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Electron-Nuclear Double Resonance Studies of Color Centers*

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The electron-nuclear double resonance (ENDOR) method is applied to the study of the interaction of F-center electrons with the first two nuclear shells in NaCl, KBr, and NaH. From the angular dependence of single-crystal ENDOR spectra, values are obtained for the isotropic magnetic interaction constants and the principal values of the magnetic and electric-quadrupole interaction tensors in NaCl and KBr. ENDOR powder spectra are obtained and analyzed to obtain isotropic and anisotropic contributions to the magnetic interaction in NaH.

I. INTRODUCTION

THE width of the broad Gaussian electron-paramagnetic-resonance (EPR) absorption lines exhibited by F centers in alkali halides is known to be due to the hyperfine interaction of the trapped electron with the neighboring nuclei.[1] In most crystals no resolved structure is observed. However, by using isotopically enriched crystals it is possible to separate the first- and second-shell contributions to the linewidth and to deduce therefrom values of the isotropic hyperfine-interaction constants for both shells. When the first-shell contribution is predominant and the spin of the nearest neighbor nuclei is $\frac{3}{2}$, theory[1] predicts a resolved nineteen-line spectrum with a characteristic distribution of intensities. In at least two crystals, NaF[2] and NaH,[3] this occurs. In such cases an unambiguous assignment of the first-shell contact term may be made directly from the line spacing. The second-shell contribution may also be computed, though with much reduced accuracy, from the apparent resolution of the pattern. Both of the above methods suffer from an inherent lack of accuracy and neither yields information on the anisotropic magnetic or electric quadrupolar interactions. In fact the anisotropic magnetic interaction is partly responsible for the limitations of the methods. In spite of the crudeness of the assumed isotropic Hamiltonian and the limited data obtainable directly from the EPR spectra, the isotropic interaction constants are found to be remarkably accurate. The values obtained are very useful in initially interpreting the more detailed information available from electron-nuclear double resonance (ENDOR) studies.

The ENDOR method, introduced by Feher[4] and applied by him to F centers in KCl, increases the resolution of the hyperfine structure by several orders of magnitude. This method, to be discussed briefly below, permits the direct observation of both the isotropic and anisotropic magnetic interactions of the various neighboring equivalent sets of nuclei (shells) in complete detail. Often the electric quadrupolar couplings are revealed as well. The ENDOR method has been applied with conspicuous success to F centers in LiF.[5] In the present paper we report further application of the method to F centers in NaCl, KBr, and NaH.

II. THEORETICAL MODEL

Feher assumed an electron-nuclear interaction axially symmetric about the line from the center of the vacancy to the nucleus concerned.[4] This assumption, strictly correct for the first-shell nuclei which occupy axially symmetric sites, is found to apply with high accuracy even to the magnetic interactions of the second-shell nuclei occupying sites of lower symmetry. This is an accidental feature, however, and departures from perfect axial symmetry are visible even in Feher's original work.[4] Moreover the electric quadrupole interaction departed widely from the assumed symmetry in the second shell. An asymmetric Hamiltonian is thus required. In order to represent the angular dependence more accurately the assumption of axial symmetry will not be made here. This will involve only a very minor increase in complexity, while permitting a quantitative measure of the departure from axial symmetry.

The part of the Hamiltonian of interest in ENDOR experiments is that describing the interaction of the equivalent nuclei in a given shell with their surroundings. Ignoring direct and indirect interactions between nuclei this may be written, for a given set of equivalent nuclei, in the form

$$\mathcal{H}=\mathcal{H}_M+\mathcal{H}_Q, \tag{1}$$

where $\mathcal{H}_M$, the magnetic part, includes the interaction with the external field and the isotropic and anisotropic interaction with the center electron. $\mathcal{H}_Q$, the asymmetric electric quadrupolar interaction, is well known from studies of quadrupole effects in nuclear magnetic resonance in solids.[6] The corresponding first-order ENDOR frequencies due to this set of nuclei are

$$h\nu_{\text{ENDOR}}=\pm g\mu_0 H+h\nu_M+h\nu_Q, \tag{2}$$

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* This research supported by a grant from the National Science Foundation.

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

[2] N. Lord, Phys. Rev. **105**, 756 (1957).

