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Temperature dependence of the ground-state cubic-field splitting for the ^6S iron-group ion in sodium fluoride*

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Iron-group impurities in x-irradiated NaF have been studied using electron paramagnetic resonance. Special attention was given to the measurement and understanding of the temperature dependence of a $^6S_{5/2}$ spectrum, which previously had been attributed to Fe^{3+} located substitutionally at a cation site with octahedral symmetry. Concentration measurements and comparisons with the work of others indicate that the spectrum is also consistent with NaF:Cr^+. The effective-spin-Hamiltonian parameters were measured for temperatures in the range of 21 to 198 K, and indicate 65% decrease in the fine-structure constant from 60 to 198 K, and a similar but less-well-defined increase in the transition width. The superhyperfine constants associated with the surrounding F^- ligands show little temperature dependence, and all parameters appear to have constant values below 60 K. The temperature dependence of the fine-structure constant has been interpreted according to the splitting of ionic states by the electron-phonon interaction mechanism, and calculations indicate possible agreement with data for a reasonable choice of atomic parameters.

I. INTRODUCTION

This paper presents measurements and calculations of the temperature dependence of the cubic-field ground-state splitting for a ^{6}S iron group in sodium fluoride.

Andrews and Kim[1] (hereafter referred to as AK) have described measurements of the spin-Hamiltonian parameters for the NaF:Fe^{3+} spectrum as a function of temperature. Their work indicates that the change in that spectrum over the temperature range of 77 to 180 K is mainly due to changes in the fine-structure constant and the linewidth of the individual transitions. A complete explanation for the large change in these parameters was not given. In this paper we extend their work to a temperature range of 21 to 198 K, but discuss the new results according to two models for the paramagnetic center. We will show that the measured parameters are also consistent with the interpretation that the center is due to Cr^+ rather than Fe^{3+} (such a center has previously been described by Hall *et al.*[2]). We shall interpret the temperature dependence of the ground-state splitting $3a$ according to the theory of the splitting of ionic states by the electron-phonon interaction (called SEPI), which is due to Shrivastava.[3]

In using the SEPI mechanism, we have differed somewhat from the original work by (i) finding it necessary to include higher orders in the orbit-lattice interaction, (ii) using an exact phonon spatial average rather than the long-wavelength approximation, (iii) treating the cubic-field strength Dq as a somewhat adjustable parameter, and (iv) using separate Debye temperatures for the longitudinal and transverse phonon modes.

We have applied the theory to both Cr^+ and Fe^{3+} in NaF, and have recalculated it for MgO:Mn^{++} as a check. Our recalculation for MgO:Mn^{++} is smaller than Shrivastava's by a factor of 10 (i.e., a factor of 2 larger than the experiment), but the inclusion of higher-order terms in the interaction results in an effect an order of magnitude larger than experiment. For NaF, we show that a somewhat reasonable choice of parameters can provide an approximate fit to our data.

The experimental procedures are presented in Sec. II, the experimental results in Sec. III. The identification of the paramagnetic center is discussed in Sec. IV, and an interpretation of the temperature dependence of $3a$ according to the SEPI theory is presented and discussed in Sec. V. A conclusion is drawn in Sec. VI.

II. EXPERIMENTALS

These experiments were performed at X band using homodyne detection. The system was based on the Varian V4500 EPR spectrometer, and made use of a Varian V4560 100-kHz multipurpose microwave cavity. Temperatures of and above 77 K were obtained by standard liquid-nitrogen Dewar and gaseous-nitrogen flow techniques. For temperature below 77 K, a special transfer tube was constructed similar to that described by Rannon and Hyde,[4] and was used to deliver cold He gas to a quartz flow Dewar. Temperatures were measured by placing calibrated carbon composition resistors above and below the sample cavity, and the sample temperature was taken to be the average of the temperatures at these two resistors. The temperature gradient within the flow Dewar generated an uncertainty at the sample of about ± 2 K at $T = 60$ K, and this uncertainty decreased with temperature.

Commercially grown (Harshaw Chemical Co.) single crystals of NaF containing natural impurities were used in all of the experiments presented here. A segment of a single crystal was typically oriented via x-ray diffraction, and cut into rectangular prisms having approximate dimensions 3×3×15 mm. The long axis in most of these experiments was along a [100] direction.

The preparation of the paramagnetic center involved x irradiation and optical bleaching. The former was accomplished at the exit port of a Phillips type 12045 x-ray diffraction unit using a molybdenum target operated at 50 keV and 20 mA. X-irradiation exposures of 60 to 100 h at room temperature were required. The bleaching process refers to the reduction of the interfering F-center resonance, and involved exposure of the x-irradiated crystal to a high-pressure Hg lamp (Illumination Industries type AHG-1, 1000 W) for not longer than a few hours. Before reaching the sample, the light from this lamp passed through a heat filter (water), and a glass condensing lens.

Most of the samples in this experiment were rotated about a [001] direction, and an angle θ was defined as being that between the external magnetic field and the [100] direction. During a given run, the [100] direction was found from the EPR anisotropy. At temperatures near or above 77 K, where only the spectrum in question is observed, $\theta \approx 0°$ was found by comparing the observed spectrum to that described by AK. We defined $\theta = 0°$ to be the orientation that corresponded to a local maximum in the signal height of the spectrum. At temperatures below 77 K, the g anisotropy of a spectrum associated[5] with Ni^+ was used to define $\theta = 0°$.

