

Hyperfine Interaction Constants of the F -Center Electron with the Lattice in Alkali Halides (with NaCl Structure)*

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On the basis of the de Boer model for the F center, one can obtain expressions for the coupling constants in the hyperfine interaction of the F electron with a nucleus of the lattice. These constants can be determined experimentally by means of "electron nuclear double resonance." The comparison of the theoretical expressions and the empirical values permits an estimate of the importance of the several factors determining these coupling constants. The formal similarity between the magnetic dipole-dipole constants and the contribution of the F electron to the electric quadrupole coupling constants is exploited. The measured magnetic constants are used in the discussion of the quadrupole constants. It is shown that the polarization of the lattice, as a result of the displacement of the ions in the first few shells around the negative-ion vacancy, is important in determining the electric quadrupole coupling constant. This conclusion is in qualitative agreement with Kojima's calculations in LiF. It also explains the fact that while the magnetic interaction shows negligible deviation for "axial" symmetry at sites of lower symmetry, this is not true for the electric quadrupole interaction.

I. INTRODUCTION

THE de Boer model of the F center in ionic crystals assumes this defect to consist of an electron trapped by a negative-ion vacancy. The model implies the occurrence of a hyperfine interaction of the F electron with the nuclei at the lattice sites. The general form of the interaction with any specific nucleus is well known. Using the transformation properties of "spherical tensors,"¹ one can easily establish the dependence of the various terms in the spin Hamiltonian on the relative orientations of the radius vector from the vacancy to the given site, the principal axis of the "electric field gradient" tensor, and an external constant magnetic field. The electron-nuclear double resonance (ENDOR) technique² has been used by several investigators³ to observe the hyperfine spectrum of the F center. The specific angular dependence of the observed absorption lines permits ready identification of the lattice sites responsible for them. Besides the qualitative verification of the de Boer model, these experiments suggest the possibility of a more detailed check for the theory. The most obvious program is to calculate the isotropic coupling constant which is proportional to the square of the magnitude of the F electron wave function at the given site. This was done by Adrian and Gourary⁴ and by Kojima.⁵ Both assume the F -electron wave function to consist of a spherically symmetric component, centered on the vacancy. This function is orthogonalized

with respect to the core orbitals centered on all the lattice sites. The complete, orthonormalized F electron wave function φ_F has the following form

$$\varphi_F(\mathbf{r}) = N[\psi_F(\mathbf{r}) - \sum_{n,l,\alpha} \langle F | n l 0, \alpha \rangle \psi_{n l 0}(\mathbf{r} - \mathbf{R}_\alpha)], \quad (1)$$

where N is a normalizing constant. (n, l) assumes values appropriate for core orbitals, α labels the lattice sites. The overlap integrals involving two core orbitals centered at two different sites are neglected. The spherically symmetric function $N\psi_F$ is calculated from a variational ansatz. The results of this calculation suggest that most of the charge of the F electron is concentrated within the volume of the (missing) negative ion, and that the major contribution to this charge arises from the spherically symmetric density $(N\psi_F)^2$. The other terms in φ_F largely determine the values of $|\varphi_F|^2$ outside of the vacancy, i.e., the "contact" hyperfine constant.^{5a}

We shall discuss the magnetic dipole-dipole and the electric quadrupole hyperfine constants. We shall show that the preceding description of φ_F is consistent with observation and that it implies that the polarization of the lattice by the F center is an important factor in the electric quadrupole hyperfine interaction. This conclusion is in agreement with the calculation of Kojima. Kojima's calculation suggests that the main contribution to this polarization is due to the displacement (relaxation) of the ions in the first few shells into the vacancy.

In the following paper it is shown that the sign of the electric quadrupole coupling constant can be determined from the "ENDOR" (electron nuclear double resonance) data. Thus, the experiment permits an estimate of the sign and magnitude of the ion displacements. The displacements calculated by Kojima seem to have the correct sign and magnitude.

An interesting "by product" of the theory is the

^{5a} The preceding discussion and the rest of this paper applies only to the ground state of the electron.

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¹ M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), Chap. 5.

² G. Feher, *Phys. Rev.* **103**, 834 (1956); **105**, 1122 (1957).

³ W. C. Holton, thesis, University of Illinois, 1960 (unpublished).

⁴ Barry S. Gourary and Frank J. Adrian in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 10.

⁵ T. Kojima, *J. Phys. Soc. Japan* **12**, 918 (1957).

evidence it gives that the calculated asymptotic value of the nuclear quadrupole antishielding factor for Cl^- is too large.

In Sec. II, we introduce a general spin Hamiltonian to describe the hyperfine interaction of the F electron with a given nucleus; in Sec. III, the magnetic dipole term is considered in detail. In Sec. IV, the electric quadrupole term is considered, and an approximate relation for the corresponding coupling constant is derived.

II. THE HYPERFINE SPIN HAMILTONIAN

In this section we shall introduce the formalism and Hamiltonian on which we shall base the discussion in the main sections of this paper.

The interaction of an electron with a stationary nucleus can be formulated in terms of two types of coupling, magnetic and electric. These correspond, respectively, to the interaction of the nuclear magnetic and electric multipole moments with the magnetic and electric fields associated with the electron. The ordinary Coulomb interaction of the electron with the nuclear charge (electric monopole moment) is always treated separately, the other interactions are lumped together and are referred to as the hyperfine interaction. The dominant terms of this interaction involve the nuclear magnetic dipole and electric quadrupole moments, respectively.⁶ These are coupled to the magnetic field and electric field gradient due to the electron.

The magnetic field associated with the electron arises from its orbital motion and from its intrinsic magnetic dipole moment. The latter is also associated with an anomalous "contact" interaction, due to the possible overlap of the electronic wave function with the nucleus. This contact interaction is well known from the theory of the Dirac equation where it characterizes "S" states. In the present problem it is convenient to include the contact term all contributions due to that part of the electronic wave function which is spherically symmetric about the given nucleus. Evidently, then the "ordinary" magnetic dipole-dipole interaction is associated only with that part of the electronic wave function which is not spherically symmetric about the center of the given nucleus (i.e., vanishes at that point).

The quantum-mechanical discussion of the hyperfine interaction is greatly simplified by the use of the concept of the irreducible spherical tensors. Such a tensor of rank L consists of $2L+1$ functions which, under a space rotation, transform among themselves according to the L th irreducible representation of the three-dimensional rotation group.⁷ In particular, if L is an integer, these $2L+1$ functions transform like the spherical harmonics of order L . The hyperfine interaction evidently has to consist of sums of invariants or contractions of pairs of tensors of equal rank.

⁶ Recall that parity conservation excludes permanent nuclear magnetic 2^{2n} poles and electric 2^{2n+1} poles.

⁷ Sections 17 and 18 of reference 1.

The Wigner-Eckart⁸ theorem permits a simple calculation of the matrix elements of spherical tensors between states of sharp angular momentum, and leads to an explicit separation of the features of the interaction depending on the detailed physical description from those that are geometric in character (symmetry properties).⁸ In particular, this theorem asserts that the matrix elements of all tensors of rank $L=\text{integer}$, between states belonging to the same angular momentum \mathbf{J} , are proportional to a tensor of the same rank constructed from \mathbf{J} . These tensors, for $L=1; 2$, are listed in Eq. (3). In the present problem, we are concerned with a representation in which the nuclear and electronic spins (\mathbf{I}, \mathbf{S}) are each conserved. As a final preliminary remark, we recall that an interaction spin Hamiltonian is calculated by taking the expectation of the complete Hamiltonian within a given manifold of states of the unperturbed Hamiltonian. This amounts to an appropriate averaging over all the space variables in the complete Hamiltonian.

We shall now deduce expressions for the several terms in the hyperfine spin Hamiltonian which will be particularly convenient for the following discussion.

The ordinary magnetic dipole-dipole interaction is usually written as

$$-\frac{3(\mathbf{u}_e \cdot \mathbf{r})(\mathbf{u}_N \cdot \mathbf{r}) - \mathbf{u}_e \cdot \mathbf{u}_N r^2}{r^5} = 2g_N\beta_N \frac{3(\mathbf{S} \cdot \mathbf{r})(\mathbf{I} \cdot \mathbf{r}) - \mathbf{S} \cdot \mathbf{I} r^2}{r^5}, \quad (2)$$

where $\mathbf{u}_e = 2\beta\mathbf{S}$ = the electronic magnetic dipole operator, $\mathbf{u}_N = g_N\beta_N\mathbf{I}$ = the nuclear magnetic dipole operator, and \mathbf{r} = the electronic coordinate measured from the (point) nuclear dipole as origin.