[3] W. T. Doyle and W. L. Williams, Phys. Rev. Letters **6**, 537 (1961).

[4] G. Feher, Phys. Rev. **105**, 1122 (1957).

[5] W. C. Holton, H. Blum, and C. P. Slichter, Phys. Rev. Letters **5**, 197 (1960).

[6] M. H. Cohen and F. Reif, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 321.

with similar expressions holding for each set of equivalent nuclei. The expressions for the frequencies are simplest when referred to principal axes at the nuclear site. Following Feher[4] we choose a right-handed system with the x_3 axis in the direction of the line from the nuclear site to the center of the vacancy. The x_1 axis is chosen to lie in a [100] direction. From the symmetry of the sites it is clear that these are principal axes for the nuclei in the first-two shells. When the principal axes are not apparent from symmetry, they may be determined by appropriate procedures.[7] We shall, however, be interested only in the first-two shells here.

The quadrupole contribution to the ENDOR frequency, referred to the principal axes, is given by[8]

$$h\nu_Q=\frac{3eQV_{33}}{I(2I-1)4}(3\cos^2\theta-1+\eta_Q\sin^2\theta\cos2\varphi)(m-\tfrac{1}{2}), \quad (3)$$

where e is the electronic charge, Q is the quadrupole moment of the nucleus, V_{33} is the x_3 component of the electric field gradient at the nucleus, h is Planck's constant, I is the nuclear spin, m is the larger of the two nuclear magnetic quantum numbers in the allowed $\Delta m=\pm1$ transition, and $\eta_Q=(V_{11}-V_{22})/V_{33}$ is the asymmetry parameter. The subscripts indicate partial derivatives. No limits may be placed upon η_Q since it is not known which of the axes is the major axis of the field gradient tensor. The angles θ and φ are the polar angles of the steady magnetic-field direction relative to the principal axes.

The magnetic interaction in F centers with an asymmetric Hamiltonian has been discussed by Deigen and Zevin.[9] Similar results can be obtained in more symmetric form as follows. The magnetic interaction may be written[8]

$$\mathcal{H}_M=a\mathbf{I}\cdot\mathbf{S}+\mathbf{I}\cdot B\cdot\mathbf{S}, \quad (4)$$

where a is the well-known isotropic Fermi contact interaction,

$$a=\frac{\mu_0\mu_I}{SI}\frac{8\pi}{3}|\psi(0)|^2, \quad (5)$$

and B is a traceless tensor representing the anisotropic part of the magnetic interaction. The elements of B are given by

$$B_{ij}=A_{ij}+\tfrac{1}{3}a\delta_{ij}, \quad (6)$$

with

$$A_{ij}=\frac{\mu_0\mu_I}{SI}\int\frac{x_j}{r^3}\frac{\partial^2|\psi|^2}{\partial x_i}dV, \quad (7)$$

where μ_0 and μ_I are the Bohr magneton and nuclear magneton, respectively, S and I are the electronic and nuclear spins, x_i is the ith rectangular coordinate, and r is the radius vector from the nuclear site. Clearly, $B_{ij}=0$ for $i\neq j$ for the first two nuclear shells, since for these sites B is referred to principal axes. The ENDOR frequencies corresponding to $\mathcal{H}_M$ are easily shown to be

$$h\nu_M=\tfrac{1}{2}a+\tfrac{1}{2}b(3\cos^2\theta-1+\eta_M\sin^2\theta\cos2\varphi), \quad (8)$$

where $b=B_{33}/2$ and $\eta_M=(B_{11}-B_{22})/B_{33}$. The angles are the same as those appearing in Eq. (3). The similar angle dependence of the two terms $h\nu_Q$ and $h\nu_M$ is evident. In the presence of axial symmetry $\eta_Q=\eta_M=0$ and the expressions for the ENDOR frequencies reduce to those given by Feher.[10]

The experimental results will be used to obtain values of the isotropic coupling constant a/h and the tensor components $B_{ii}/2h$ and $eQV_{ii}/2h$. They will be given directly in Mc/sec.

