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Electric Field Effects in Electron-Nuclear Double-Resonance Spectroscopy of *F* Centers. II. Theoretical Considerations*

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Three separate theoretical estimates of the electric field perturbations of the isotropic hyperfine interaction between the *F* center's electron and its nearest-neighbor nuclei are presented. Calculations of this effect were made for the first-, second-, and fourth-nearest-neighbor interactions in KCl, KBr, NaCl, and LiF. Simple hydrogenic, LCAO (linear combination of atomic orbitals), and semicontinuum wave functions were used. Comparison is made with the experimental data for KCl, KBr, and NaCl.

I. INTRODUCTION

The first measurement of electric field effects in ENDOR spectroscopy was reported by Reichert and Pershan.[1] Later, Usmani and Reichert reported the results of an extensive study of the effects of electric field perturbations on ENDOR spectra of *F* centers in alkali halides.[2] These perturbations were measured for the first, second, and fourth shell nuclei in three host lattices: KCl, KBr, and NaCl. An effective nuclear spin Hamiltonian was developed to predict theoretically the splitting and lineshapes of the electric field perturbed ENDOR spectra. In principle, all the parameters of the spin Hamiltonian become functions of the applied electric field, but only the change in the isotropic part of the hyperfine interaction was detected. The values of the change in the isotropic hyperfine interaction with the applied electric field, $\partial a/\partial E$, were determined for the three shells in all the host lattices by using the spin Hamiltonian interpretation of the ENDOR data. We shall henceforth refer to this paper as I.

In this paper we have made several simple theoretical calculations of the magnitude of the electric field parameters $\partial a/\partial E$ that were measured in I. These calculations have considered two mechanisms by which the external electric field affects the hyperfine coupling between the *F*-center electron and the nearest-neighbor nuclei. Section II describes the theoretical estimates of the magnitude of these two effects. Section III discusses some of the assumptions made in these calculations and Sec. IV summarizes the conclusions.

II. THEORY

When a uniform electric field is applied to an alkali halide crystal containing *F* centers, two mechanisms should be considered which produce the electric field induced variations of the *F* center's hyperfine interaction with its surrounding nuclei. (1) The electronic electric field effect originating from the direct interaction of the applied electric field with the *F*-center electron. In calculating this effect we shall assume that the surrounding nuclei are at fixed positions and the *F*-center electronic cloud is polarized by the applied field. This polarization may be calculated, using a perturbation expansion, by the mixing of even and odd electronic ground- and excited-state wave functions. This mixing produces the change in the hyperfine interaction. (2) The ionic polarization of the crystal lattice, in which the cation and anion sublattices remain rigid but are displaced with respect to each other. This produces a variation in the local crystalline environment of the *F* center and subsequently produces a change in its hyperfine interaction with the surrounding nuclei. This effect is called the ionic electric field effect. We shall treat these two physical effects as being completely independent in these calculations. This is obviously only an approximation since, for example, the motion of the ionic sublattice will alter the ground-state wave function of the *F*-center electron. However, such effects are much smaller than the direct interaction calculated and will be neglected in these discussions.

A. Electronic Polarization

The first mechanism to be considered is the direct interaction of the electric field on the *F* center's electron. Here we shall consider the surrounding ions to be stationary and permit only polarization of the electronic cloud. Such a calculation is directly analogous to the theories of atomic polarization. Reichert[3] has discussed in detail the necessary conditions for the existence of linear electric field effects in host lattices having nuclear spins, paramagnetic defects or paramagnetic impurities situated at sites which lack inversion symmetry. The local nuclear environment about the *F* center (as measured by the ENDOR spectrum) provides such a physical system. Given the ground- and excited-state wave functions of the *F*-center electronic system, it should be possible to calculate directly the observed electric field effects. The obvious problem is the choice of the proper electronic wave functions, or, turning the question around, whether the experimentally measured values of the electric field parameters can help select,

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* Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force under Contract No. F 44620-69-C-0077.

[1] J. F. Reichert and P. S. Pershan, Phys. Rev. Letters **15**, 780 (1965).

[2] Z. Usmani and J. F. Reichert, Phys. Rev. **180**, 482 (1969).

[3] J. F. Reichert, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967), p. 745.

among the many wave functions that have been theoretically predicted, the proper one to describe the F center's excited state. (The ground-state functions can be chosen presumably by comparison with the unperturbed ENDOR spectrum.) The isotropic hyperfine interaction constant a is given by the expression

$$a=\langle 0|\mathcal{H}_{\mathrm{HF}}|0\rangle , \tag{1}$$

where $|0\rangle$ is the F center's electronic ground-state wave function and

$$\mathcal{H}_{\mathrm{HF}}=(8\pi/3)gg_N\beta\beta_N\delta(\mathbf{r}-\mathbf{R}_N) \tag{2}$$

is the spatial part of the isotropic hyperfine interaction between the nuclear spin $\mathbf{I}$ and the electron spin $\mathbf{S}$, and $\mathbf{r}$ and $\mathbf{R}_N$ are the position vectors of the electron and nucleus, respectively. The operator $\mathcal{H}_{\mathrm{HF}}$ is of even parity with respect to the nucleus at the origin. The electric-field operator $\mathcal{H}_E=e\mathbf{E}\cdot\mathbf{r}$, considered as a perturbation, is however of odd parity and will mix excited states $|i\rangle$ into the ground state. In the presence of an external electric field, the perturbed ground state wave functions can be written

$$|E\rangle=|0\rangle+\sum_{i\neq 0}\frac{\langle i|\mathcal{H}_E|0\rangle}{E_0-E_i}|i\rangle+\text{higher-order terms}, \tag{3}$$

where only the first-order corrections have been included. Using these new wave functions one can calculate the change in the hyperfine interaction due to the applied electric field to be

$$\Delta a=\langle E|\mathcal{H}_{\mathrm{HF}}|E\rangle-\langle 0|\mathcal{H}_{\mathrm{HF}}|0\rangle . \tag{4}$$