Equation (2) can be rewritten as a contraction of two spherical tensors of rank 2:

$$-\frac{16\pi}{5}g_N\beta_N \sum_{m=-2}^2 (-1)^m Y_m^{(2)}(\theta, \varphi) / r^3 \mathbf{Y}_{-m}^{(2)}(\mathbf{I}, \mathbf{S}), \quad (3)$$

where $\mathbf{Y}_m^{(2)}$ are the symmetrized solid harmonics of order 2, listed below.

$$\begin{aligned} \left(\frac{4}{5}\pi\right)^{\frac{1}{2}} \mathbf{Y}_{\pm 2}^{(2)}(\mathbf{I}, \mathbf{S}) &= \left(\frac{3}{2}\right)^{\frac{1}{2}} \mathbf{I}_{\pm 1} \mathbf{S}_{\pm 1}, \\ \left(\frac{4}{5}\pi\right)^{\frac{1}{2}} \mathbf{Y}_{\pm 1}^{(2)}(\mathbf{I}, \mathbf{S}) &= (\sqrt{3}/2) (\mathbf{I}_0 \mathbf{S}_{\pm 1} + \mathbf{I}_{\pm 1} \mathbf{S}_0), \\ \left(\frac{4}{5}\pi\right)^{\frac{1}{2}} \mathbf{Y}_0^{(2)}(\mathbf{I}, \mathbf{S}) &= \frac{1}{2} (3\mathbf{I}_0 \mathbf{S}_0 - \mathbf{I} \cdot \mathbf{S}), \end{aligned}$$

and

$$\begin{aligned} \left(\frac{4}{3}\pi\right)^{\frac{1}{2}} \mathbf{Y}_{\pm 1}^{(1)}(\mathbf{I}) &= \mathbf{I}_{\pm 1} = \mp \left(\frac{1}{2}\right)^{\frac{1}{2}} (\mathbf{I}_x \pm i\mathbf{I}_y), \\ \left(\frac{4}{3}\pi\right)^{\frac{1}{2}} \mathbf{Y}_0^{(1)}(\mathbf{I}) &= \mathbf{I}_0 = \mathbf{I}_z. \end{aligned}$$

The corresponding spin Hamiltonian is obtained upon taking the expectation of Eq. (3) in the electronic state

⁸ Section 18 of reference 1.

$\psi_e(\mathbf{r})$, and is

$$\frac{16\pi}{5} g_N \beta_N \sum_{m=-2}^2 (-1)^m \times \left[\int |\psi_e(\mathbf{r})|^2 Y_m^{(2)}(\theta, \varphi) / r^3 d\tau \right] \mathcal{Y}_{-m}^{(2)}(\mathbf{I}, \mathbf{S}). \quad (4)$$

The contact (isotropic magnetic) interaction is

$$-\frac{8\pi}{3} \mathbf{u}_e \cdot \mathbf{u}_N |\psi_e(0)|^2 = -\frac{8\pi}{3} 2g_N \beta_N |\psi_e(0)|^2 \mathbf{S} \cdot \mathbf{I}. \quad (5)$$

The electric quadrupole-quadrupole interaction is (by analogy to the classic expression) written as

$$\int \rho_e \rho_N \frac{3(\mathbf{r}_e \cdot \mathbf{r}_N)^2 - r_e^2 r_N^2}{r_e^5} d\tau_e d\tau_N, \quad (6)$$

where $\rho_e(\mathbf{r}_e)$ and $\rho_N(\mathbf{r}_N)$ are, respectively, the electronic and nuclear charge densities, and $r_e/r_N \geq 1$.

Equation (6) can be written as a contraction of two spherical tensors of rank 2:

$$\frac{16\pi}{5} \frac{1}{4} \sum_{m=-2}^2 (-1)^m \left[\int |\psi_e(\mathbf{r}_e)|^2 Y_m^{(2)}(\theta_e, \varphi_e) r_e^{-3} d\tau \right] \times \left[\int |\psi_N(\mathbf{r}_N)|^2 Y_{-m}^{(2)}(\theta_N, \varphi_N) d\tau_N \right]. \quad (7)$$

This expression reduces according to the Wigner-Eckart⁷ theorem to

$$-\frac{e^2 Q}{4I(2I-1)} \frac{16\pi}{5} \sum_{m=-2}^2 (-1)^m \times \left[\int |\psi_e(\mathbf{r}_e)|^2 Y_m^{(2)}(\theta_e, \varphi_e) r_e^{-3} d\tau_e \right] \mathcal{Y}_{-m}^{(2)}(\mathbf{I}), \quad (8)$$

where Q is the nuclear quadrupole moment, defined as the expectation of $Y_0^{(2)}(\theta_N, \varphi_N)$ in the state with sharp spin \mathbf{I} and $M_I = I$.

It is convenient to interpret Eq. (8) as the contraction of the electric field gradient tensor of the electron with the nuclear quadrupole moment tensor operator. The integrals in Eqs. (4) and (8) are identical, this similarity between the dipolar and quadrupolar coupling constants will be utilized in Sec. III.

If the given electron interacts with the nucleus of an ion, a more careful calculation is necessary to account for an important second-order effect. In this case the electron distorts the closed shells of the ionic core and the nucleus interacts with an "effective" field gradient. The theory of this effect has been worked out by Sternheimer and co-workers.⁹ They were able to show

⁹ R. M. Sternheimer, Phys. Rev. **84**, 244 (1951); H. M. Foley, R. M. Sternheimer, and D. Tycko, *ibid.* **93**, 734 (1954).

that the effective field gradient due to a charge density $\rho(\mathbf{r})$ can be associated with an effective charge distribution $[1 - \gamma(r)]\rho(\mathbf{r})$. The function $\gamma(r)$ and its asymptotic value as r tends to infinity, γ_∞ , have been reported for several ions.^{9,10}

For the present problem, we have to include in the effective field gradient two additional factors: the effective positive charge associated with the negative vacancy, and the polarization of the lattice as a result of the defect.¹¹ Thus, using Eqs. (4), (5), and (8) the complete hyperfine spin Hamiltonian for the interaction of the F electron and the nucleus at a site α can be written in the following form:

$$\mathcal{H}_\alpha = a_\alpha \mathbf{S} \cdot \mathbf{I}_\alpha + 2 \left(\frac{4\pi}{5} \right)^{\frac{1}{2}} \sum_{m=-2}^2 (-1)^m b_{m,\alpha} \mathcal{Y}_{-m}^{(2)}(\mathbf{I}_\alpha, \mathbf{S}) + \frac{2}{3} \left(\frac{4\pi}{5} \right)^{\frac{1}{2}} \sum_{m=-2}^2 (-1)^m Q_{m,\alpha} \mathcal{Y}_{-m}^{(2)}(\mathbf{I}_\alpha), \quad (9)$$

where the following abbreviations have been introduced for the coupling constants:

$$a_\alpha = 2g_N \beta_N (8\pi/3) |\varphi_F(\mathbf{R}_\alpha)|^2 = \text{the contact (isotropic) magnetic coupling constant}, \quad (10)$$

$$b_{m,\alpha} = g_N \beta_N \langle \varphi_F | 2(4\pi/5)^{\frac{1}{2}} Y_m^{(2)}(\theta_\alpha, \varphi_\alpha) / r_\alpha^3 | \varphi_F \rangle = \text{the magnetic dipole-dipole coupling constant (tensor)}, \quad (11)$$

$$Q_{m,\alpha} = \frac{3e^2 Q_\alpha}{4I_\alpha(2I_\alpha-1)} q_{m,\alpha} = \text{the electric quadrupole coupling constant (tensor)}, \quad (12)$$

and

$$q_{m,\alpha} = [2(\frac{4}{5}\pi) (-1)^m Y_{-m}^{(2)}(-\theta_0, -\varphi_0) Y_0^{(2)}(0,0) / R_\alpha^3 + q_{m,\alpha}(\text{pol.})] (1 - \gamma_{\infty,\alpha}) - \langle \varphi_F | (1 - \gamma_\alpha(r)) 2(\frac{4}{5}\pi)^{\frac{1}{2}} Y_m^{(2)}(\theta_\alpha, \varphi_\alpha) / r_\alpha^3 | \varphi_F \rangle = \text{the effective electric field gradient tensor at site } \alpha. \quad (13)$$

In Eq. (13) the first term accounts for the effective charge of the vacancy at $(R_\alpha, \theta_0, \varphi_0)$ and $q_{m,\alpha}(\text{pol.})$ is the field gradient associated with the lattice polarization.

The integrations indicated in Eqs. (11) and (13) become improper when the range of integration includes the α th site ($r = R_\alpha$). In this case these integrals are to be interpreted as Cauchy principle parts. This is equivalent with the more common statement that one is to exclude in these integrals the contribution from the part of the F -electron charge density which is spherically

¹⁰ R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956).

¹¹ These points are discussed in Sec. IV.

symmetric about R_α .¹² ($r_\alpha, \theta_\alpha, \varphi_\alpha$) are the coordinates in a local coordinate system with its origin at the α th site. In the following we shall, whenever possible, simplify the notation by dropping the subscript α .