III. EXPERIMENTAL METHODS

The ENDOR method consists in saturating an EPR transition of an inhomogeneously broadened line and simultaneously irradiating with a frequency capable of causing transitions between the hyperfine sublevels. The EPR resonance is monitored and an indication is observed when ENDOR transitions occur due to temporary partial desaturation of the EPR signal. One usually employs an EPR bridge spectrometer tuned to the dispersion mode.[11] The signal klystron is locked to an external cavity. Narrow banding is achieved by field modulation. The magnetic field is tuned to the center of the dispersion line and the steady EPR signal is bucked out at the output.

When a steady-state ENDOR signal may be observed, as with F centers, amplitude modulation of the ENDOR power may be used in place of field modulation to obtain a narrow bandwidth.[12] With the AM ENDOR method one tunes the bridge to the absorption mode and locks the signal klystron to the sample cavity itself, with a considerable gain in stability and signal-to-noise ratio. The AM ENDOR method was used in all the experiments to be reported here.

A maximum sensitivity X-band superheterodyne magic-tee-bridge spectrometer of conventional design[13] was used. The intermediate frequency was 30 Mc/sec. Both signal and local oscillators were equipped with afc. The signal klystron was locked to the sample cavity using the FM cavity-discriminator method. The local oscillator was stabilized with a 30-Mc/sec discriminator. Five-hundred-cycle/sec narrow-band amplification was used for all the ENDOR runs. Phase-sensitive detection was used since it was at hand. The ENDOR frequencies were generated by commercial signal generators (General Radio 1001-A, Hewlett-

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[7] G. M. Volkoff, Can. J. Phys. **31**, 820 (1953).

[8] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961),

[9] M. F. Deigen and V. Ia. Zevin, Soviet Phys.-JETP **7**, 790 (1958).

[10] Equation (8) is consistent with the results of Deigen and Zevin (reference 9). Note that they define the parameter b differently. Here $b=B_{33}/2=(2A_{33}-A_{11}-A_{22})/6$.

[11] G. Feher, Phys. Rev. **114**, 1219 (1959).

[12] W. T. Doyle, Rev. Sci. Instr. **33**, 118 (1962).

[13] G. Feher, Bell System Tech. J. **36**, 449 (1957).

Packard 650-A). They were 100% amplitude modulated with an external 500-cps sine-wave audio oscillator. The rf was amplified by two cascaded Instruments for Industry model 500 wide-band amplifiers driving a three-turn rectangular coil in the mid-plane of the TE_{102} reflection cavity (unloaded $Q \approx 3000$ at room temperature). Rf currents of several hundred ma could be obtained over the frequency range employed. The microwave frequency used was 9050 kMc/sec corresponding to resonant fields of about 3200 gauss. The spectrometer was equipped with stainless-steel waveguide and coaxial ENDOR feed to permit low-temperature operation. Measurements were made at both 77° and 1.25°K.

The alkali halide samples used were all Harshaw single crystals. The sodium hydride was commercial powder from the same stock used for earlier measurements on the resolved F-center EPR spectrum.[3] To prevent reaction with atmospheric moisture the hydride samples were handled in a dry box and irradiated in an hermetically sealed aluminum container. After irradiation all samples were handled in subdued light to avoid development of complex centers.

The F centers were produced by x irradiation using a Norelco high-intensity source operated at 50 kv and 40 ma. The crystals were exposed for times varying from minutes to over 24 hr, at a distance of a few centimeters from the target. Aside from intensity variations no dependence of the ENDOR spectrum upon total dose was noted.

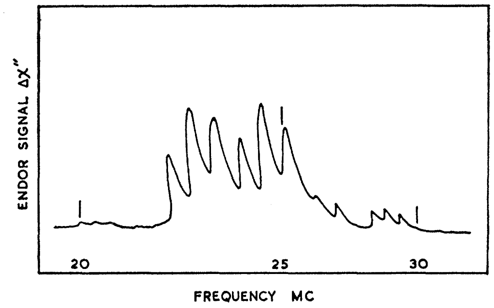

FIG. 1. Typical amplitude-modulated ENDOR spectrum of F centers in KBr. This part of the spectrum is due to the second-shell bromine nuclei. The angle between the steady magnetic field and a [100] direction in the crystal, θ_H, is 35°. This curve was taken at a temperature of 1.25°K. In this and in the following experimental traces the distortion is due to the use of a curvilinear chart recorder.

