic terms, the charge compensating vacancies are not "bound" to the Fe^{3+} site [see Fig. 5(b)].

The computed temperature dependence of a (see Fig. 4) deserves some comments with regard to the existing theoretical expression for a . The fine-structure constant a decreases as T increases. This tendency is consistent with the existing speculation.¹⁹ The decrease of a is practically linear in T . This linear relation leads to a linear dependence of a on the lattice constant d ,

¹⁷ L. H. Ahrens, *Geochim Cosmochim. Acta.* **2**, 155 (1952).

¹⁸ N. S. Gill, and R. S. Nyholm, *J. Chem. Soc.* **1959**, 3997 (1959).

¹⁹ W. Low, *Ref. 11*, p. 118.

for the case of the linear expansion of the lattice. Quantitatively, however, the amount of change (approximately 60%) of a between 77 and 180°K does not appear to be easily compatible with the existing theories on a . According to the theories on the S -state ions, the fine structure constant is given in a certain approximation by the following²⁰:

$$a = K\lambda^4/E_{PS}^4, \quad (7)$$

where K is the matrix element of the potential V of the cubic crystalline field, and E_{PS} and λ are the energy spacing between the 4P and 6S states of the Fe^{3+} ion in the lattice and the spin-orbit coupling constant respectively. λ seems to be less significant in the T dependence of a . The reason is the following: Experimentally, the spectroscopic splitting factor g is practically insensitive to temperature changes in the range between 77 and 180°K. This means that the change of λ over the same temperature range, if any, is not significant. It is possible that E_{PS} is temperature-dependent. However, it is hard to imagine that it could change enough to produce the observed temperature dependence of a . Thus, K becomes a factor to produce the temperature dependence of a . The wave function used for the matrix element is more or less insensitive to the temperature change. Consequently, the possible T dependence of K originates from the temperature dependence of the cubic field potential V . Simple calculations by means of Eq. (7) and a linear thermal expansion of the lattice produce about 2 to 3% change of a over this temperature range. This is just too small to account for the observed change (60%) of a . The possibility that the computer fitting is not necessarily unique appears to be very remote, because the values of the parameters involved in the computation for Fig. 4 (see also Sec. IV) have been varied in wide ranges and the most optimum values of a at different temperatures have been obtained and plotted in Fig. 4. Thus, no simple satisfactory explanation for the observed T dependence of a appears to be immediately available. It is hoped that electron-nuclear-double-resonance (ENDOR) studies of the same samples examined in the present paper may provide some additional information concerning the interaction of the S -state ion with its environment. Further efforts in this direction are being made in this laboratory.

VI. CONCLUSION

EPR studies of x-irradiated single crystals of NaF containing iron as an impurity have been conducted

²⁰ S. A. Al'tschuler and B. M. Kozyrev, Ref. 4, p. 72.

near 4.2°K and at temperatures between 77 and 180°K.

Three (EPR) spectra with isotropic g values have been distinguished: One is the well-known F -center spectrum; the second is centered near $g=2.002$, and exhibits a partially resolved structure which is anisotropic; the third is centered near $g=4.334$, and corresponds to the Fe^+ spectrum that was previously determined by Bleaney and Hayes.¹ The first two spectra are readily observable near 77°K, while the Fe^+ spectrum is observed near 4.2°K.

The observed anisotropy of the second spectrum has been successfully described in terms of a spin Hamiltonian consisting of (i) a Zeeman term for an effective spin $S=\frac{5}{2}$, (ii) a fine-structure term for an S -state ion located at the center of a cubic crystalline field, and (iii) a hyperfine interaction term pertaining to six equivalent nuclei of spin $\frac{1}{2}$ each. The spin Hamiltonian has led to the identification of the ion responsible for the spectrum to be $\text{Fe}^{3+}(^6S_{5/2})$ located at a cation site, interacting with the cubic crystalline field and with the nearest-neighbor fluorine nuclei. The results indicate that the charge-compensating vacancies (two cation-ion vacancies per Fe^{3+}) are far from the site of Fe^{3+} and do not disturb the cubic crystalline field surrounding Fe^{3+} .

As the temperature is raised from 77 to 180°K, the Fe^{3+} spectrum changes in both its structure and amplitude. Computer analyses of the observed temperature dependence have indicated that the changes are due primarily to the temperature dependence of the fine structure constant (a), and the width (W) of individual lines composing the Fe^{3+} spectrum. The analyses also have yielded that a decreases almost linearly by approximately 60% over the temperature range and W increases as the square root of the temperature.

The results are consistent qualitatively with the existing theories of the S -state ion. Quantitatively, however, the change (60%) of a from 77 to 180°K is just too big to be satisfactorily accounted for by the corresponding change (2 to 3%) expected from the theoretical expression for a . Similar studies on S -state ions are being conducted in order to examine further this point of concern.

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