It is convenient to impose on the local coordinate system the condition that its polar axis be directed toward (or away from) the vacancy. This choice does not necessarily make the local coordinate system unique, but any such system has the merit of permitting a simple statement of the restrictions imposed on the tensors $\mathbf{b}_\alpha, \mathbf{q}_\alpha$, by the symmetries of the α th site.¹³

Specifically, if the α th site lies on a plane of reflection symmetry, then the local polar axis is normal to that principal axis of these tensors which is normal to the symmetry plane. Hence

$$\begin{aligned} b_{1,\alpha} &= \mp b_{-1,\alpha}, & q_{1,\alpha} &= \mp q_{-1,\alpha}, \\ b_{2,\alpha} &= \mp b_{-2,\alpha}, & q_{2,\alpha} &= \mp q_{-2,\alpha}. \end{aligned} \quad (14)$$

If the α th site lies on an n -fold axis of rotation symmetry, then the local polar axis is itself a principal axis, hence

$$b_{\pm 1,\alpha} = 0 = q_{\pm 1,\alpha}, \quad (15)$$

and

$$b_{2,\alpha} = b_{-2,\alpha}; \quad q_{2,\alpha} = q_{-2,\alpha}. \quad (16)$$

Furthermore, if $n \geq 3$, then we have also

$$b_{\pm 2,\alpha} = 0 = q_{\pm 2,\alpha}. \quad (17)$$

For a fcc lattice, if we denote the vacancy by (000), then the site symmetries listed in Table I are easily verified.

III. THE MAGNETIC DIPOLE-DIPOLE COUPLING CONSTANT TENSOR

In this section we shall use the approximate F -electron wave function Eq. (1) to obtain approximations for the tensor \mathbf{b} defined by Eq. (11). We shall use these together with some experimental results to estimate the contributions to \mathbf{b} arising from the F -electron charge density inside and outside of the volume of the α th ion. These estimates will be used in the next section in the discussion of the contribution of the F electron charge density to the "effective" field gradient tensor acting at the α th site [Eq. (13)].

$$I_{0,\alpha} = -2\pi \int_{R_\alpha - R_i}^{R_\alpha + R_i} dr \int_{(\tau^2 + R_\alpha^2 - R_i^2)/2rR_\alpha}^{-1} r^2 N^2 \psi_F^2(r) \frac{3(rx - R_\alpha)^2 - (r^2 - 2rR_\alpha x + R_\alpha^2)}{(r^2 - 2rR_\alpha x + R_\alpha^2)^{3/2}} dx, \quad (21)$$

where $x = \cos\theta$. The integration with respect to x is elementary, and leads to

$$I_{0,\alpha} = (2/R_\alpha^3) \left[\frac{1}{2} \int_{R_\alpha - R_i}^{R_\alpha + R_i} N^2 \psi_F^2(r) d\tau + \int_{R_\alpha - R_i}^{R_\alpha + R_i} N^2 \psi_F^2(r) f\left(\frac{r}{R_i}\right) d\tau \right], \quad (22)$$

¹² See Appendix A for additional comments.

¹³ The symmetries of a site consist at any subgroup of the lattice point group which maps the vacancy and the site into themselves. The invariance of \mathcal{H} under these transformations T requires that $T\mathbf{b}T^{-1} = \mathbf{b}$. The known transformation laws for spherical tensors immediately lead to the results quoted above (see reference 1, Chap. V).

¹⁴ The identity of the right sides of Eqs. (18a) and (18b) is proved in O. Kellogg, *Foundations of Potential Theory* (Dover Publications, Inc., New York, 1953), pp. 152-155.

TABLE I. The symmetries of site in an fcc lattice.

Site type	Site location	Symmetry group of site
(n00)	Fourfold axis of rotation symmetry	C_{4v}
(nnn)	Threefold axis of rotation symmetry	C_{3v}
(nm0)	Twofold axis of rotation symmetry	C_{2v}
(nm0), (nnm) $m \neq n, \bar{n}$	Plane of reflection symmetry	C_s

Consider first the zero component of \mathbf{b} :

$$\frac{b_0}{g_N \beta \beta_N} = \int \varphi_F^2(\mathbf{r}) \frac{3 \cos^2 \theta_\alpha - 1}{r_\alpha^3} d\tau \quad (18a)$$

$$= \frac{\partial^2}{\partial z^2} \int \frac{\varphi_F^2(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\tau' \Big|_{\mathbf{r} = \mathbf{R}_\alpha} + \frac{4\pi}{3} \varphi_F^2(\mathbf{R}_\alpha), \quad (18b)$$

where the integral in Eq. (18a) is to be interpreted as a Cauchy principal part.^{12,14} \mathbf{r} is the radius vector from the center of the vacancy (origin).

($N\psi_F$) is spherically symmetric about the vacancy, hence its contribution to b_0 can be determined with the help of (18b). It is

$$\frac{2}{R_\alpha^3} \int_{r \leq R_\alpha} N^2 \psi_F^2(r) d\tau - \frac{8\pi}{3} N^2 \psi_F^2(R_\alpha). \quad (19)$$

We shall now estimate the contribution to $b_{0,\alpha}$ due to the part of $N\psi_F$ which does not overlap the α th ion. For this purpose we shall restrict the region of integration for the integral in Eq. (18a) to the space outside of a sphere of radius R_i (= ionic radius) about \mathbf{R}_α .

From Eq. (18b) we conclude that the integral over the region $r \geq R_\alpha + R_i$ vanishes. The integral over the region $r \leq R_\alpha - R_i$ is just

$$\frac{2}{R_\alpha^3} \int_{r \leq R_\alpha - R_i} N^2 \psi_F^2(r) d\tau. \quad (20)$$

It remains to evaluate the integral

where

$$f = \frac{1}{16} \left\{ \left(\frac{r}{R_i} \right)^3 - 2 \left(\frac{r}{R_i} \right) \left[\left(\frac{R_\alpha}{R_i} \right)^2 + 3 \right] + \left[\left(\frac{R_\alpha}{R_i} \right)^4 + 2 \left(\frac{R_\alpha}{R_i} \right)^2 - 3 \right] \left(\frac{r}{R_i} \right)^{-1} \right\}. \quad (23)$$

A similar calculation can be made to determine $I_{i,\alpha}$, the contribution to $b_{0,\alpha}$ of the part of $N\psi_F$ which overlaps the α th ion. However, if we consider Eq. (19), it is evident that

$$I_{i,\alpha} = \frac{2}{R_\alpha^3} \left[\frac{1}{2} \int_{R_\alpha - R_i \leq r \leq R_\alpha} N^2 \psi_F^2(r) d\tau - \frac{1}{2} \int_{R_\alpha \leq r \leq R_\alpha + R_i} N^2 \psi_F^2(r) d\tau - \int_{R_\alpha - R_i \leq r \leq R_\alpha + R_i} N^2 \psi_F^2(r) f \left(\frac{r}{R_i} \right) d\tau \right] - (8\pi/3) N^2 \psi_F^2(R_\alpha). \quad (24)$$

Combining Eqs. (18a), (20), (22), and (24), we obtain

$$\begin{aligned} \frac{b_{0,\alpha}}{g_{N,\alpha} \beta \beta_N} = & \frac{2}{R_\alpha^3} \left[\int_{r \leq R_\alpha - R_i} N^2 \psi_F^2(r) d\tau + \frac{1}{2} \int_{R_\alpha - R_i \leq r \leq R_\alpha + R_i} N^2 \psi_F^2(r) d\tau + C_{1,\alpha}(R_i) \right] \\ & + \left\{ \frac{2}{R_\alpha^3} \left[\frac{1}{2} \int_{R_\alpha - R_i \leq r \leq R_\alpha} N^2 \psi_F^2(r) d\tau - \frac{1}{2} \int_{R_\alpha \leq r \leq R_\alpha + R_i} N^2 \psi_F^2(r) d\tau - C_{1,\alpha}(R_i) \right] \right. \\ & \left. - (8\pi/3) N^2 \psi_F^2(R_\alpha) \right\} + C_{2,\alpha}. \quad (25) \end{aligned}$$

In Eq. (25), the group of terms in the first pair of square brackets represents the effect of the part of $N\psi_F$ which does not overlap the α th ion. It is shown in Appendix B to be less than

$$\int_{r \leq R_\alpha} N^2 \psi_F^2(r) d\tau \leq 1.$$

The terms inside of the curly braces represent the effect of the part of $N\psi_F$ which overlaps the α th ion.

$$C_{1,\alpha}(R_i) = \int_{R_\alpha - R_i \leq r \leq R_\alpha + R_i} N^2 \psi_F^2(r) f \left(\frac{r}{R_i} \right) d\tau \quad (26)$$

and $C_{2,\alpha}$ accounts for the contribution of the part of $|\varphi_F(\mathbf{r}) - N\psi_F(\mathbf{r})|^2$ which is centered on the α th site. The remaining contributions to $b_{0,\alpha}$ consist of two- or three-centered integrals involving at least one core

orbital on a site other than α . These contributions are assumed to be negligible.