EPR concentration measurements (see Sec. IV) were based upon the method introduced by Singer.[6] That is, a properly oriented ruby single crystal was used as a secondary concentration standard. Our ruby was calibrated against the following primary standards: F centers in KCl, bis acetyl acetonate Cu(II), $MnSO_4 \cdot H_2O$, and $CuSO_4 \cdot 5H_2O$.

III. EXPERIMENTAL RESULTS

The effective spin Hamiltonian for an Fe^{3+} ion located substitutionally at a cation site and surrounded by six F^- ions in octahedral coordination has been given by AK as

$$\mathcal{H} = g\,\mu_B\,\vec{S}\cdot\vec{H}_0 + F(\alpha) + H_{SHF} \quad , \tag{1}$$

where the first term is the Zeeman interaction for $S = \frac{5}{2}$, μ_B is the electronic Bohr magneton, H_0 the external static magnetic field, and g is the spectroscopic splitting factor.

The second term in Eq. (1) refers to the fine structure appropriate to an $S = \frac{5}{2}$ ion in octahedral symmetry, and is given by[7]

$$F(\alpha) = \tfrac{1}{6}\,\alpha[S_x^4 + S_y^4 + S_z^4 - \tfrac{1}{5}S(S+1)(3S^2 + 3S - 1)] \quad , \tag{2}$$

where x, y, and z refer to the crystalline axes, and α is the fine-structure constant.

The third term represents the superhyperfine interaction of the central ion with the six fluorine ions in the first shell. Because of the cubic symmetry, it may be written[8]

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

where z' denotes the direction of the external field and is the preferred direction for both S and the fluorine nuclear spins, θ_n denotes the angle between H_0 and the axis along which rests the nth ligand, and δ and γ refer to the isotropic and anisotropic superhyperfine constants, respectively.

The Hamiltonian (1) leads to a large number of transitions. In the presence of a magnetic field satisfying the condition

$$\alpha/g\mu_B H_0 \ll 1 \quad ,$$

the fine-structure terms lead to the following transitions[7]:

$$(9)\; M_S = \pm\tfrac{1}{2} \rightarrow \mp\tfrac{1}{2} \;:\; H = H_0 \quad ,$$

$$(8)\; M_S = \pm\tfrac{3}{2} \rightarrow \pm\tfrac{1}{2} \;:\; H = H_0 \pm \tfrac{5}{2}p(\alpha/g\mu_B) \quad ,$$

$$(9)\; M_S = \pm\tfrac{5}{2} \rightarrow \pm\tfrac{3}{2} \;:\; H = H_0 \mp 2p(\alpha/g\mu_B) \quad ,$$

where $H_0 = h\nu/g\mu_B$, ν is the constant microwave frequency, and $p = \frac{1}{5}(l^2m^2 + m^2n^2 + n^2l^2)$, l, m, and n being the direction cosines of H_0 with respect to the cubic axes of the crystal. The numbers in parentheses on the left denote relative intensities. Since there are three sets of paired fluorine nuclei in the first shell, and since each pair has three possible orientations in the external magnetic field, a given fine-structure line will be split into not more than $3^3 = 27$ transitions. Thus for a given crystal orientation, there may be as many as 135 transitions.

When the interval between any two adjacent transitions is smaller than their widths, as is the case here, a partially resolved spectrum results. Analysis then requires a computer synthesis. Using an IBM 360 computer (W.S.U. Computing and Data Processing Center, Detroit, Mich.) we have found the constants α, γ, and δ that correspond to the recorded spectra. Our computer program, however, differs in some respects from that used by AK.

AK used two special orientations to separately eliminate effects of fine and anisotropic hyperfine structure, but we were only able to use one such orientation. That is, for $\theta \approx 32°$, the effects of fine structure vanish ($p = 0$). This orientation was used by us to obtain less ambiguous determinations of γ and δ. The parameter α was determined for

$\theta = 0°$ where the fine structure has maximum effect ($p = 1$).

AK determined a good fit to the data by incrementing each parameter over a wide range. We have used a nonlinear least-squares technique[9] whereby the program converges upon a set of parameters, and generates a corresponding hypothetical spectrum with a minimum standard deviation relative to the measured spectrum. This widely used method has the advantage of efficiently finding at least one good set of parameters, while bypassing a host of poor sets. Occasionally, more than one set of equally good parameters were found, and these were used to set limits on the certainty of the results.

Figure 1 shows examples of spectra for $T = 56$ K and $T = 198$ K, $\theta = 0°$. The measured spectrum corresponds to the solid line, the computed spectrum to dots. The fit seems adequate for low temperatures, but not as good for the high temperature, where the weakness of the spectrum together with possible interference from other impurities made data both difficult to acquire and to analyze.