By using the proper wave functions and forming the ratio of the change in the hyperfine interaction to the unperturbed interaction it is easy to show that

$$\Delta a/a=2eE\Delta^{-1}\{[\langle i|Z|0\rangle\langle 0|\delta(\mathbf{r}-\mathbf{R}_N)|i\rangle]\times[\langle 0|\delta(\mathbf{r}-\mathbf{R}_N)|0\rangle]^{-1}\} . \tag{5}$$

Here we have considered only one excited state $|i\rangle$, and $\Delta=E_0-E_i$ is the energy separation between ground and excited state and $\mathcal{H}_E=eEZ$ for $\mathbf{E}$ along the Z axis (parallel to the axis of symmetry of the crystal). This general expression will be used to calculate the electric-field parameter in the following calculations. Various published values for the ground- and excited-state electronic wave functions will be substituted in this expression to see which will give the best fit.

Note that only one excited state $|i\rangle$ was included in the calculation of Eq. (5). This assumption seems justified from the optical Stark-effect measurements of Chiarotti *et al.*[4] and the theoretical calculations of Fowler *et al.*[5] They predict, however, that a $2s$ state should lie very close to the $2p$ excited state. Since the electric field perturbation only admixes states of odd parity into the even ground state, the $2s$ state will not contribute to the perturbed ground state $|E\rangle$ in Eq. (3). Kübler and Friauf[6] have theoretically calculated the complete energy-level diagram for F centers in various alkali halides. Their calculations show that the only low-lying excited state of odd parity between the valence and conduction band is the $2p$ state. Thus the assumption of one excited state seems justified.

1. *Hydrogenlike Wave Functions*

Consider the simple hydrogenlike wave functions of Gourary and Adrian[7] for both the ground and excited state of the F-center electron. These functions were calculatedf rom the point-ion lattice model. They are written

$$\psi_g(1S)=[2(4\pi)^{1/2}](\xi/R_0)^{3/2}e^{-\xi r/R_0} \tag{6}$$

and

$$\psi_e(2P)=(3/4\pi)^{1/2}(2/\sqrt{3})(\xi'/R_0)^{5/2}(r\cos\theta)e^{-\xi' r/R_0} . \tag{7}$$

Here ξ and ξ' are the variational parameters determined by minimizing the energy and are tabulated in Ref. 7. Substituting the wave functions (6) and (7) in Eq. (5), one obtains

$$(\Delta a/a)_{\text{shell-}I}=\frac{64eER_0\xi'^5e^{(\xi-\xi')}}{\Delta(\xi+\xi')^5} . \tag{8}$$

The calculation of matrix elements of Eq. (5) is given in Appendix A. These data are tabulated in terms of the rate of change of the hyperfine interaction with electric field, $\partial a/\partial E$, which is defined by

$$\Delta a=\left(\frac{\partial a}{\partial E}\right)E .$$

Thus

$$\left(\frac{\partial a}{\partial E}\right)_{\text{shell-}I}=\frac{64eR_0\xi'^5e^{(\xi-\xi')}}{\Delta(\xi+\xi')^5}a_{\text{shell-}I} \tag{9}$$

or more generally one can write for the Nth nuclear shell

$$\left(\frac{\partial a}{\partial E}\right)_{\text{shell-}N}=\frac{64e[\sqrt{(N)}R_0]\xi'^5e^{\sqrt{(N)}(\xi-\xi')}}{\Delta(\xi+\xi')^5}a_{\text{shell-}N} . \tag{10}$$

By using the tabulated values of R_0, ξ, ξ' and Δ from Ref. 7 and the hyperfine interaction constants from Ref. 8 in Eq. (10) the electric field parameter $\partial a/\partial E$ has been calculated for the first, second, and fourth shell nuclei in KCl, KBr, NaCl, and LiF. These results are tabulated in Table I.

It should be pointed out that the theoretical calculations of the electric field effects require sufficiently

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[4] G. Chiarotti and U. M. Grassano, Phys. Rev. Letters **16**, 124 (1966).

[5] W. Beall Fowler, E. Calabrese, and D. Y. Smith, Solid State Commun. **5**, 569 (1967).

[6] Jügen K. Kübler and Robert J. Friauf, Phys. Rev. **140**, A1742 (1965).

[7] B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957); in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, pp. 124–247.

[8] W. C. Holton and H. Blum, Phys. Rev. **125**, 89 (1962).

Table I. Electric field parameters of F centers in alkali halides.

Crystal	Shell	Electric field parameter ($\partial a/\partial E$) in Hz/V cm^{-1}			
		Experimental	Hydrogenlike wave functions	Semicontinuum functions	LCAO wave functions
KCl	I	0.9 ±0.05	0.58	⋯	0.56
	II	0.25±0.03	0.22	⋯	⋯
	IV	0.05±0.005	0.04	⋯	⋯
KBr	I	1.0 ±0.05	0.59	⋯	0.58
	II	2.0 ±0.05	1.53	⋯	⋯
	IV	0.33±0.02	0.21	⋯	⋯
NaCl	I	2.0 ±0.5	1.32	1.24	1.26
	II	0.5 ±0.05	0.31	0.37	⋯
	IV	⋯	0.12	⋯	⋯
LiF	I	⋯	0.34	⋯	0.31
	II	⋯	0.16	⋯	⋯
	IV		0.006	⋯	⋯

detailed wave functions to give a true picture of the electronic charge distribution near the nuclei. The use of the simple hydrogenlike wave functions give a reasonably good picture of the electronic charge distribution everywhere except in the immediate vicinity of the ions. To account for such rapid fluctuations, the wave functions of the electron need to be orthogonalized to the ion-core orbitals. The effects of such orthogonalization of the F center's envelope function to the ion-core orbitals on the calculations of $\partial a/\partial E$ will be discussed later.