In estimating the contribution of the F -electron charge density to the electric field gradient at the α th site, we shall have to distinguish the part of $\varphi_F(\mathbf{r})$ which overlaps the α th ion from that which does not overlap the α th ion. Hence we shall have to return to Eq. (25). No such distinction is necessary for the discussion of $b_{0,\alpha}$. For this purpose it is, therefore, more convenient to rewrite Eq. (25) in the form

$$b_{0,\alpha}/g_{N,\alpha} \beta \beta_N = (2/R_\alpha^3) C_{3,\alpha} + b_{0,\alpha}', \quad (27)$$

where

$$C_{3,\alpha} = \int_{r \leq R_\alpha} N^2 \psi_F^2(r) d\tau, \quad (28)$$

$$b_{0,\alpha}' = -(8\pi/3) N^2 \psi_F^2(R_\alpha) + C_{2,\alpha}. \quad (29)$$

The calculations of Kojima⁵ and Adrian and Gourary⁴ suggest that

$$0.8 \leq C_{3,\alpha} \leq 1. \quad (30)$$

In order to estimate $b_{0,\alpha}'$ we calculated $(2g_{N,\alpha} \beta \beta_N / R_\alpha^3) \times (b_{0,\alpha})^{-1}$ using the values of $b_{0,\alpha}$ determined by "ENDOR" experiments.¹⁵ The results are tabulated in Table II. Evidently

$$|b_{0,\alpha} - 2g_{N,\alpha} \beta \beta_N / R_\alpha^3| (b_{0,\alpha})^{-1} < 0.9.$$

Furthermore, it seems that

$$b_{0,\alpha} \sim 2g_{N,\alpha} \beta \beta_N / R_\alpha^3,$$

may be a good asymptotic relation. This relation is suggested by the exponential decrease of $b_{0,\alpha}'$ with R_α due to the corresponding decrease in φ_F .

¹⁵ The data were taken from reference 3, Table I.

TABLE II. Comparison of the experimental $b_{0,\alpha}$ with the theoretical asymptotic expression.

Material	Ion	$(R_\alpha/a)^2$ a	1	2	3	4	5	6
		$(2g_{N,\alpha} \beta \beta_N / R_\alpha^3) (b_{0,\alpha})^{-1}$						
LiF	Li	1.19	...	1.08	...	1.18
LiCl	Li	1.06
NaF	Na	0.48
NaCl	Na	0.30
KCl	K	0.13	...	0.73
KBr	K	0.14
LiF	F	...	0.22	...	1.03	...	0.91	...
NaF	F	1.21
LiCl	Cl	...	0.18	...	1.00	...	1.04	...
NaCl	Cl	...	0.13
KCl	Cl	...	0.18	...	0.28	...	0.57	...

a = interionic distance.

To conclude our discussion of the magnetic dipole-dipole coupling constant (tensor), we shall now consider the other components of \mathbf{b} :

$$\frac{\mp b_{\pm 1, c}}{g_{N, \alpha} \beta \beta_N} = (6)^{\frac{1}{2}} \int \varphi_F(\mathbf{r}) \frac{\cos \theta_\alpha \sin \theta_\alpha \exp(\pm i \varphi_\alpha)}{r_\alpha^3} d\tau, \quad (31)$$

$$\frac{b_{\pm 2, \alpha}}{g_{N, \alpha} \beta \beta_N} = \left(\frac{3}{2}\right)^{\frac{1}{2}} \int \varphi_F(\mathbf{r}) \frac{\sin^2 \theta_\alpha \exp(\pm 2i \varphi_\alpha)}{r_\alpha^3} d\tau. \quad (32)$$

Evidently, only those components of $\varphi_F^2(\mathbf{r})$ which depend on φ_α can contribute to $b_{m, \alpha}$, $m \neq 0$. But this implies that $b_{m, \alpha}$, $m \neq 0$ consist of sums of multicentered integrals involving at least one core orbital centered on a site other than α . Thus, we might expect these components of \mathbf{b} to be extremely small. This conclusion is confirmed by the fact that no experimental determination of these components has yet been reported. Feher² seems to be the only worker who actually looked for "axial asymmetry"¹⁶ in the magnetic hyperfine interaction [of (1,1,0) sites]. He found that his resolution was insufficient to observe $b_{2,110}$.¹⁷

IV. THE ELECTRIC FIELD GRADIENT (QUADRUPOLE COUPLING) TENSOR

In this section we shall utilize the similarity of the magnetic coupling tensor \mathbf{b} , Eq. (11), and the contribution of the F electron to the effective field gradient tensor Eq. (13). The experimentally determined magnetic coupling constant and the theoretical discussion of this constant in Sec. III will be used to obtain an estimate of the importance of the several factors contributing to the electric quadrupole coupling constant.

The field gradient at the α th site in a cubic lattice with an F center arises from four factors: First, the effective unit positive charge associated with the negative-ion vacancy¹⁸; second, the F electron charge density; third, the equilibrium lattice polarization associated with the F center; finally, the gradient of the Madelung field in a perfect lattice evaluated at the displaced position of the α th ion.

A. The Lattice Polarization

The lattice polarization results from two different effects, first the radial relaxation of the ions about the vacancy, which lowers the symmetries of all sites other

TABLE III. Kojima's calculated polarization of LiF.

Shell ^a	Displacement of ions into the vacancy	Dipole moment induced on ions (core distortion)
1	0.074 <i>a</i>	0.002 <i>ae</i>
2	0.026 <i>a</i>	0.006 <i>ae</i>

^a The set of ions located at a distance $R = (n)^{\frac{1}{2}}a$ from a given site are called the n th shell (of neighbors).

than the vacant one. Second, the electric field associated with the vacancy leads to a small distortion of the ion cores, i.e., induces an electric dipole moment on them. Kojima⁵ calculated both effects for the first two shells of ions about the vacancy. His results are summarized in Table III.

The contribution of the displacement and core distortion of ions in the two first shells to the components of the field-gradient tensor at sites in these shells were calculated from Kojima's results, as shown in Table IV.

In the following we shall always combine the gradient of the Madelung field with the field gradient due to lattice polarization. We shall refer to the resultant term as the polarization field gradient. Table IV suggests that the contribution of the lattice polarization, and particularly the displacement of ions, to the field-gradient tensor is of the same order as that of the vacancy charge. Since the main contribution appears to be due to the ion displacement, we shall henceforth neglect the contribution of the distortion of the ionic cores to the field gradient. Table IV suggests furthermore that the sign of $q_{m, \alpha}(\text{pol.})$ might be determined by the direction of the displacement of the ions. In order to investigate the validity of the preceding observation, we calculated the field gradient at sites in the first two shells due to the displacement of the ions in the first six shells. The field gradients were calculated to second order in the fractional displacements ζ_α . That is, $(a\zeta_\alpha)$ is the displacement of the ions in the α th shell towards

TABLE IV. Field gradient due to lattice polarization calculated from Kojima's results for LiF.

Shell	m^a	$q_m(\text{pol.}) (2/R_\alpha^3)^{-1} b$				
		Due to displacement of ions in shell 1	Due to core distortion in shell 1	Due to displacement of ions in shell 2	Due to core distortion in shell 2	Gradient of the Madelung field ^c
1	0	0.156	-0.004	0.110	0.025	-0.118
2	0	0.831	-0.023	-0.109	-0.025	-0.010
	2 ^d	0.276	-0.008	-0.005	-0.001	

^a The components not listed, vanish identically because of the symmetry of the sites.

^b The field gradient is normalized to the gradient of the field due to the effective positive charge of the vacancy.

^c Here we used the Madelung potential for ionic crystals of the structure of NaCl, calculated by F. W. de Wette and B. R. A. Nijboer, *Physica* **24**, 1105 (1958).

^d $q_{2, \alpha} = (1/e\sqrt{6})(\delta^2 V/\delta x_\alpha^2 - \delta^2 V/\delta y_\alpha^2)$. The local y axis is chosen in the (100) plane through the vacancy and the α th site (located in the second shell).

¹⁶ Axial asymmetry refers here to the independence of the spin Hamiltonian of φ_α .

¹⁷ Note that the symmetries of sites for which $(R_\alpha/a)^2 = 1, 3, 4$ imply that $b_{m, \alpha} = 0$ for $m \neq 0$. It is, however, quite possible that a more careful analysis of presently available "ENDOR" data will permit a determination of $b_{2,110}$.

¹⁸ All available evidence indicates that alkali halides are very nearly ideal ionic crystals. Thus, the charge at each lattice site is $|e|$.

the center of the vacancy.

$$\begin{aligned}
 q_{0,1}(\text{pol.})(2/R_1^3)^{-1} &= [(1.78\zeta_1 + 4.41\zeta_1^2) - 21.6\zeta_1^2] \\
 &\quad + (3.20\zeta_2 + 0.41\zeta_2^2 + 13.82\zeta_2\zeta_1) \\
 &\quad - (1.14\zeta_3 + 0.25\zeta_3^2 + 1.75\zeta_3\zeta_1) \\
 &\quad - (3.04\zeta_4 + 6.11\zeta_4^2 - 12.30\zeta_4\zeta_1) \\
 &\quad - (0.01\zeta_5 + 0.38\zeta_5^2 - 1.46\zeta_5\zeta_1) \\
 &\quad + (0.52\zeta_6 + 0.67\zeta_6^2 - 1.36\zeta_6\zeta_1). \quad (33)
 \end{aligned}$$

Here $(-21.6\zeta_1)2/R_1^3$ is the Madelung field gradient, and we neglected the effect of the distortion of the ionic cores. If $\zeta_1 \leq 0.104$, then the contribution of displacement of the ions in the first shell is larger than the Madelung field gradient. Hence in this case the net contribution of the displacement of ions in the first shell has the same sign as ζ_1 . But the contribution of the displacements of ions in the second shell has the same sign as ζ_2 (and ζ_1). Hence even when ζ_1 slightly exceeds 0.104, the signs of $q_{0,1}(\text{pol.})$ and of ζ_1 are probably equal. It has been observed that it may not be consistent to include the effect of the displacement of ions in the second shell, while neglecting the effect of the displacement of ions in the third and fourth shells. However, even if we make the rather extreme assumption that $\zeta_2 = \zeta_3 = \zeta_4 = \zeta$, and $\zeta_1 = 0.104$, the signs of $q_{0,1}(\text{pol.})$ and of ζ_1 are equal, provided that $\zeta \leq 0.356$. This seems rather conclusive evidence that, for the displacements to be expected in practice, $q_{0,1}(\text{pol.})$ and ζ_1 have the same sign. In particular a positive $q_{0,1}(\text{pol.})$ always indicates a positive (inward) displacement of the ions.