The results for parameters at $T = 77$ K are shown in Table I along with those determined by AK. We differ notably in values for W and δ, where W is the half-width of a transition, and is defined here to be that of a Gaussian line shape as measured between points of maximum slope. The descrepancies may be due to the differing analytical techniques. In particular, we did not attempt to find a value for W that was the same for all orientations, as did AK. Instead, we noticed a possible orientational dependence for W. This may not seem surprising when we consider that the width of a single transition may be greatly influenced by the anisotropy of the second shell. Also, the width may be influenced by an anisotropic relaxation time. Preliminary measurements using the saturation method showed that the product of the spin-spin and spin-lattice relaxation times was definitely anisotropic, and reached a local maximum for $\theta = 0°$. The values for W given here were obtained for that orientation alone, and were smaller than those obtained at other orientations.

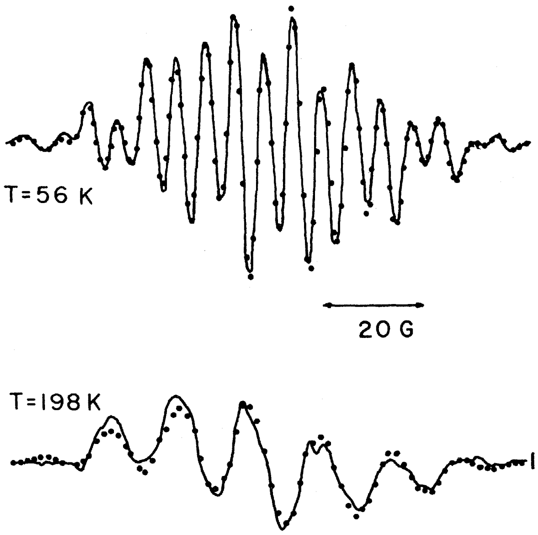

FIG. 1. Observed (solid line) and computed (dots) spectra at $T = 56$ K and $T = 198$ K. The approximate noise level of the recorded spectrum is indicated, in the latter case, by the vertical line on the right-hand side of the figure.

TABLE I. EPR parameters at $T = 77$ K.

Parameter	Present work	Andrews and Kim[a]
g	2.0012	2.002 ± 0.0008
α (10^{-4} cm^{-1})	2.36 ± 0.2	2.29 ± 0.05
δ (10^{-4} cm^{-1})	12.6 ± 0.15	12.8 ± 0.03
γ (10^{-4} cm^{-1})	1.7 ± 0.1	1.7 ± 0.1
W (G)	3.97	4.69

[a] Reference 1.

The temperature dependence of the Hamiltonian parameters α, γ, and W is shown in Fig. 2. We find no definite temperature dependence in δ, and only a slight indication in γ. W and α, however, change rapidly for temperatures above 70 K, but approach somewhat constant values below 70 K. These trends agree with those obtained by AK. We made no effort to observe a temperature dependence in g; AK report none.

IV. MODEL FOR THE PARAMAGNETIC CENTER

The proper identification of the center requires some discussion. Recent mass-spectrograph analyses of our samples (some of which were also used in the AK study) indicate the presence of Mn (2ppm), Fe (8ppm), Cr ($\lesssim$ 0.1ppm), Ni ($\lesssim$ 0.1ppm), Nb (4ppm), and Pr (1ppm), where typical concentrations for the various samples are indicated in parentheses. In addition to the above, a high Si background and some organic contaminants were reported.

Our observations have enabled us to identify some Ni^+ spectra corresponding to those described by Hayes and Wilkens,[5] and the Fe^+ spectrum described by Bleaney and Hayes.[10] Mn, Nb, and Pr all have large nuclear spins, and should show characteristic hyperfine structure, six lines for Mn and Pr ($I = \frac{5}{2}$) and 10 for Nb ($I = \frac{9}{2}$). We have only observed Mn^{++} here. No indication of Si or organic materials was observed. We are left with the two possibilities, Fe and Cr.

We have performed concurrent EPR concentra-

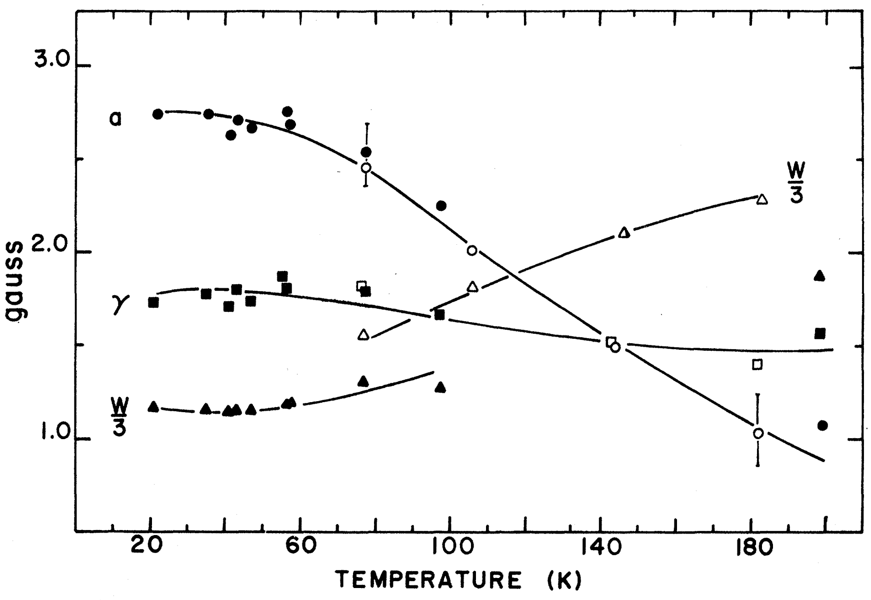

FIG. 2. Temperature dependence of W, γ, and α. The solid data points refer to the present work, the open data points to the work of Andrews and Kim. The solid lines only serve to indicate the trend in the data.