2. *Semicontinuum Wave Functions*

Next, consider the wave functions used by Fowler.[9] These are variational functions, used in the semicontinuum model of F centers in alkali halides, which gave the optical absorption and emission energies in good agreement with experiments. These functions are

$$\psi_g(1S)=(\alpha^3/7\pi)^{1/2}(1+\alpha r)e^{-\alpha r} \tag{11}$$

and

$$\psi_e(2P)=(\beta^5/\pi)^{1/2}(r\cos\theta)e^{-\beta r}, \tag{12}$$

where α and β are the variational parameters given as $\alpha=0.56a_0^{-1}$, $\beta=0.42a_0^{-1}$ for NaCl, and a_0 is the Bohr radius.

Substituting these wave functions into the general expression for the change in hyperfine interaction with electric field [Eq. (5)] one can show that for the Nth nuclear shell

$$\left(\frac{\partial a}{\partial E}\right)_{\text{shell-}N}=\frac{8(\surd(N)R_0)e\beta^5(144\alpha+24\beta)e^{\surd(N)(\alpha-\beta)R_0}}{3\Delta(1+\surd(N)\alpha R_0)(\alpha+\beta)^6}a_{\text{shell-}N}. \tag{13}$$

The values of $\partial a/\partial E$ are calculated for the first and second shell nuclei in NaCl using the values of α, β, and R_0 in Eq. (13). The results are given in Table I. These wave functions, again, are the modified hydrogenlike s- and p-type functions, and should also be orthogonalized to the ion-core orbitals.

3. *Linear-Combination-of-Atomic-Orbitals (LCAO) Wave Functions*

The molecular orbital model of the F-center[10] assumes that the F-center electron is shared among the six nearest-neighbor positive ions. The molecular orbital wave functions are constructed from the linear combination of the six atomic orbitals (LCAO) as

$$\psi(\mathbf{r})=\sum_{i=1}^{6}C_i\phi_i(\mathbf{r}-\mathbf{R}_i). \tag{14}$$

Here $\phi_i(\mathbf{r}-\mathbf{R}_i)$ is the appropriate ionic wave function of the valence electron, centered at the ith positive ion. The ϕ's are assumed orthogonal to each other, and any overlap integrals between ϕ_i and ϕ_j for $i\neq j$ have been neglected in this calculation. These molecular orbitals must satisfy the symmetry of the crystal's point group.

When the surrounding positive ions are numbered as in Fig. 1, the six linearly independent molecular orbitals derived from group theoretical arguments are:

(i) The totally symmetric ground-state wave function of the F center electron

$$|\Gamma_1{}^+\rangle=\frac{1}{\surd6}[\phi_1+\phi_2+\phi_3+\phi_4+\phi_5+\phi_6]; \tag{15}$$

(ii) the doubly degenerate, symmetric excited-state wave function

$$\begin{aligned}|\Gamma_{3u}{}^+\rangle&=\frac{1}{\surd12}[2\phi_1+2\phi_2+\phi_3+\phi_4-\phi_5-\phi_6],\\|\Gamma_{3v}{}^+\rangle&=\frac{1}{\surd4}[\phi_3+\phi_4-\phi_5-\phi_6];\end{aligned} \tag{16}$$

(iii) the triply degenerate antisymmetric excited-state wave functions

$$\begin{aligned}|\Gamma_{4x}{}^-\rangle&=\frac{1}{\surd2}[\phi_1-\phi_2],\\|\Gamma_{4y}{}^-\rangle&=\frac{1}{\surd2}[\phi_3-\phi_4],\\|\Gamma_{4z}{}^-\rangle&=\frac{1}{\surd2}[\phi_5-\phi_6].\end{aligned} \tag{17}$$

In a free alkali atom, ϕ_i would be a pure s function. But the nonsymmetrical crystal field associated with the vacancy will polarize the alkali atom, thus mixing a large amount of p function into the wave function ϕ_i.

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[9] W. Beall Fowler, Phys. Rev. **135**, A1725 (1964).

[10] See Ref. 1 and A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, Phys. Rev. **91**, 1066 (1953).

Thus we write

$$\phi_i = [\gamma^{1/2}\psi_{is}(\mathbf{r}-\mathbf{R}_i) + (1-\gamma)^{1/2}\psi_{ip\sigma}(\mathbf{r}-\mathbf{R}_i)]. \quad (18)$$

The functions ψ_{is} and $\psi_{ip\sigma}$ are, respectively, the s and p orbitals of alkali atom i. The fraction of s character of the atomic orbital is represented by γ which has been set equal to 0.6 for our calculation.[11] Table II gives the $\psi_{ip\sigma}$ orbitals used in forming the orthonomal set of atomic orbitals.

Application of an electric field along the z direction will mix the ground state $|\Gamma_1^+\rangle$ with any state of $|\Gamma_{4z}^-\rangle$ symmetry. The electric field perturbation $\mathcal{H}_E$, which has odd parity with respect to the vacancy site, will not mix the $|\Gamma_{3u}^+\rangle$ and $|\Gamma_{3v}^+\rangle$ states into $|\Gamma_1^+\rangle$. The state functions $|\Gamma_{4x}^-\rangle$ and $|\Gamma_{4y}^-\rangle$ behave like p_x and p_y orbitals, and hence the matrix elements $\langle\Gamma_1^+|Z|\Gamma_{4x}^-\rangle = \langle\Gamma_1^+|Z|\Gamma_{4y}^-\rangle = 0$. Therefore, the only state of the $|\Gamma_{4z}^-\rangle$ symmetry is

$$|\Gamma_{4z}^-\rangle = \frac{1}{\sqrt{2}}[\phi_5(\mathbf{r}-\mathbf{R}_5) - \phi_6(\mathbf{r}-\mathbf{R}_6)], \quad (19)$$

which is the excited state of the system. These LCAO wave functions may now be substituted into the general expression for the electric field parameter. The result of this calculation, given in Appendix B, is

$$(\partial a/\partial E)_{\text{shell-}I} = \frac{2eR_0}{\Delta} a_{\text{shell-}I}. \quad (20)$$

The values of $\partial a/\partial E$ for the first shell nuclei in KCl, KBr, and NaCl have been calculated using the tabulated values of R_0, a, and Δ in Eq. (20). The results are given in Table I.