Using the same notation as in Eq. (33), we obtain the following expression for $q_{0,2}(\text{pol.})$:

$$\begin{aligned}
 q_{0,2}(\text{pol.})(2/R_2^3)^{-1} &= (10.38\zeta_1 - 0.37\zeta_1^2 + 33.70\zeta_1\zeta_2) \\
 &\quad - [(4.07\zeta_2 + 3.68\zeta_2^2) + 15.18\zeta_2^2] \\
 &\quad - (4.00\zeta_3 - 3.81\zeta_3^2 + 20.05\zeta_3\zeta_2) \\
 &\quad + (1.24\zeta_4 + 0.10\zeta_4^2 + 2.69\zeta_4\zeta_2) \\
 &\quad - (1.16\zeta_5 + 7.10\zeta_5^2 + 19.55\zeta_5\zeta_2) \\
 &\quad + (2.75\zeta_6 + 5.94\zeta_6^2 - 1.80\zeta_6\zeta_2). \quad (34)
 \end{aligned}$$

Here $(-15.18\zeta_2^2)(2/R_2^3)$ is the Madelung field gradient. Again the most important contribution is due to the displacement of the ions in the first shell. Hence the

signs of ζ_1 and $q_{0,2}(\text{pol.})$ are equal for any displacements to be expected in practice. Note that a negative $q_{0,2}$ always indicates a negative (outward) displacement of the ions.

Finally, using the convention that the (local) y_α axis lies in the (100) plane through the vacancy and the α th site, we have

$$\begin{aligned}
 q_{2,2}(\text{pol.})(2/R_2^3)^{-1} &= (3.39\zeta_1 + 2.33\zeta_1^2 + 6.29\zeta_1\zeta_2) - (0.16\zeta_2 + 1.00\zeta_2^2) \\
 &\quad + (5.93\zeta_3 + 1.19\zeta_3^2 + 16.85\zeta_3\zeta_2) \\
 &\quad + (1.74\zeta_4 + 1.06\zeta_4^2 + 1.91\zeta_4\zeta_2) \\
 &\quad - (6.62\zeta_5 + 13.95\zeta_5^2 - 23.2\zeta_5\zeta_2) \\
 &\quad - (1.08\zeta_6 + 0.92\zeta_6^2 + 2.75\zeta_6\zeta_2). \quad (35)
 \end{aligned}$$

Again, the sign of $q_{2,2}(\text{pol.})$ and of ζ_1 are equal for the expected displacements, and a negative $q_{2,2}(\text{pol.})$ always indicates a negative (outward) displacement.

B. The Approximate Effective Field Gradient

We have already noted in Sec. I that if a nucleus is embedded in an ion, then the nuclear quadrupole moment interacts with an "effective" field gradient. Foley and Sternheimer show that this effective field gradient can be calculated by replacing the actual (source) charge density $\rho(\mathbf{r})$ by an effective density $[1 - \gamma(r)]\rho(\mathbf{r})$.¹⁹ The calculations of these authors show that $1 - \gamma(r) \approx 1$ for $r \leq$ the ionic radius. Furthermore, $\gamma(r)$ reaches its asymptotic value, γ_∞ , very rapidly. Hence, a reasonable approximation of the effective field gradient is just to correct the field gradient due to charge densities outside of the ionic volume by multiplying it by $(1 - \gamma_\infty)$. This approximation enables us to use the approximate expression for \mathbf{b} , derived in the preceding section, to estimate the contribution of the F electron to the effective field gradient at the α th nucleus. If we substitute Eq. (25) into Eq. (12) and combine the result with Eq. (13), we obtain the following approximation for $q_{0,\alpha}$:

$$\begin{aligned}
 q_{0,\alpha} &= \frac{2}{R_\alpha^3} (1 - \gamma_{\infty,\alpha}) - \left[\left(\frac{b_{0,\alpha}}{g_{N,\alpha}\beta\beta_N} - \frac{2C_\alpha}{R_\alpha^3} \right) \right. \\
 &\quad \left. + \frac{2C_\alpha}{R_\alpha^3} (1 - \gamma_{\infty,\alpha}) \right] + q_{0,\alpha}(\text{pol.})(1 - \gamma_{\infty,\alpha}), \quad (36)
 \end{aligned}$$

where

$$\begin{aligned}
 C_\alpha &= \int_{r \leq R_\alpha - R_i} N^2 \psi_F^2(r) d\tau \\
 &\quad + \frac{1}{2} \int_{R_\alpha - R_i \leq r \leq R_\alpha + R_i} N^2 \psi_F^2(r) d\tau + C_{1,\alpha}, \quad (37)
 \end{aligned}$$

$$C_{1,\alpha} = \int_{R_\alpha - R_i \leq r \leq R_\alpha + R_i} N^2 \psi_F^2(r) f(r/R_i) d\tau. \quad (26)$$

TABLE V. Values of the parameters $C_{1,\alpha}$ defined by Eq. (26).

Crystal	$C_{1,1}$		$C_{1,2}$	$C_{1,3}$	
	Gourary and Adrian	Kojima		Gourary and Adrian	Kojima
LiF	-0.203	-0.024	...
	-0.086 ^a	+0.009	...	-0.002 ^a	-0.022
KCl	-0.160	...	-0.016	-0.006	...

^a These entries were calculated using the results of the improved calculation of Gourary and Adrian. The other entries were calculated using the results of the simple point ion lattice calculation of Gourary and Adrian.

¹⁹ See R. M. Sternheimer and D. Tycko, Phys. Rev. **93**, 734 (1954); Eq. (12).

TABLE VI. Parameters of the spherically symmetric part of the F -electron wave function.

Crystal	k_1a		k_2a	
	Gourary and Adrian	Kojima	Gourary and Adrian	Kojima
LiF	2.26		1.86	
	2.611 ^a	2.96	2.637 ^a	1.626
KCl	2.37		2.44	

^a These values are the results of the improved calculation. The other values quoted from Gourary and Adrian result from the simple point ion lattice calculation.

The three sets of terms in Eq. (36) represent, respectively, the contributions of the effective positive charge of the vacancy, the F -electron charge density, and the lattice polarization. A regrouping of terms in Eq. (36) leads to a more convenient expression for $q_{0,\alpha}$,

$$q_{0,\alpha} = q_{0,\alpha}(\text{pol.})(1 - \gamma_{\infty,\alpha}) - [(b_{0,\alpha}/g_{N,\alpha}\beta\beta_N) - (2/R_\alpha^3)] + (1 - C_\alpha)(-\gamma_{\infty,\alpha})(2/R_\alpha^3). \quad (38)$$

We shall now proceed to estimate the parameter $(1 - C_\alpha)$. This requires in turn the calculation of the parameter $C_{1,\alpha}$ defined by Eq. (26), (c.f. Table V). To calculate this parameter one requires the analytic expression for $N\psi_F$. Kojima and Gourary and Adrian used similar expressions in their calculations of $N\psi_F$. Kojima's expression is

$$N\psi_F(r) \propto \frac{\sin k_1 r}{r}, \quad r \leq 0.9a$$

$$\propto e^{-k_2 r}, \quad r \geq 0.9a. \quad (39)$$

Gourary and Adrian use

$$N\psi_F(r) \propto \frac{\sin k_1 r}{r}, \quad r \leq \chi a$$

$$\propto \frac{e^{-k_2 r}}{r}, \quad r \geq \chi a \quad (40)$$

where a is the interionic distance. $\chi = 1$ in all cases except the improved calculation for LiF. In the latter case, χ is used as a variational parameter and determined to be 0.9. Some values of k_1a and k_2a are listed in Table VI.

The limits of integration for the integrals which determine C_α involve the "ionic radius" R_i . The value chosen for this parameter was $a/2$. The error involved in this approximation is of the same order as that introduced by approximating $1 - \gamma(r)$ by a step function. This approximation will now be discussed in some detail.