tion measurements on all observed spectra. Our results for the Mn^{++}, Ni^{+}, and Fe^{+} spectra (≈ 2, 0.2, and 0.1 ppm, respectively) appear to be consistent with the mass-spectrograph values. The EPR concentration for the remaining spectrum (Sec. III), however, appears to be about 0.01 ppm. This is in contrast to the 1-ppm estimate provided by AK, and is also significantly less than the mass-spectrograph value for Cr. On the basis of mass-spectrograph and EPR concentration measurements, the number of spins in this spectrum is consistent with both Fe and Cr.

Table II shows the EPR parameters determined for $NaF:Cr^{+}$ at $T = 77$ K by Hall *et al.*,[2] and those determined using electron-nuclear double resonance (ENDOR) at liquid-He temperatures by Ziegler and Seidel.[11] They are remarkably similar to ours. Whether we have observed Fe^{3+} or Cr^{+} is complicated by both ions having practically the same effective-spin Hamiltonian. The only differences arise from the expected hyperfine structure of ^{57}Fe ($I = \frac{1}{2}$, 2%) and ^{53}Cr ($I = \frac{3}{2}$, 9.5%). Confirmation of the $NaF:Cr^{+}$ model has come through the ENDOR workers who have measured the hyperfine constant A^{53} to be $20.71 \times 10^{-4}\,cm^{-1}$. Using this value for A^{53}, a hypothetical $(Cr + {}^{53}Cr)^{+}$ EPR spectrum was constructed, and then treated as an experimental spectrum. The changes in the parameters that resulted when this hypothetical spectrum was fit to the Fe^{3+} Hamiltonian (1) were negligible, and we conclude that our technique is incapable of detecting the presence of ^{53}Cr in the EPR spectrum. An observation of the contribution of ^{53}Cr to the wings of the EPR spectrum would have been definitive, but low impurity concentrations made this impossible.

In Table III, we list the parameters for Cr^{+} and Fe^{3+} in several solids. We can begin to see two trends. The g shift, $\Delta g = g - 2.0023$, is negative for Cr^{+} but positive for Fe^{3+} ($g = 2.0023$ is the free-electron value), and for a given material, the cubic splitting parameter α is smaller for Cr^{+} than for Fe^{3+}. If we assume that the paramagnetic center of interest is Fe^{3+}, then these trends are not manifest in NaF (compare Tables I and II). We note that there is some theoretical reason for believing that Δg should be negative for Cr^{+} and positive for Fe^{3+}. Watanabe[12] has calculated such shifts for $NaCl:Cr^{+}$ and Fe^{3+} in II-VI compounds. Finally, the table shows that γ is much higher for Fe^{3+} in the perouvskite fluorides than for Cr^{+}. Recent calculations[13] agree with this qualitative observation, and have also obtained good quantitative agreement for γ in $NaF:Cr^{+}$.

The above analysis suggests that the Fe^{3+} center discussed by AK may well be due to $NaF:Cr^{+}$. This

TABLE II. EPR parameters attributed to NaF : Cr^{+}.

Parameter	Hall *et al.*[a] $T = 77$ K	Ziegler and Seidel[b] $T \approx 4$ K
g	2.001 ± 0.001	...
α (10^{-4} cm^{-1})	2.2 ± 0.2	...
δ (10^{-4} cm^{-1})	12.5 ± 0.5	12.645
γ (10^{-4} cm^{-1})	1.5 ± 0.5	1.53

[a] Reference 2. [b] Reference 11.

TABLE III. EPR parameters for Cr^+ and Fe^{3+} in various substances.

	Cr^+			Fe^{3+}		
Material	g	α (10^{-4} cm^{-1})	γ (10^{-4} cm^{-1})	g	α (10^{-4} cm^{-1})	γ (10^{-4} cm^{-1})
$KMgF_3$ [a]	2.0005	4.5	1.83	2.0031	51	6
$KCdF_3$ [a]	•••	•••	•••	2.0027	53	5.67
MgO[b,a]	1.9996	41.3	•••	2.0037	205	•••
ZnS[a]	1.9995	3.9	•••	2.019	127	•••
ZnSe[c]	2.0016	5.35	•••	•••	48.3	•••

[a] Reference 37, p. 440.

[b] G. Rius and A. Herre, Solid State Commun. 11, 795 (1972).

[c] G. H. Azarbayejani and C. Kikuchi, University of Michigan Technical Report No. 04381-9-T, 1966, p. 16 (unpublished).

conjecture will be taken into consideration in Sec. V.

V. INTERPRETATION OF THE TEMPERATURE DEPENDENCE OF $3a$

A. Introduction

The first treatment of the temperature dependence of 3α was given by Walsh *et al.*,[14] who showed that such a dependence could be described in terms of an implicit and explicit temperature behavior. The implicit dependence refers to changes in 3α brought on by changes in the interionic distance via thermal expansion. He showed that the effect in $MgO{:}Mn^{++}$ and $MgO{:}Fe^{3+}$ could largely be explained in this way. On the other hand, the effect in $ZnS{:}Mn^{++}$ could not be explained by thermal expansion alone. The leftover dependence was termed explicit.