No molecular orbital calculations were performed for second and fourth nearest neighbors. The complexity in forming suitable linear combinations of atomic orbitals for so many sites did not seem to make the calculation worthwhile. Thus we have limited our calculations to only the nearest-neighbor effects.

B. Ionic Polarization

In the previous discussion we have neglected any effect due to the motions of the ions in the applied electric field. This omission must now be justified. If one assumes that the externally applied uniform electric field causes both the anion and cation sublattices to be equally displaced in opposite directions, one can show the ionic displacement to be[12]

$$\Delta R_{\text{ionic}} = \frac{3(\epsilon - n^2)E}{4\pi N e^*(n^2+2)}, \quad (21)$$

where E is the Maxwell average electric field $=(1/\epsilon)E_{\text{applied}}$, ϵ is the static dielectric constant, n is the index of refraction of the host lattice, N is the number of ion pairs per unit volume, and e^* is the effective ionic charge as calculated in Ref. 13. Using Tessman, Kahn, and Shockley's[14] values for the above parameters, ΔR, has been calculated for four different host lattices KCl, KBr, NaCl, and LiF. In order to estimate the change in the hyperfine interaction due to this ionic motion we shall consider two simple theoretical models.

TABLE II. $\psi_{ip\sigma}$ orbitals. Here, $Y_1^0 = (3/4\pi)^{1/2}\cos\theta$, $Y_1^{\pm 1} = \pm(3/8\pi)^{1/2}\sin\theta e^{\pm i\phi}$ are spherical harmonics.

Ion	$\psi_{p\sigma}$
1	$(1/\sqrt{2})[Y_1^1 - Y_1^{-1}]f(r)$
2	$-(1/\sqrt{2})[Y_1^1 - Y_1^{-1}]f(r)$
3	$-i/\sqrt{2}[Y_1^1 + Y_1^{-1}]f(r)$
4	$i/\sqrt{2}[Y_1^1 + Y_1^{-1}]f(r)$
5	$-Y_1^0 f(r)$
6	$Y_1^0(f(r)$

If one assumes that the wave functions of the F center are unchanged by the ionic motion then it is possible simply to form the ratio of $\Delta a/a$ using the Gourary and Adrian ground-state functions with $R_0 + \Delta R$ substituted for R_N. Thus since $a = \langle\psi_g|\mathcal{H}_{\text{HF}}|\psi_g\rangle = \text{const}|\psi_g|^2$ we have for this ratio

$$\frac{\Delta a}{a} = \frac{|\psi_{1S}(R_0+\Delta R)|^2 - |\psi_{1S}(R_0)|^2}{|\psi_{1S}(R_0)|^2}. \quad (22)$$

The spatial dependence of the ground-state wave function is

$$\psi_{1S}(r) \propto e^{-\xi r/R_0}, \quad (23)$$

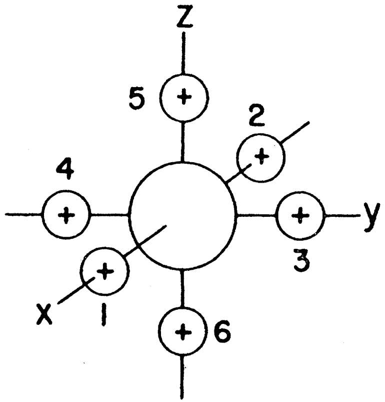

FIG. 1. Various atomic orbitals used in the molecular-orbital calculation of the F-center wave functions.

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[11] See Ref. 10.

[12] N. Bloembergen, in *Proceedings of the Colloque Ampere* (*Magnetic and Electric Resonance and Relaxation*), *1962*, edited by J. Smidt (North-Holland Publishing Co., Amsterdam, 1963), p. 39.

[13] B. Szigeti, Trans. Faraday Soc. **45**, 155 (1949).

[14] J. Tessman, A. Kahn, and W. Schokley, Phys. Rev. **92**, 890 (1953).

TABLE III. Ionic electric field effect ($\partial a/\partial E$) for the first-shell nuclei.

Substance	e^*	ϵ	n	N	ΔR (cm)	($\partial a/\partial E$) in Hz/V cm^{-1} Ionic	($\partial a/\partial E$) in Hz/V cm^{-1} Exp.
KCl	$0.8e$	4.68	1.46	1.6×10^{22}	1.69×10^{-17}	0.04	0.9 ± 0.05
KBr	$0.76e$	4.78	1.53	1.4×10^{22}	1.85×10^{-17}	0.04	1.0 ± 0.05
NaCl	$0.74e$	5.62	1.50	2.2×10^{22}	1.41×10^{-17}	0.12	2.0 ± 0.5
LiF	$0.87e$	9.27	1.39	6.2×10^{22}	0.62×10^{-17}	0.04	...

so that

$$\frac{\Delta a}{a}=e^{-2\xi(\Delta R/R_0)}-1\simeq-2\xi\left(\frac{\Delta R}{R_0}\right),$$

or

$$\left(\frac{\partial a}{\partial E}\right)_{\text{ionic}}=2\xi\left(\frac{\Delta R}{R_0}\right)\left(\frac{a}{E}\right).\tag{24}$$

The electric field parameters $\partial a/\partial E_{\text{ionic}}$ have been estimated by using the values of ξ, R_0, a and the calculated values of ΔR, in Eq. (24). The results are given in Table III.