Foley and Sternheimer plot $1 - \gamma(r)$ for Cs^+ , Rb^+ , and Cl^- .²⁰ In all three ions $1 - \gamma(r) \approx 1$ for small distances

from the origin, it has a small negative minimum at $r \approx 0.8 \text{ \AA}$ and then rises rapidly. $1 - \gamma(r) \approx 0.9(1 - \gamma_\infty)$ at $r \approx 2.2 \text{ \AA}$ for the alkali ions, and at $r \approx 2.7 \text{ \AA}$ for the halogen ion. At the ionic radii suggested by Gourary and Adrian,⁴ $1 - \gamma(r) \approx 0.7(1 - \gamma_\infty)$ for the alkalis, and $1 - \gamma(r) \approx 0.5(1 - \gamma_\infty)$ for the halogen. This suggests that a reasonable estimate of the error introduced by approximating $1 - \gamma(r)$ by a step function can be obtained by comparing the resulting value of C_α with the value obtained by approximating $1 - \gamma(r)$ by three line segments. [The second approximation does not change the form of Eq. (38), though it requires a re-definition of C_α .] This calculation was done for C_2 in KCl. The nuclear antishielding factor was written in the form

$$1 - \gamma(r) = 1; \quad r \leq r_1 = 1.06 \text{ \AA}$$

$$= 1 - \gamma_\infty \frac{r - r_2}{r - r_1}; \quad r_1 \leq r \leq r_2 = 2.65 \text{ \AA}$$

$$= 1 - \gamma_\infty; \quad r_2 \leq r.$$

In this approximation $C_2 = 0.839$. In the step-function approximation,

$$1 - \gamma(r) = 1; \quad r \leq R_i$$

$$= 1 - \gamma_\infty; \quad r \geq R_i.$$

$C_2(R_i = 1.64 \text{ \AA}) = 0.850$ and $C_2(R_i = a/2 = 1.57) = 0.878$. This result suggests that in view of the inaccuracy of $1 - \gamma(r)$ and $N\psi_F$ any refinement of the step-function approximation of $1 - \gamma(r)$ is probably unwarranted. We may conclude further that the values of C_α calculated in the step-function approximation are slightly too large for halogen ions and probably slightly too small for the alkali ions. These conclusions are evidently unaffected by the further approximation of letting $R_i = a/2$.

In Table VII, we list values of $(1 - C_\alpha)$ for KCl and LiF. For LiF we compare the values calculated from Kojima's results with those obtained from both the "simple" and the "improved" point ion lattice calculations of Gourary and Adrian.

In Table VIII we list the values of the several terms in Eq. (38), calculated for Li^+ sites in the first shell of LiF. "ENDOR" data were used to calculate the second term, the other terms were calculated from the theory.

TABLE VII. Values of the parameters $1 - C_\alpha$ defined by Eqs. (37) and (38).

Crystal	$1 - C_1$		$1 - C_2$	$1 - C_3$	
	Gourary and Adrian	Kojima	Gourary and Adrian	Gourary and Adrian	Kojima
LiF	0.609			0.069	
	0.369 ^a	0.284		0.015 ^a	0.036
KCl	0.541		0.122	0.029	

²⁰ Reference 9, Fig. 2. in the second paper. The curves are incorrect, and the correct asymptotic values, $1 - \gamma_\infty$, are reported in reference 10. Still the qualitative features of the curves are probably reliable.

^a These entries were calculated using the results of the improved calculation of Gourary and Adrian. The other entries were calculated using the results of the simple point ion lattice calculation of Gourary and Adrian.

TABLE VIII. The calculated field gradient in LiF at Li⁺ sites in the first shell.

$q_{0,1}(\text{pol.})(1-\gamma_\infty)^a$	$-\left[(b_0/g_N\beta\beta_N)-(2/R_\alpha^3)\right]$	$(1-C_1)(-\gamma_\infty)(2/R_\alpha^3)$		q_0		$(e^2Q/4h)q_0$ in kc/sec ^b	
		Gourary and Adrian	Kojima	Gourary and Adrian	Kojima	Gourary and Adrian	Kojima
0.031 ^c	0.039	-0.111 ^d	...	-0.041	...	+35.7	...
0.031	0.039	-0.065 ^e	-0.050	+0.005	+0.020	+4.4	-17.4
0.019 ^f	0.039	-0.111 ^d	...	-0.053	...	+46.2	...
0.019	0.039	-0.065 ^e	-0.050	-0.007	+0.008	+6.1	-7.0

^a The entries in the first four columns are in 10²⁴ cm⁻².

^b $Q = -0.1 \times 10^{-24}$ cm².

^c Calculating $q_{0,1}(\text{pol.})$ from Table VI, and using $\gamma_\infty = 0.259$.

^d Using the results of the point ion lattice calculation of Gourary and Adrian.

^e Using the results of the improved calculation of Gourary and Adrian.

^f This value includes the contribution of the displacements of the ions in the third and fourth shells, assuming these to be equal to the displacement of the ions in the second shell. This overestimates the effect of the farther ions, and constitutes a lower bound on $q_0(\text{pol.})$.

Equation (33) shows that $q_{0,1}(\text{pol.})$ is over estimated if one includes only contributions due to the displacements of ions in the first two shells. The displacements of ions in the third and fourth shells tend to decrease $q_{0,1}(\text{pol.})$. Hence, the assumption that the displacements of ions in the second, third, and fourth shells are all equal, and that the displacements of ions in the farther shells may be neglected probably underestimates $q_{0,1}(\text{pol.})$.

To date no experimental determination of the electric quadrupole coupling constant for Li⁺ in LiF has been reported. This suggests that the simple point-ion lattice calculation results in a $N\psi_F$ which is too diffuse. However, both the improved point-ion lattice results and Kojima's calculation seem in accord with the experimental evidence. On the other hand, even a small outward displacement of the ions would, because of the reversal of the sign of $q_{0,1}(\text{pol.})$, lead to a calculated value of $q_{0,1}$ which is probably too large to be consistent with the experimental evidence. Thus it is evident that the contribution of $q_{0,1}(\text{pol.})$ to $q_{0,1}$ is important.

C. Estimates of the Polarization Field Gradient

Of particular interest is the fact that Eq. (38) enables us to estimate $q_{0,\alpha}(\text{pol.})$ from the experimental ("ENDOR") data.²¹ Such an estimate is subject to three sources of uncertainty.

First the nuclear quadrupole moment, Q_α , is only known to within 20%. This means that the experimental value of $q_{0,\alpha}$ is only determined within this accuracy.

Second, there is an uncertainty about the reliability of the calculated values of γ_∞ . This complication seems to affect mainly the halogen ions. Thus, molecular observations seem to suggest that for Cl⁺ $(1-\gamma_\infty) \approx 10$ rather than the calculated value of 57.6. The same observations show, however, reasonable agreement with the calculated values of $(1-\gamma_\infty)$ for the alkali ions.²²

²¹ In order to calculate $q_0(\text{pol.})$ from Eq. (38), it is essential to know both magnitude and sign of q_0 . The "ENDOR" data are known to determine $|Qq_0|$. In the following paper it is shown that the same data also determine the sign of this parameter.

²² Charles H. Townes in *Handbuch der Physik* (Springer-Verlag, Berlin, 1958), Vol. 38/1, p. 416.

Rewriting Eq. (38) as

$$q_{0,\alpha}(\text{pol.}) = \{q_{0,\alpha} + [(b_{0,\alpha}/g_{N,\alpha}\beta\beta_N) - (2/R_\alpha^3)] - (1-C_\alpha)(-\gamma_{\infty,\alpha})(2/R_\alpha^3)\} (1-\gamma_{\infty,\alpha})^{-1}, \quad (41)$$

it is evident that an error in $\gamma_{\infty,\alpha}$ may lead to an error in the sign of the $q_{0,\alpha}(\text{pol.})$ deduced from the experimental values of $q_{0,\alpha}$ and $b_{0,\alpha}$. We shall return to this point.

The third source of uncertainty in the estimate of $q_{0,\alpha}(\text{pol.})$ is due to the uncertainty in the parameter C_α . This uncertainty is primarily due to the uncertainty in $N\psi_F$. Other factors contributing to it are the uncertainty in $1-\gamma(r)$ and the step function approximation of this function. This point has already been discussed. The uncertainty in $1-C_\alpha$ affects the estimated magnitude of $q_{0,\alpha}(\text{pol.})$: It may also lead to an error in the sign of the estimate of $q_{0,\alpha}(\text{pol.})$. With the possible exception of lithium salts this problem does not seem to occur for ions in the first shell. This is because in this case the third term in Eq. (41) does not seem to determine the sign of $q_0(\text{pol.})$. The rapid decrease of $1-C_\alpha$ with R_α suggests that the uncertainty in this factor may be of little consequence for sites in the third and farther shells.

To illustrate the preceding discussion, Eq. (41) was used to estimate $q_{0,1}(\text{pol.})$ and $q_{0,2}(\text{pol.})$ in KCl. The values of the various terms in Eq. (41) (divided by $2/R_\alpha^3$) are listed in Table IX.