The rare earths have attracted similar attention. The first calculations of an explicit contribution to the ground-state splitting were made by Huang[15] and Menne.[16] These involved applications of the orbit-lattice interaction of $CaF_2{:}Gd^{3+}$, but the results were generally orders of magnitude too small or of the wrong sign.

The first such calculation for the iron group was given in Shrivastava's theory of the splitting of ionic states by the electron-phonon interaction[17] (called SEPI). His application of the SEPI theory to $MgO{:}Mn^{++}$ yielded an effect 20 times larger than the residual explicit effect measured by Walsh *et al.* The functional form derived in the SEPI theory was also successfuly applied[3] to $ZnS{:}Mn^{++}$ but no detailed calculation was presented in that paper. Harvey[18] has discussed the theory, and has suggested that its validity is questionable for the somewhat covalent ZnS. He has emphasized the need for more experimental evidence.

AK have pointed out that the temperature dependence of 3α for the $NaF{:}Fe^{3+}$ spectrum is much too large to be accounted for by thermal expansion alone. This, and the more complete data now available, have prompted us to carry out a SEPI calculation. It was our original contention that a dominant explicit effect in an ionic solid such as NaF might be a more appropriate test for the theory than has been either MgO or ZnS.

The implicit contribution to the temperature dependence is estimated in Sec. V B. An outline of the SEPI calculation is presented in Sec. V C, and the results in Sec. V D are discussed in Sec. V E.

B. Implicit contribution

Ionic theories[19] of 3α show a dependence on the interionic distance R such that

$$\alpha = K/R^{5n} , \tag{4}$$

where K contains all the atomic parameters and the matrix elements that enter into a perturbation calculation, and where $n \approx 4$ (this value has been approximately verified by hydrostatic experiments[20]) is typical for the ionic theories. If the only effect of the temperature is to change R, then the fractional change in 3α due to R can be found from Eq. (4) to be

$$\frac{d}{dT} \ln \alpha = -5nr, \tag{5}$$

where r is the coefficient of linear expansion.

In Fig. 3, the dotted line represents the variation of α with T as is implied by Eq. (5). Values for α in this temperature range were taken from James and Yates,[21] and we have set $\alpha(T=0) = 2.52 \times 10^{-4}\,cm^{-1}$. We note the large difference between the implicit contribution and our data. We take this to mean that a large explicit temperature dependence exists in $\alpha(T)$, and to our knowledge, this is the most dramatic instance of such an effect.

C. Explicit contribution

Central to the SEPI theory is the orbit-lattice interaction[22] $\mathcal{H}_{OL}$, which can be thought of as rep-

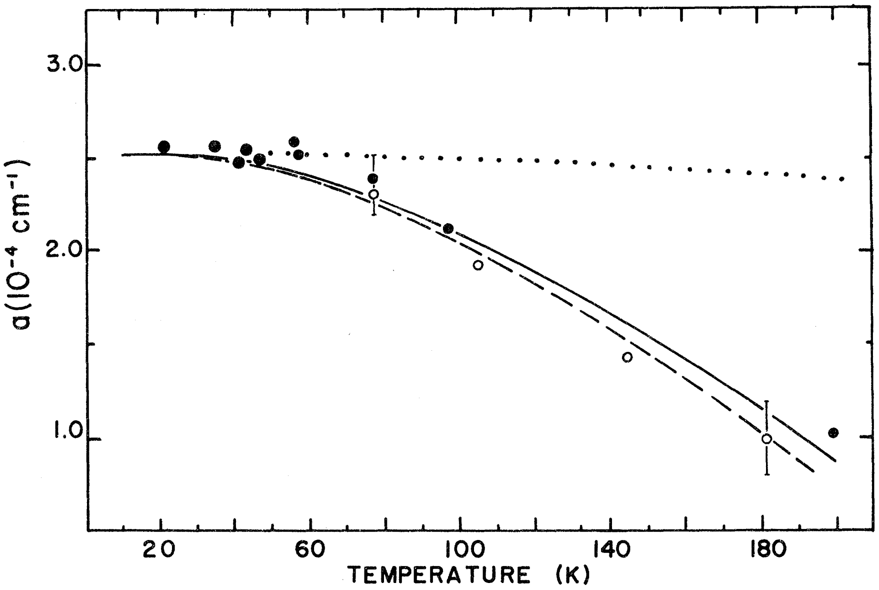

FIG. 3. Theoretical contributions to the temperature-dependent fine-structure constant. The implicit contribution for $n=4$ is given by the dotted line. The implicit-plus-explicit contribution is given by the dashed (NaF : Fe^{3+}) and solid (NaF : Cr^{+}) lines.

resenting the change in the electronic energy of the central paramagnetic ion due to the movement of the ligands about their equilibrium positions. In the SEPI theory, several excited states are admixed by the cubic field, and then coupled to the ^6S ground state by the spin-orbit interaction. These same excited states are sensitive to the movement of the ligands. So, as the temperature increases, the ligand movement increases, and an indirect change in the splitting of the ground-state levels occurs.