It is clear from these results that this ionic effect cannot account for the observed electric field perturbations. This calculation predicts an effect which is one order of magnitude smaller than the experimental results. An independent estimate of this ionic effect can be made by considering "Seidel's rule."[15] Seidel has found an empirical relationship between the hyperfine interaction of the nearest neighbor nuclei and the interionic distance for various alkali halide host materials. He has shown that

$$a=\text{const}\times(1/R^3).\tag{25}$$

Differentiating this expression to find the rate of change of a with respect to a change in lattice spacing, one finds

$$\left(\frac{\Delta a}{a}\right)=3\left(\frac{\Delta R}{R}\right),\tag{26}$$

which gives results of the same order of magnitude as Eq. (24).

Bailey and Doyle have measured the change in the hyperfine interaction with applied uniaxial stress.[16] Although uniaxial stress produces a significantly different type of local lattice distortion from an applied electric field, it is still possible to use these data to estimate the order of magnitude of the change in a with a change in R. Ignoring the tensorial properties of these uniaxial stress measurements we have estimated this effect by using an average value of the experimentally determined $\partial a/h\partial P$ and found $\Delta a/a\sim3(\Delta R/R)$, which again agrees with the previous two calculations. Since all three independent estimates show the ionic contribution to be one order of magnitude smaller than the direct electronic effect, its omission seems justified.

III. DISCUSSION

In calculating the electric field parameters we have chosen to estimate the ratio $\Delta a/a$ rather than the change in the hyperfine interactions directly. The reason for this should be explained. The simple hydrogenic function of Gourary and Adrian (GA) [Eqs. (6) and (7)] do not predict the correct order of magnitude of the hyperfine constant. This is because these functions have not been properly orthogonalized to the various ion cores.

The method of orthogonalizing the F-center electronic wave functions to the ion-core orbitals, has been used by Gourary and Adrian very successfully in predicting correct values of the hyperfine interaction constants. According to this method, one writes the orthonormalized wave functions of the F-center electron as

$$\psi^F=N[\psi_F-\sum_i\langle\phi_i|\psi_F\rangle\phi_i].\tag{27}$$

Here N is the normalization factor, ψ_F is the simple s- and p-type hydrogenlike wave functions used above, or any other F-center electronic orbital functions. The ϕ_i's are the ion-core orbitals, which one takes as the Hartree-Fock functions of the free ions. Using this method, one gets

$$\langle\Psi_g{}^F|\delta(\mathbf{r}-\mathbf{R}_N)|\psi_g{}^F\rangle \simeq A_N\langle\psi_g(1S)|\delta(\mathbf{r}-\mathbf{R}_N)|\psi_g(1S)\rangle=A_N|\psi_g(1S)|^2,\tag{28}$$

where $A_N\sim100$ is the amplifying factor, which gives the correct order of magnitude for the electron density at the nuclear sites and thus good agreement with the experimental values of a. Using the same argument, one could assume that the use of the GA method would yield properly orthogonalized excited state functions and thus

$$\langle\Psi_g{}^F|\delta(\mathbf{r}-\mathbf{R}_N)|\Psi_e{}^F\rangle \simeq B_N\langle\psi_g(1S)|\delta(\mathbf{r}-\mathbf{R}_N)|\psi_e(2P)\rangle,\tag{29}$$

where B_N is a new amplifying factor which would be expected to be of the same order as A_N. Thus by forming the ratio of $\Delta a/a$ these two large amplifying factors will cancel, since

$$\frac{\langle\Psi_g{}^F|\delta(\mathbf{r}-\mathbf{R}_N)|\Psi_e{}^F\rangle}{\langle\psi_g{}^F|\delta(\mathbf{r}-\mathbf{R}_N)|\psi_g{}^F\rangle}=\frac{B_N\langle\psi_g(1S)|\delta(\mathbf{r}-\mathbf{R}_N)|\psi_e(2P)\rangle}{A_N\langle\psi_g(1S)|\delta(\mathbf{r}-\mathbf{R}_N)|\psi_g(1S)\rangle} \simeq\frac{\langle\psi_g(1S)|\delta(\mathbf{r}-\mathbf{R}_N)|\psi_e(2P)\rangle}{\langle\psi_g(1S)|\delta(\mathbf{r}-\mathbf{R}_N)|\psi_g(1S)\rangle}.\tag{30}$$

The use of the GA method of orthogonalizing the F center's electronic wave functions to the ion-core orbitals requires the use of $\langle\Psi_g{}^F|Z|\Psi_e{}^F\rangle$ in Eq. (33) in Appendix A. Consequently, this should give a different result than the matrix element $\langle\psi_g(1S)|Z|\psi_e(2P)\rangle$ for the simple hydrogenlike s- and p-type ground- and excited-state wave functions. Wood,[17] however, has

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[15] H. Seidel, Z. Physik **165**, 218 (1961).

[16] C. E. Bailey and W. T. Doyle (unpublished).

[17] R. F. Woods and U. Öpik (unpublished).

pointed out that such orthogonalization of F center's electronic wave functions to the ion-core orbitals, lowers the oscillator strengths for the $1S \rightarrow 2P$ optical transitions only by 5 to 10%. We can, therefore, expect an error of approximately the same order of magnitude in the value of the matrix element $\langle \psi_g(1S) | Z | \psi_e(2P) \rangle$. This, then, explains the reason for obtaining the correct order of magnitude for the electric field parameter $\partial a / \partial E$ from the simple hydrogenlike wave functions.