The positive sign of $q_{0,1}(\text{pol.})$ is certain. In fact $1-C_1$ is probably overestimated. As already noted, the step function approximation of $1-\gamma(r)$ inherently leads to such an overestimate. Furthermore, the $N\psi_F$ used in calculating C_1 was obtained by a simple point-ion lattice calculation. Theoretical considerations, and the results of the improved calculation in LiF suggest that such $N\psi_F$ tend to be too diffuse. Finally, the error in the calculated value, $1-\gamma_{\infty,1}=13.8$ is probably small and certainly not sufficient to affect the sign of $q_{0,1}(\text{pol.})$. Thus, we conclude that the ions in the first shell displace into the vacancy.

In calculating the entries in the second row of Table IX the calculated value of $1-\gamma_{\infty,2}=57.6$ was used. The negative sign of $q_{0,2}(\text{pol.})$ implies, if correct, an outward

TABLE IX. The experimental values of the lattice polarization field gradients in KCl.

Shell (α)	$(e^2Q/2h)q_{0,\alpha}$ in Mc/sec	$(q_{0,\alpha})(2/R_\alpha)^{-1}$ $\times (1-\gamma_\infty)^{-1}$	$[(b_{0,\alpha}/g_{N,\alpha}\beta\beta_N) - (2/R_\alpha)^3]$ $\times [(2/R_\alpha)^3(1-\gamma_\infty)]^{-1}$	$-(1-C_\alpha)(-\gamma_\infty)$ $\times (1-\gamma_\infty)^{-1}$	$q_{0,\alpha}(\text{pol.})$ $\times (2/R_\alpha)^{-1}$
1	0.40 ^a	0.37	0.45	-0.50	0.32
2	$\pm 0.013^b$	± 0.007	0.083	-0.120	$-0.030, -0.044^c$

^a Quoted in reference 3. Sign is determined in the following paper.

^b Quoted in reference 2. Sign is not determined.

^c Uncertainty is due to the undetermined sign of $q_{0,2}$. It will be shown below that $q_{0,2}$ is in fact positive. (See footnote 23.)

displacement of the ions. As already noted, the step function approximation of $1-C_2$ tends to underestimate this factor. Thus, the only way in which the sign of $q_{0,2}(\text{pol.})$ can be made positive is by decreasing the value of $1-\gamma_{\infty,2}$ by a factor of at least 1.3 or 1.6 depending on the sign of $q_{0,2}$. It is, of course, possible that an improved calculation will lead to a $N\psi_F$ which is concentrated enough to reduce $1-C_2$ sufficiently to assure a positive sign of $q_{0,2}(\text{pol.})$. However, the previously mentioned data on polar molecules²² seem to suggest that the calculated value of $1-\gamma_{\infty,2}$ is indeed too large.

The same approximation as used in deriving Eq. (38) for $q_{0,\alpha}$ can be applied to the other components of the effective field gradient tensor. Using the step function approximation for $1-\gamma(r)$, we obtain, on substituting Eq. (11) into Eq. (13),

$$q_{m,\alpha} = [q_{m,\alpha}(\text{pol.}) - b_{m,\alpha}''/g_{N,\alpha}\beta\beta_N](1-\gamma_{\infty,\alpha}) - b_{m,\alpha}'/g_{N,\alpha}\beta\beta_N; \quad m \neq 0. \quad (42)$$

Here $b_{m,\alpha}'$ is the contribution to $b_{m,\alpha}$ of that part of $\varphi_F(\mathbf{r}) - N\psi_F(r)$ which overlaps the α th ion. As noted in the discussion of the magnetic coupling constants, $b_{m,\alpha}'$ consists of sums of two-centered integrals, involving two core orbitals, one centered on the α th site and one on a different site. $b_{m,\alpha}''$ is the contribution to $b_{m,\alpha}$ of that part of $\varphi_F(\mathbf{r}) - N\psi_F(r)$ which does not overlap the α th ion. It consists of sums of two- and three-centered integrals, involving two core orbitals centered on sites β and γ where $\alpha \neq \beta, \gamma$. In view of the factor r_α^{-3} in the integrands it is reasonable to assume that $b_{m,\alpha}' \gg b_{m,\alpha}''(1-\gamma_{\infty,\alpha})$.

As noted previously, the constants $b_m, m \neq 0$, are probably negligibly small. Hence one might expect the major contribution to $q_{m,\alpha}, m \neq 0$, to be due to $q_{m,\alpha}(\text{pol.})$. Thus, we obtain the following approximate expression for $q_{m,\alpha}$,

$$q_{m,\alpha} = q_{m,\alpha}(\text{pol.})(1-\gamma_{\infty,\alpha}), \quad m \neq 0. \quad (43)$$

Equation (43) implies that if $m \neq 0$ then the signs of $q_{m,\alpha}$ and $q_{m,\alpha}(\text{pol.})$ are equal. But, Eq. (35) suggests that the signs of q_1 and $q_{2,2}(\text{pol.})$ are equal. Hence we may expect $q_{2,2}$ and the displacement of the ions in the first shell to have equal signs.

According to Feher, in KCl, $b_{2,2} \approx 0$ and

$$|(e^2Q/2h)(6)^{1/2}q_{2,2}| = 0.077 \text{ Mc/sec.}^2$$

This suggests that the approximate expression, Eq. (42), might be applicable in this case. We may thus infer

from the positive sign of $q_{0,1}(\text{pol.})$ that $q_{2,2} > 0$. Hence we may resolve the uncertainty in the sign of $q_{0,2}$.²³

V. CONCLUSIONS

It was shown that a wave function such as Eq. (1) leads to a consistent interpretation of the observed hyperfine interaction constants of the F electron with the lattice. Specifically, the conclusion that most of the F -electron charge density is spherically symmetric and concentrated within the vacancy is consistent with the observed magnetic dipole-dipole coupling tensor \mathbf{b} . However, for the first few shells the contribution of the F -electron charge density within the volume of the α th ion is of the same order as that of the (spherically symmetric) density concentrated in the vacancy. An asymptotic expression was derived for $b_{0,\alpha}$. This expression is independent of the F -electron density at the α th site and of the properties of the α th ion. It depends only on the distance of the α th site from the vacancy.

It was shown that the polarization of the lattice leads to an important contribution to the effective field gradient tensor, and probably accounts for any observable deviation of the electric quadrupole interaction from axial symmetry. Kojima's calculations suggest that the distortion of the ionic cores is a minor effect, and that the main contribution to the lattice polarization field gradient $\mathbf{q}(\text{pol.})$ is due to the displacement of the ions in the first few shells (into the vacancy). Hence, the experimental values of \mathbf{q} might be useful in investigating this displacement. Using the experimental data, it has been shown that in LiF and KCl the ions displace into the vacancy. This agrees with Kojima's calculation for LiF.

Additional "ENDOR" experiments are required to

²³ Feher quotes

$$\left| \frac{eQ}{2\hbar} \frac{\partial^2 V}{\partial x^2} \right| = 0.032 \text{ Mc/sec}, \quad \left| \frac{eQ}{2\hbar} \frac{\partial^2 V}{\partial y^2} \right| = 0.045 \text{ Mc/sec}.$$

Since he could not observe $|(eQ/2\hbar)\partial^2 V/\partial z^2|$, he assumes that

$$|eq_{0,2}| = \left| \frac{\partial^2 V}{\partial z^2} \right| = \left| \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} \right| = \left(\frac{eQ}{2\hbar} \right)^{-1} (0.013) \text{ Mc/sec},$$

and hence

$$|\sqrt{6}eq_{2,2}| = \left| \frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2} \right| = \left(\frac{e^2Q}{2\hbar} \right)^{-1} (0.077) \text{ Mc/sec}.$$

Thus $q_{2,2} > 0$ implies that

$$\partial^2 V/\partial y^2 < 0, \quad \partial^2 V/\partial x^2 > 0,$$

and hence,

$$\partial^2 V/\partial z^2 = -(eQ/2\hbar)^{-1} (0.013) \text{ Mc/sec} < 0.$$

complement the available data on the hyperfine interaction constants \mathbf{b} and \mathbf{q} . These data would be helpful in checking the asymptotic expression for $b_{0,\alpha}$ and the validity of our conclusion that for $m \neq 0$ $b_{m,\alpha}$ is negligible. From the electric quadrupole coupling tensor one could calculate $\mathbf{q}(\text{pol.})$. These results could in turn be used to estimate the ion displacements in the shells close to the vacancy. Specifically, one might proceed as follows: Assuming first that only the displacements of ions in the first shell contribute to $q_{0,100}(\text{pol.})$, this displacement can be deduced from the desired value of $\mathbf{q}(\text{pol.})$. Next, one could calculate the ion displacement in the first three shells, on the assumption that they are the only factors determining the observed $\mathbf{q}(\text{pol.})$ at sites in the first two shells. (This would require the solution of three equations involving the three unknowns.) Proceeding in this way one should be able to estimate the limits to which the calculated ion displacements tend.

Finally it has been shown that the calculated value of $1-\gamma_\infty$ for Cl^- is probably too large. This conclusion probably applies also to the other halogens.