For an electronic state characterized by the vibrational quantum number N_k, Shrivastava gives the phonon-induced shift of an energy level, Γ_0, to second order in H_{OL} as

$$\Delta_{\Gamma_0}=\sum_{i,k';j,l,m}\frac{\langle\Gamma_0,N_k|\mathcal{H}_{\mathrm{OL}}(j,l,m)|\Gamma_i,N_{k'}\rangle\langle\Gamma_i,N_{k'}|\mathcal{H}_{\mathrm{OL}}(j,l,m)|\Gamma_0,N_k\rangle}{E_i-E_0}\ , \tag{6}$$

where E_0 and E_i denote the electronic energies of the states $|\Gamma_0,N_k\rangle$ and $|\Gamma_i,N_{k'}\rangle$, respectively. The sum is over the excited states and the normal modes (referenced by the indices j, l, and m) of the metallic complex. If $|\Gamma_0\rangle$ represents, in turn, $|_1\Gamma_8\rangle$ and $|_1\Gamma_7\rangle$ of the $^6S_{5/2}$ ground state, then the change in the fine-structure constant will be given by

$$\Delta\alpha=\tfrac{1}{3}(\Delta_{_1\Gamma_8}-\Delta_{_1\Gamma_7})\ . \tag{7}$$

The forms for $|\Gamma_0\rangle$ and $|\Gamma_i\rangle$ can be found in the literature,[17,23,24] and involve the $^6S_{5/2}$ ground-state cubic eigenfunctions, the spin-orbit constant ζ for a single $3d$ electron, and the $^4\Gamma_4$ components of the excited-state cubic eigenfunctions, and their corresponding energies relative to the ground state. Those excited states pertinent to the SEPI theory arise from the ^4G, ^4P, and ^4F quartets, and are given explicitly by Blume and Orbach[23] after taking care to change the sign of the mixing coefficient of the ^4G state[24] (see also Orbach and Stapleton[22]). Our expressions are different from those given by Shrivastava, where it does not appear that this correction has been made.

Shrivastava used only the lowest-order ($l=2$) terms in Eq. (6), and also the free-ion value for the ensuing $3d$ electron radial averages $\langle r^2\rangle$. We have found it useful to include the $l=4$ terms for the following reasons. A significant contribution to $\Delta\alpha$ should come from the state having large ^4P character[17] because only that character is directly coupled to the ground state. The first nonvanishing matrix elements with ^4P occur for $l=4$ terms in the orbit-lattice interaction. Also, the $l=4$ terms are proportional to the cubic-field strength parameter Dq, which is typically larger than what would be indicated when using free-ion values of $\langle r^4\rangle$.

In carrying out the calculation, the energies of the unperturbed quartets were obtained from Moore,[25] and the mixing coefficients and new energies of the admixed cubic states were found by solving the secular matrix given by Watanabe.[26]

Matrix elements of the electron operators appearing in Eq. (6) were found using the method of Racah as given by Blume and Orbach. Reference was made to the 3-j and 6-j symbols tabulated by Rotenberg *et al.*[27] Considerable human error was eliminated by rechecking these matrix elements with the aid of a computer subroutine for the generation of the 3-j symbols.

The result, which includes contributions from several of the normal modes, can be written in the form

$$\begin{aligned}\Delta\alpha=-\sum_{k'}\{&\Delta(\Gamma_{5g}2,0)f(Q(\Gamma_{5g}0),k')\\&+\Delta(\Gamma_{5g}4,0)f(Q(\Gamma_{5g}0),k')\\&+\Delta(\Gamma_{3g}4,\theta)f(Q(\Gamma_{3g}\theta),k')\\&+\Delta(\Gamma_{3g}4,e)f(Q(\Gamma_{3g}e),k')\}\ ,\end{aligned}\tag{8}$$

where

$$\begin{aligned}f(Q(\Gamma_{jg}m),k')=&\langle N_k|Q(\Gamma_{jg}m)|N_{k'}\rangle\\&\times\langle N_{k'}|Q(\Gamma_{jg}m)|N_k\rangle\ ,\end{aligned}\tag{9}$$

and where the $Q(\Gamma_{jg}m)$ contain the normal-mode structure the symmetries of which are formally indicated in parentheses. The terms of the form $\Delta(\Gamma_{jg}l,m)$ denote contributions associated with a given vibration mode, and represent lengthy expressions, which we have omitted here for the sake of brevity.

The temperature dependence is derived from Eq. (9), and may involve several approximations. Shrivastava attributed some of the overestimate of the temperature dependence in MgO:Mn^{++} to use of the long-wavelength approximation. We have chosen to carry out the phonon spatial averages in the exact manner introduced by Menne.[28] Our results are stated within the Debye approximation, and can be summarized by an expression of the form

$$\begin{aligned}\Delta\alpha=-\sum_\sigma\frac{C_0T^2}{v_\sigma^3}\int_0^{\Theta'_\sigma/T}\frac{x}{e^x-1}\{&[\Delta(\Gamma_{5g}2,0)+\Delta(\Gamma_{5g}4,0)]\\\times\langle[R_k^\sigma(\Gamma_{5g}0)]^2\rangle&+\Delta(\Gamma_{3g}4,\theta)\langle[R_k^\sigma(\Gamma_{3g}\theta)]^2\rangle\\&+\Delta(\Gamma_{3g}4,3)\langle[R_k^\sigma(\Gamma_{3g}e)]^2\rangle\}dx\ ,\end{aligned}\tag{10}$$