It should also be pointed out explicitly that we have neglected all electric field perturbations of the ion-core orbitals and thus any effects of the electric field on this orthogonalization procedure. Such effects should be quite small.

So far in this discussion the question of the proper electric field to be used for the calculation of Eq. (5) has been ignored. All the experimental and theoretical values quoted in Table I were calculated using the applied electric field, that is the applied voltage divided by the thickness of the sample.

Tessman, Kahn, and Shockley[14] used an effective internal electric field Eq. (31) in their calculation of the polarizability of individual alkali and halide ions, i.e. the calculation of the static dielectric constant. The local field as seen by an atom at a particular point is given as

$$\mathbf{E}_{\text{eff}} = \mathbf{E} + \frac{4\pi \mathbf{P}}{3}. \tag{31}$$

Here $4\pi \mathbf{P}/3$ is the Lorentz correction factor. In the calculation of static dielectric constants the use of this effective field seems justified since the individual ions have a highly localized charge distribution at the point at which this effective field is calculated.

Mott and Gurney,[18] however, have suggested that the normal Lorentz correction factor $4\pi \mathbf{P}/3$ may not be correct for some crystals because of the extended nature of the electronic charge distribution and consequently overlapping of the neighboring ions. Dixon[19] has used the same approach to justify the use of the applied electric field in describing the electrically induced nuclear quadrupole shifts. He argues that since the bonding electrons occupy a rather large volume near the resonant nucleus, most of the variation of the local electric field is smoothed out, and the applied field represents the proper quantity to be used.

Brodksy and Burstein[20] have found that in calculating the dielectric constants in III-V compounds, with nonlocalized valence-band wave functions, the appropriate effective field is the macroscopic field. In calculating the electric field effects in nuclear magnetic resonance of Ga and As nuclei in GaAs, Gill and Bloembergen[21] also found it necessary to assume the effective field equal to the macroscopic applied field.

In our calculations of electronic electric field parameter $\partial a / \partial E$, the matrix elements are evaluated over two or three atomic spacing and hence $\mathbf{E}$ will be represented by the average field over such a distance, i.e., the applied electric field. However, this question cannot be considered closed and because of the many approximations in the basic theory of this effect, it is not possible to conclude that the assumptions made in using the applied field are responsible for the discrepancy between theory and experiment.

IV. CONCLUSIONS

Three theoretical estimates of the electric field effects in the ENDOR spectrum of F centers have been presented. In view of the many simplifying assumptions made in these calculations the agreement between experiment and theory is remarkable. It seems apparent that just including the single $2p$ excited state is sufficient to explain most of the observed effect. The question of internal electric field remains unresolved. In fact, if these electric field measurements are to have any significance in unraveling information about excited states of defects, better theoretical estimates must be made of the average of the internal field over these defects.

There is still the open question as to what predictions of electric field effects would be available from a pseudopotential model of the F center's wave functions. The solution of this problem is bequeathed by the two experimentalist authors to their theoretical colleagues.

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APPENDIX A: CALCULATION OF $\Delta a/a$ FROM HYDROGENLIKE WAVE FUNCTIONS

From Eq. (5), we have

$$\Delta a/a = 2eE\Delta^{-1}\{[\langle 0 | Z | i \rangle \langle i | \delta(\mathbf{r} - \mathbf{R}_N) | 0 \rangle] \times [\langle 0 | \delta(\mathbf{r} - \mathbf{R}_N) | 0 \rangle]^{-1}\}. \tag{32}$$

Using the wave functions from Eqs. (6) and (7), we have

$$\begin{aligned}\langle 0 | Z | i \rangle &= \langle \psi_g(1S) | Z | \psi_e(2P) \rangle \\ &= K_0 K_1 \int_0^\infty \int_0^\pi \int_0^{2\pi} e^{-\xi r/R_0}(r \cos\theta) \\ &\qquad \times (r \cos\theta e^{-\xi' r/R_0}) r^2 dr d(\cos\theta) d\phi \\ &= (32\pi K_0 K_1)[R_0/(\xi+\xi')]^5,\end{aligned} \tag{33}$$

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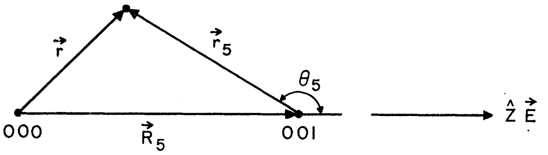

FIG. 2. Definition of coordinates.

where

$$K_0=[2/(4\pi)^{1/2}](\xi/R_0)^{3/2},\qquad K_1=(3/4\pi)^{1/2}(2/\sqrt{3})(\xi'/R_0)^{5/2} \tag{34}$$

and

$$\langle 0|\delta(\mathbf{r}-\mathbf{R}_N)|i\rangle=K_0K_1\int_0^\infty\int_0^\pi\int_0^{2\pi}e^{-\xi r/R_0}\delta(\mathbf{r}-\mathbf{R}_N)\times(r\cos\theta e^{-\xi' r/R_0})r^2dr\,d(\cos\theta)d\phi. \tag{35}$$

For the first-nearest-neighbor nucleus at the 001 lattice site (on the z axis)

$$\delta(\mathbf{r}-\mathbf{R}_N)=(1/r^2)\delta(r-R_0)\delta(\cos\theta-1)\delta(\phi). \tag{36}$$

Using (36) in Eq. (35) and on integration, we get

$$\langle 0|\delta(\mathbf{r}-\mathbf{R}_N)|i\rangle=K_0K_1e^{-(\xi+\xi')}\text{ for the first shell.} \tag{37}$$

In general, for the Nth shell (with electric field parallel to the symmetry axis from vacancy to the Nth shell nucleus) we have

$$\langle 0|\delta(\mathbf{r}-\mathbf{R}_N)|i\rangle=K_0K_1e^{-\surd(N)(\xi+\xi')}. \tag{38}$$