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APPENDIX A

Classically the potential energy of interaction between the electronic magnetization density $\mathbf{u}_e |\varphi_F(\mathbf{r})|^2$ and the nuclear magnetic point dipole \mathbf{u}_N can be written as

$$\lim_{\epsilon \rightarrow 0} \left[- \int_{|\mathbf{r}-\mathbf{R}_\alpha| \geq \epsilon} \mathbf{u}_e \varphi_F^2(\mathbf{r}) \cdot \left(\nabla_\alpha \cdot \mathbf{u}_N \nabla_\alpha \frac{1}{r_\alpha} \right) d\tau - \mathbf{u}_N \cdot \nabla_\alpha \int_{|\mathbf{r}-\mathbf{R}_\alpha| \leq \epsilon} \mathbf{u}_e \varphi_F^2(\mathbf{r}) \cdot \nabla_\alpha \frac{1}{r_\alpha} d\tau \right]. \quad (\text{A1})$$

If $\varphi_F^2(\mathbf{r})$ is differentiable this reduces to¹⁴

$$- \sum_{i,j=1}^3 \mu_{ei} \mu_{Nj} \left[\lim_{\epsilon \rightarrow 0} \int_{|\mathbf{r}-\mathbf{R}_\alpha| \geq \epsilon} \varphi_F^2(\mathbf{r}) \frac{\partial^2}{\partial x_{\alpha,i} \partial x_{\alpha,j}} \frac{1}{r_\alpha} d\tau - \frac{4\pi}{3} \varphi_F^2(\mathbf{R}_\alpha) \delta_{ij} \right] \quad (\text{A2})$$

$$= 2g_N \beta \beta_N \left[\sum_{i,j=1}^3 S_i I_j \lim_{\epsilon \rightarrow 0} \int_{|\mathbf{r}-\mathbf{R}_\alpha| \geq \epsilon} \varphi_F^2(\mathbf{r}) \times \frac{3x_{\alpha,i} x_{\alpha,j} - \delta_{ij} r_\alpha^2}{r_\alpha^5} d\tau - \frac{4\pi}{3} \varphi_F^2(\mathbf{R}_\alpha) S \cdot I \right]. \quad (\text{A3})$$

It is a simple matter to verify the following:

(1) If $\varphi_F^2(\mathbf{r})$ is spherically symmetric about \mathbf{R}_α , the integral over $|\mathbf{r}-\mathbf{R}_\alpha| \geq \epsilon$ vanishes.

(2) If $\varphi_F^2(\mathbf{r})$ is not spherically symmetric about \mathbf{R}_α , it vanishes at \mathbf{R}_α .

Thus we may identify the second term in Eq. (A3) with the contribution of the component of $\varphi_F^2(\mathbf{r})$ which is spherically symmetric about \mathbf{R}_α . It is usually included in the contact interaction. Thus the ordinary magnetic dipole-dipole interaction in the hyperfine Hamiltonian may be interpreted either as associated with that part of the electronic wave function which does not overlap the nucleus, or alternatively as associated with the part of the wave function which is not spherically symmetric about the point nucleus. The argument in the case of the interaction between the gradient of the electric field due to the electronic charge density $e|\varphi_F(\mathbf{r})|^2$ and the nuclear electric (point) quadrupole moment Q follows the same lines and will be omitted.

APPENDIX B

We propose to prove that

$$C_{1,\alpha} = \int_{R_\alpha - R_i \leq r \leq R_\alpha + R_i} N^2 \psi_F^2(r) f\left(\frac{r}{R_i}\right) d\tau \leq \frac{1}{2} \int_{R_\alpha - R_i \leq r \leq R_\alpha} N^2 \psi_F^2(r) d\tau - \frac{1}{2} \int_{R_\alpha \leq r \leq R_\alpha + R_i} N^2 \psi_F^2(r) d\tau, \quad (\text{B1})$$

where

$$f\left(\frac{r}{R_i}\right) = \frac{1}{16} \left\{ \left(\frac{r}{R_i}\right)^4 - 2\left(\frac{r}{R_i}\right)^2 \left[\left(\frac{R_\alpha}{R_i}\right)^2 + 3 \right] + \left[\left(\frac{R_\alpha}{R_i}\right)^4 + 2\left(\frac{R_\alpha}{R_i}\right)^2 - 3 \right] \left(\frac{r}{R_i}\right)^{-1} \right. \\ \left. = \frac{1}{16} \left\{ \left(\frac{r}{R_i}\right)^2 - \left[\left(\frac{R_\alpha}{R_i}\right)^2 + 3 - 2\left(\left(\frac{R_\alpha}{R_i}\right)^2 + \frac{3}{2}\right)^{\frac{1}{2}} \right] \right\} \right. \\ \left. \times \left\{ \left(\frac{r}{R_i}\right)^2 - \left[\left(\frac{R_\alpha}{R_i}\right)^2 + 3 \right] + 2\left(\left(\frac{R_\alpha}{R_i}\right)^2 + \frac{3}{2}\right)^{\frac{1}{2}} \right\} \right\} \left(\frac{r}{R_i}\right)^{-1}. \quad (\text{B2})$$

Differentiating $f(r/R_i)$ with respect (r/R_i) , we obtain

$$f'\left(\frac{r}{R_i}\right) = \frac{1}{16} \left\{ \left(\frac{r}{R_i}\right)^2 - \left[\left(\frac{R_\alpha}{R_i}\right)^2 + 3 - 2\left(\frac{R_\alpha}{R_i}\right) \left(\left(\frac{R_\alpha}{R_i}\right)^2 + 3 \right)^{\frac{1}{2}} \right] \frac{1}{3} \right\} \\ \times \left\{ \left(\frac{r}{R_i}\right)^2 - \left[\left(\frac{R_\alpha}{R_i}\right)^2 + 3 + 2\left(\frac{R_\alpha}{R_i}\right) \left(\left(\frac{R_\alpha}{R_i}\right)^2 + 3 \right)^{\frac{1}{2}} \right] \frac{1}{3} \right\} \\ \times \left(\left(\frac{R_\alpha}{R_i}\right)^2 + 3 \right)^{\frac{1}{2}} \left[\frac{1}{3} \right] \left(\frac{r}{R_i}\right)^{-2}. \quad (\text{B3})$$

Hence

$$f'\left(\frac{r}{R_i}\right) < 0, \quad \text{for} \quad \left(\frac{R_\alpha - R_i}{R_i}\right)^2 \leq \left(\frac{r}{R_i}\right)^2 \\ \leq \left[\left(\frac{R_\alpha}{R_i}\right)^2 + 3 + 2\left(\frac{R_\alpha}{R_i}\right) \left(\left(\frac{R_\alpha}{R_i}\right)^2 + 3 \right)^{\frac{1}{2}} \right] \frac{1}{3} \quad (\text{B4})$$

and

$$f'\left(\frac{r}{R_i}\right) > 0, \quad \text{for} \quad \left[\left(\frac{R_\alpha}{R_i}\right)^2 + 3 + 2\left(\frac{R_\alpha}{R_i}\right) \left(\left(\frac{R_\alpha}{R_i}\right)^2 + 3 \right)^{\frac{1}{2}} \right] \frac{1}{3} \\ \leq \left(\frac{r}{R_i}\right)^2 \leq \left(\frac{R_\alpha + R_i}{R_i}\right)^2. \quad (\text{B5})$$

But

$$f(R_\alpha/R_i) = -\frac{1}{16} [4(R_\alpha/R_i)^2 + 3] (R_\alpha/R_i) < -\frac{1}{2} \\ \text{if } R_\alpha \geq R_i, \quad (\text{B6})$$

and

$$f(R_\alpha + R_i/R_i) = -\frac{1}{2}. \quad (\text{B7})$$

Hence, combining Eqs. (B4)–(B7), we have

$$f(r/R_i) \leq -\frac{1}{2} \quad \text{if} \quad R_\alpha \leq r \leq R_\alpha + R_i, \quad (\text{B8})$$

and consequently

$$\int_{R_\alpha \leq r \leq R_\alpha + R_i} N^2 \psi_{F^2}(r) f\left(\frac{r}{R_i}\right) d\tau \\ \leq -\frac{1}{2} \int_{R_\alpha \leq r \leq R_\alpha + R_i} N^2 \psi_{F^2}(r) d\tau. \quad (\text{B9})$$

Now,

$$f(R_\alpha - R_i/R_i) = \frac{1}{2}. \quad (\text{B10})$$

Hence combining Eqs. (B4) and (B10), we have

$$f(r/R_i) \leq \frac{1}{2} \quad \text{if} \quad R_\alpha - R_i \leq r \leq R_\alpha, \quad (\text{B11})$$

and consequently

$$\int_{R_\alpha - R_i \leq r \leq R_\alpha} N^2 \psi_{F^2}(r) f\left(\frac{r}{R_i}\right) d\tau \\ \leq \frac{1}{2} \int_{R_\alpha - R_i \leq r \leq R_\alpha} N^2 \psi_{F^2}(r) d\tau, \quad (\text{B12})$$

and combining Eqs. (B9) and (B12) we obtain (B1). This concludes our proof. Inserting Eq. (B1) into Eq. (25) it is evident that the terms in the first pair of square brackets is bounded by

$$\int_{r \leq R_\alpha} N^2 \psi_{F^2}(r) d\tau.$$