where

$$x=h\omega_{k\sigma}/k_BT\ ,\quad C_0=k_B^2/2\pi^2R^2\rho h\ ,\quad \Theta'_\sigma=\Theta_D^\sigma/\sqrt{2}\ ,$$

and where k_B is the Boltzmann constant, R is the metal-ligand distance, ρ is the density of the solid, h is Plank's constant, Θ'_σ is the reduced Debye temperature, and v_σ is the velocity of sound. Terms such as $R_k(\Gamma_{jg}m)$ refer to the projection of a phonon with wave number k and polarization σ onto the cluster mode $\Gamma_{jg}m$. The spatial averages are indicated by the brackets.

D. Results of calculation

We now present calculations for the three cases MgO:Mn^{++}, NaF:Fe^{3+}, and NaF:Cr^{+}. All integrals occurring in Eq. (10) were carried out numerically using the W. S. U. IBM 360 computer. All values for $V(\Gamma_{ig}2)$, which determines the radial dependence of $\mathcal{H}_{\mathrm{OL}}$ (see Ref. 22), were estimated from the approximately linear relationship that exists between $\langle r^2\rangle$ and $\langle r^4\rangle$ for a series such as Cr^{+}, Cr^{++}, Cr^{+++}, ... The values used for $\langle r^4\rangle$ were estimated in a manner consistent with the point-charge interpretation of Dq. Since ionic point-charge calculations yield values for Dq generally smaller than the real value, this procedure may stretch the point-charge model beyond validity. Its purpose is to compensate for the expanded 3d orbitals in the solid state.[24]

1. MgO:Mn^{++}

By using only the first term ($l=2$) in Eq. (8), and the long-wavelength approximation, we have repeated Shrivastava's original calculation. We have used the same parameters that are given in that paper, except that our values of the mixing coefficients and new excited-state energies are slightly different (principally our value for the lowest excited state is taken to be 19 518 cm^{-1} rather than 15 905 cm^{-1}). Our calculation gives a temperature dependence which is an order of magnitude smaller than Shrivastava's, or about a factor of 2 larger than the experimental data of Walsh as interpreted by Shrivastava.

If we repeat this calculation using the $l=4$ terms in Eq. (8) and the exact spatial averages, we obtain a temperature dependence which is an order of magnitude larger than experiment. Although this is less encouraging, the motivation still exists to carry out the calculation for NaF since in that case the explicit seems to dominate the implicit part.

2. NaF:Fe^{3+}

Unfortunately, there are no optical measurements of Dq for Fe^{3+} in alkali halides. Nevertheless, determinations of Dq for octahedral (FeF$_6$)$^{3+}$ complexes do exist for other substances. For instance, Breman and co-workers[29] give for (NH$_4$)$_3$[FeF$_6$] and FeF$_3$ (anhydrous) the values $Dq=1350$ and 1110 cm^{-1}, respectively.

That Dq for NaF:Fe^{3+} might have a value similar to those above is reasonable after considering the spectrochemical series. This series comprises a set of empirical relationships, one of which is that the value of Dq for a series of complexes

$[MA_6]$ having the same ligands A varies according to the central ion M. For example, Dq increases to the right for the series[30]

$$\mathrm{Mn}^{++} < \mathrm{Co}^{++} < \mathrm{V}^{++} < \mathrm{Fe}^{3+} < \mathrm{Cr}^{3+} < \mathrm{Co}^{3+} < \mathrm{Mn}^{4+} \;.$$

A recent measurement[31] gives $Dq = 780\,\mathrm{cm}^{-1}$ for NaF:Mn^{++}, so we can suspect that for NaF:Fe^{3+}

$$780 < Dq \lesssim 1400\,\mathrm{cm}^{-1} \;.$$

Let us adopt a value of Dq similar to that of FeF_3 (anhydrous), and further assume a value of R close to the FeF_3 bond length (≈ 2 Å). We use Eq. (10) together with mixing coefficients and excited-state energies appropriate to $Dq = 1100\,\mathrm{cm}^{-1}$, $\rho = 2.558$ g/cm^3, $\zeta = 400\,\mathrm{cm}^{-1}$, $\Theta'_l = 394$ K, $\Theta'_t = 230$ K, $\langle r^4\rangle = 20.9a_0^4$, and $\langle r^2\rangle = 3.09a_0^2$, where ρ is the density of NaF, Θ'_l and Θ'_t are the longitudinal and transverse reduced Debye temperatures, respectively, and a_0 is the first Bohr radius. The Debye temperatures were estimated from the frequency distributions for the acoustic modes calculated by Karo.[32] The velocity of sound as a function of temperature was taken from Vallin *et al.*,[33] where measurements for $V_l\,[100]$ and $V_t\,[110]$ and $V_t\,[100]$ are given; a simple weighted average of V_t over the two directions is adopted here.