Similarly, for the Nth shell,

$$\langle 0|\delta(\mathbf{r}-\mathbf{R}_N)|0\rangle=K_0^2e^{-\surd(N)(2\xi)}. \tag{39}$$

Using the results from Eqs. (33), (38), and (39) in Eq. (32) we get

$$\begin{aligned}(\Delta a/a)_{\text{shell-}N}&=2e\Delta^{-1}E\{[32\pi K_0K_1(R_0/(\xi+\xi'))^5]\\&\quad\times\{K_0K_1[\surd(N)R_0]e^{-\surd(N)(\xi+\xi')}\}[K_0^2e^{-\surd(N)(2\xi)}]^{-1}\} \qquad (40)\\&=64\pi e\Delta^{-1}EK_1^2[\surd(N)R_0](R_0/(\xi+\xi'))^5e^{\surd(N)(\xi-\xi')}\\&=64e\Delta^{-1}E[\surd(N)R_0]\xi'^5(\xi+\xi')^{-5}e^{\surd(N)(\xi-\xi')}, \qquad (41)\end{aligned}$$

which reduces to

$$=64eE\Delta^{-1}R_0\xi'^5(\xi+\xi')^{-5}e^{(\xi-\xi')}\text{ for the first shell.} \tag{42}$$

APPENDIX B: CALCULATION OF $\Delta a/a$ FROM LCAO WAVE FUNCTIONS

From Eq. (5), the value of $\Delta a/a$ is

$$(\Delta a/a)=(2e\Delta^{-1}E)\{[\langle 0|Z|i\rangle\langle i|\delta(\mathbf{r}-\mathbf{R}_N)|0\rangle]\times[\langle 0|\delta(\mathbf{r}-\mathbf{R}_N)|0\rangle]^{-1}\}. \tag{43}$$

Using the LCAO wave functions $|\Gamma_1^+\rangle$ and $|\Gamma_{4z}^-\rangle$ from Eqs. (15) and (19), we get

$$\begin{aligned}\langle 0|Z|i\rangle&=\langle\Gamma_1^+|Z|\Gamma_{4z}^-\rangle\\&=\left\langle\frac{1}{\sqrt{6}}(\phi_1+\phi_2+\phi_3+\phi_4+\phi_5+\phi_6)\times|Z|\frac{1}{\sqrt{2}}(\phi_5-\phi_6)\right\rangle\\&=(2\sqrt{3})^{-1}[\langle\phi_5|Z|\phi_5\rangle-\langle\phi_6|Z|\phi_6\rangle], \qquad (44)\end{aligned}$$

where any contributions from the overlap integrals have been neglected. Now recall that the atomic orbitals ϕ_5 and ϕ_6 are centered at 001 and $00\bar{1}$ ionic sites, while z is measured with respect to the vacancy site 000. Hence in order to evaluate the matrix elements in Eq. (44), it is necessary to express z in terms of the ionic coordinate systems.

From Fig. 2, it is obvious that

$$\mathbf{r}=\mathbf{R}_5+\mathbf{r}_5.$$

Therefore

$$Z=\hat{Z}\cdot\mathbf{r}=\hat{Z}\cdot(\mathbf{R}_5+\mathbf{r}_5)=R_0+r_5\cos\theta_5, \tag{45}$$

where $\hat{Z}$ is the direction of the applied electric field, $\mathbf{R}_5=\hat{z}R_0$, and the site 001 lies on the positive z axis. Similarly,

$$\mathbf{r}=\mathbf{R}_6+\mathbf{r}_6$$

or

$$Z=-R_0+r_6\cos\theta_6,\quad\text{where}\quad\mathbf{R}_6=-\hat{z}R_0. \tag{46}$$

From Table II, we have

$$\begin{aligned}\phi_5&=\gamma^{1/2}\psi_s(r_5)-(1-\gamma)^{1/2}\psi_{pz}(r_5),\\\phi_6&=\gamma^{1/2}\psi_s(r_6)+(1-\gamma)^{1/2}\psi_{pz}(r_6).\end{aligned} \tag{47}$$

Here ψ_s and ψ_{pz} are taken as the Gourary and Adrian wave functions of Eqs. (6) and (7). Using Eqs. (45)–(47) in Eq. (44), we get

$$\begin{aligned}\langle\Gamma_1^+|Z|\Gamma_{4z}^-\rangle&=(2\sqrt{3})^{-1}[\langle\{\gamma^{1/2}\psi_s(r_5)-(1-\gamma)^{1/2}\psi_{pz}(r_5)\}\\&\quad\times|(R_0+r_5\cos\theta_5)|\{\gamma^{1/2}\psi_s(r_5)-(1-\gamma)^{1/2}\psi_{pz}(r_5)\}\rangle\\&\quad-\langle\{\gamma^{1/2}\psi_s(r_6)+(1-\gamma)^{1/2}\psi_{pz}(r_6)\}|(-R_0+r_6\cos\theta_6)\\&\quad\times|\{\gamma^{1/2}\psi_s(r_6)+(1-\gamma)^{1/2}\psi_{pz}(r_6)\}\rangle]\\&=(2\sqrt{3})^{-1}[2R_0-4\gamma^{1/2}(1-\gamma)^{1/2}\langle\psi_s|r\cos\theta|\psi_p\rangle], \qquad (48)\end{aligned}$$

where we have dropped the subscripts and defined

$$\begin{aligned}\langle\psi_s(r_5)|r_5\cos\theta_5|\psi_{pz}(r_5)\rangle&=\langle\psi_s(r_6)|r_6\cos\theta_6|\psi_{pz}(r_6)\rangle\\&=\langle\psi_s|r\cos\theta|\psi_p\rangle.\end{aligned} \tag{49}$$

Using the value of $\langle\psi_s|r\cos\theta|\psi_p\rangle$ from Eq. (33) in Appendix A, we get

$$\langle\Gamma_1^+|Z|\Gamma_{4z}^-\rangle=(2\sqrt{3})^{-1}\times[2R_0-4\gamma^{1/2}(1-\gamma)^{1/2}(32R_0)\xi^{3/2}\xi'^{5/2}(\xi+\xi')^{-5}]. \tag{50}$$

For the F-center electron and the alkali ion at the 001 lattice site

$$\langle 0|\delta(\mathbf{r}-\mathbf{R}_N)|i\rangle=\langle\Gamma_1{}^+|\delta(\mathbf{r}-\mathbf{R}_5)|\Gamma_{4z}{}^-\rangle$$

$$=\left\langle\frac{1}{\sqrt{6}}(\phi_1+\phi_2+\phi_3+\phi_4+\phi_5+\phi_6)\right.$$

$$\left.\times|\delta(\mathbf{r}-\mathbf{R}_5)|\frac{1}{\sqrt{2}}(\phi_5-\phi_6)\right\rangle$$

$$=(2\sqrt{3})^{-1}|\phi_5|^2 \tag{51}$$

and

$$\langle 0|\delta(\mathbf{r}-\mathbf{R}_N)|0\rangle=\langle\Gamma_1{}^+|\delta(\mathbf{r}-\mathbf{R}_5)|\Gamma_1{}^+\rangle$$
$$=\tfrac{1}{6}|\phi_5|^2. \tag{52}$$

By using Eqs. (50)–(52) in Eq. (43) we get

$$|\Delta a|=(\partial a/\partial E)E=2ea\Delta^{-1}E\{[(2\sqrt{3})^{-1}$$
$$\times(2R_0-4\gamma)^{1/2}(1-\gamma)^{1/2}(32R_0)\xi^{3/2}\xi'^{5/2}(\xi+\xi')^{-5}]$$
$$\times[(2\sqrt{3})^{-1}|\phi_5|^2][\tfrac{1}{6}|\phi_5|^2]^{-1}\}$$

or

$$(\partial a/\partial E)=ea\Delta^{-1}[2R_0-4\gamma^{1/2}(1-\gamma)^{1/2}$$
$$\times(32R_0)\xi^{3/2}\xi'^{5/2}(\xi+\xi')^{-5}] \tag{53}$$

or

$$\partial a/\partial E\simeq 2eaR_0\Delta^{-1}\times 10^{-2}\text{ Hz/V cm}^{-1}. \tag{54}$$

Here R_0 is expressed in Å and a, the isotropic hyperfine interaction constant, is in MHz. To arrive at Eq. (54) we have neglected the second term in Eq. (53) which introduces an error of about 2 to 4%.

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Sharp-Line Luminescence of Re^{4+} in Cubic Single Crystals of Cs_2ZrCl_6 and Cs_2HfCl_6†

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Sharp-line luminescence has been observed for Re^{4+} ($5d^3$) in single crystals of Cs_2ZrCl_6 and Cs_2HfCl_6 at low temperature. Well-resolved vibronic structure is seen, forming nearly perfect mirror symmetry between emission and absorption about a zero-phonon line at 13 879 cm^{-1}. Using the assignments of Dorain and Wheeler, these are identified as being due to transitions within the $t_{2g}{}^3$ configuration from the $\Gamma_7(^2T_{2g})$ level to the ground state $\Gamma_8(^4A_{2g})$. Vibrational energies of the odd modes of the $ReCl_6{}^{2-}$ complex are found to be the same for both the ground and excited states. The flourescence lifetime of 100 μsec at 2 K suggests the presence of other modes of decay than the observed luminescence. The luminescence can be excited either by transitions into the electric dipole allowed levels arising from t_2e configuration or to the $\Gamma_8(^2T_{2g})$, ($t_2{}^3$) levels.

SHARP-LINE optical spectra of impurities in solids are known to exist primarily for the rare-earth ions and a few special cases of the $3d$ transition series.[1] The states between which the transitions take place are usually of the same configuration within an electronic shell that is shielded from interactions with the crystal electric field and with neighboring ions. These transitions which are usually forbidden for free atoms become allowed in low-symmetry electric fields or in higher-symmetry fields with the cooperation of the odd modes of vibration associated with the ion's ligands or the crystal lattice. In addition to the examples of the $3d$ transition metals, it has been shown, by Dorain and his co-workers,[2,3] that sharp-line absorption spectra are also observed when the $5d$ ions, Re^{4+} and Os^{4+}, are present in dilute concentration as impurities in suitable crystal hosts. Dorain and Wheeler[2] show that the absorption spectra of Re^{4+} in K_2PtCl_6 and Cs_2ZrCl_6 could be explained on the basis of crystal-field theory applied to the $ReCl_6{}^{2-}$ complex in a slightly distorted cubic lattice. Detailed information about the crystal-field, Racah, and spin-orbit parameters were obtained along with the magnetic properties of the low-lying states, the odd-mode vibrational energies associated with the electronic levels, and the nature of the electronic transition, i.e., electric or magnetic dipole. This paper reports the observation of narrow-line *luminescence* of Re^{4+} present as an impurity in the cubic crystals Cs_2HfCl_6 and Cs_2ZrCl_6. This system is particularly interesting since Re^{4+} is isoelectronic with Cr^{3+}, whose luminescence spectra have been the subject of many investigations.

At low temperature the luminescence spectrum reported here consists of four lines between 7000 and 7400 Å. The transitions are identified using the assignments of Dorain and Wheeler as originating from the $\Gamma_7(^2T_{2g})$ level of the $t_{2g}{}^3$ configuration of Re^{4+} and

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[1] See, for example, Gerhard H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Wiley-Interscience, Inc., New York, 1968); D. S. McClure, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 9.

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