The calculation yields a temperature dependence that is about a factor of 5 larger than the experimental dependence. We note, however, that if Dq is decreased to 650 cm^{-1} as a partial result of R increasing to the crystal bond length (2.31 Å), then the calculated behavior comes closer to the data. This last result is shown by the dashed line in Fig. 3, and where we've assumed that $\alpha(T=0) = 2.52 \times 10^{-4}\,\mathrm{cm}^{-1}$, $\langle r^2\rangle = 3.8a_0^2$, and $\langle r^4\rangle = 28a_0^4$.

3. *NaF:Cr$^+$*

Since Cr$^+$ may be responsible for the observed spectrum, we performed the calculation also for that case. We are not aware of any measurements of Dq for Cr$^+$ in any substance, so we treated Dq as an adjustable parameter. Griffith[34] gives $\zeta = 222\,\mathrm{cm}^{-1}$ for the free ion. We chose a value of $200\,\mathrm{cm}^{-1}$ under the assumption that some reduction would be present. A result in approximate agreement with the data was obtained for the values $Dq = 550\,\mathrm{cm}^{-1}$, $\zeta = 200\,\mathrm{cm}^{-1}$, $R = 2.31$ Å, $\langle r^4\rangle = 23.8a_0^4$, and $\langle r^2\rangle = 3.4a_0^2$. The other constants are unchanged. The calculated curve is shown by the solid line in Fig. 3.

E. Discussion

The application of the SEPI theory to any metallic complex is, of course, limited by one's knowledge of parameters such as Dq, ζ, R, and Θ. In our treatment, we tried to estimate all except Dq, which to some extent was adjustable. In this section we discuss justification for this fitting procedure, and comment on neglected aspects of the theory.

The motivation for fitting Dq to our data might seem lacking when one considers the order-of-magnitude overestimate achieved for MgO:Mn^{++}. For that case, however, the implicit effect is much larger than the explicit effect, and the latter does not seem to increase much with temperature. It is about the same at $T = 200$ K as it is at $T = 900$ K (this occurs also for MgO:Fe^{3+}).[18] In our case, the explicit largely dominates the implicit effect. The dramatic behavior of $\alpha(T)$ for NaF may be indicative of a single dominant mechanism, and it seemed reasonable to ask for a set of parameters that could lead to such behavior. Of course, the large number of parameters and their ensuing uncertainties makes any one set difficult to accept, but the results indicate that we are working with the right numbers.

The reader is referred to the literature for a discussion of the limitations of the SEPI theory,[17,18] and in addition, we should comment that: (i) Only the nearest-neighbor interactions were considered here. Next-nearest-neighbor effects[24] might enter via $l = 2$ terms in the orbit-lattice interaction since those terms fall off as R^{-3}. (ii) The present treatment does not take into account the reduction in the Racah parameters B and C that occurs for the central ion on entering the solid.[35] These are related to the interelectronic repulsion energies and so are proportional to the term energies. The reduction in B and C implies a reduction in the $E_l - E_0$, which in turn will tend to increase the magnitude of the temperature dependence. (iii) The theory is ionic and so is yet to stand the scrutiny of a cluster-model approach using molecular orbitals. Passeggi and Buch,[36] for instance, have shown that for simple molecules where covalency is important, the orbit-lattice matrix elements are dominated by electron transfer and overlap effects. Their results indicate that the ionic model underestimates these elements and may not even give the correct sign. We recall, however, that the g shift is negative for the ^6S spectrum we observe, and that this has been associated with ionicity.[37] The ionic Cr$^+$ is probably more suited to the SEPI theory than is the more covalent Fe^{3+}. In fact, of the parameters leading to the calculated curves in Fig. 3, those of Cr$^+$ are considerably closer to free-ion values. (iv) Finally, we note that the SEPI theory provides no explanation for the lack of much explicit temperature dependence in substances such as Fe^{3+} and Mn^{++} in MgO.

Several additional experiments could be performed to help us understand this spectrum: (i) A way to increase the spin concentration should be searched for. The higher concentrations would allow observation of any ^{53}Cr contribution in the wings. (ii) ENDOR could also be attempted (this was tried unsuccessfully in the early stages of this work). (iii) The experimental value of *n* in Eq. (4) could be found using hydrostatic pressure. (iv) Optical-EPR experiments might be performed pinning down the value of *Dq*.

VI. CONCLUSION

With the benefit of x irradiation, we have observed the EPR of several iron-group impurities in NaF. We have concentrated our efforts towards understanding the nature of a ^6S spectrum, which previously had been attributed to NaF:Fe^{3+}, and have measured its spin-Hamiltonian parameters over a temperature range of 21 to 198 K. Our results indicate that the spectrum is also consistent with NaF:Cr^{+}.

We have used the SEPI mechanism to fourth order (i.e., $l = 4$ terms) in the orbit-lattice interaction to calculate a temperature-dependent cubic-field ground-state splitting for the ^6S ion in NaF, and we have recalculated the effect for Mn^{++} in MgO. We find that reasonable values for the parameters lead to an overestimate of the effect in MgO by an order of magnitude, but approximate agreement with experiment may be found for the case of NaF. Judgment in this regard should await better data, and experimental determinations of *Dq* for NaF:Fe^{3+} or NaF:Cr^{+}. Neither model for the EPR center was seen to occupy a special position in the theory that would support positive identification of the center.

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