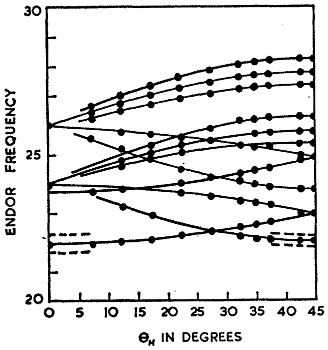

FIG. 2. Angular dependence of the second-shell spectrum of F centers in KBr. Because of the overlapping, the contribution of both isotopes of bromine are shown. The broken lines, showing the quardupole splitting of the C and D nuclei (Feher's notation, reference 4), were estimated from the width of the poorly resolved triplets due to these nuclei at θ_H equal to 45° and 0°, respectively. θ_H is the angle between the steady magnetic field and the [100] axis of the crystal.

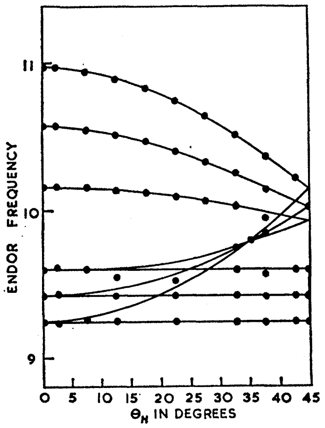

FIG. 3. Angular dependence of the first-shell ENDOR spectrum of F centers in KBr. Axial symmetry is apparent in the vanishing of the quadrupolar splitting of the b nuclei at 35°.

IV. EXPERIMENTAL RESULTS

ENDOR spectra of F centers have been observed in single crystals of KCl, NaCl, and KBr, and in powdered samples of KCl and NaH. The first- and second-shell spectra have been analyzed to determine the coupling constants defined above. In virtually all of the single-crystal work additional splittings beyond those predicted by the simple first-order theory was observed. In some cases, e.g., in the NaCl first-shell spectrum, the additional splitting was large enough to obscure the expected first-order quadrupole effects. These finer details of the spectra have not yet been analyzed. They are, however, very well defined experimentally and their analysis should throw further light upon the structure of the F center.

Single-Crystal Spectra

A typical single-crystal spectrum is shown in Fig. 1 where the ENDOR spectrum due to the second-shell nuclei in KBr is displayed. As expected from EPR measurements[1] the second-shell interaction predominates in this crystal. The pattern of ENDOR lines is complicated by overlapping of the spectra of the two isotopes of bromine. The complexity is evident in Fig. 2 showing the angular dependence of the spectrum. Figure 3 shows the first-shell angular dependence for KBr. Similar results were obtained for NaCl and they are shown in Figs. 4 and 5. The experimental results are summarized in Table I where the isotropic interaction constants and the principal values of the tensors representing the anisotropic magnetic interaction and the electric quadrupole interaction are tabulated. Our

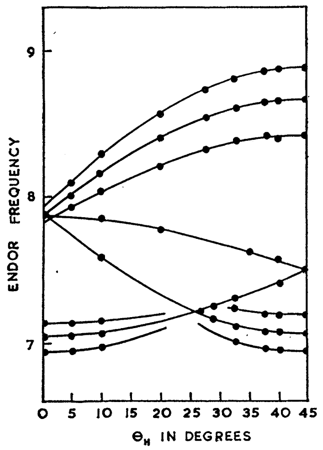

FIG. 4. Angular dependence of the second-shell Cl^{35} contribution to the ENDOR spectrum of F centers in NaCl. Both the magnetic and quadrupolar interactions are very nearly axially symmetric about the x_3 axis.

single-crystal studies of KCl corroborate those of Feher and are not presented here.

The first-shell interactions were all found to be axially symmetric within the experimental error of about 0.05 Mc/sec. As was found with KCl, the second-shell interactions are very nearly axially symmetric $(B_{11}\approx B_{22})$. The constant $B_{33}/2=b$ is the same as that appearing in Feher's Hamiltonian. The isotropic magnetic interaction constants are in good agreement with the EPR linewidth measurements.[1] Preliminary ENDOR results reported by Lord[14] are shown for comparison. Agreement is satisfactory except for $a(1)$. This may indicate an erroneous choice of sign for the $g\mu_0 H$ term of Eq. (2) in the earlier work. The theory predicts two identical sets of ENDOR lines separated by twice the nuclear magnetic resonance frequency. Both sets must be observed if the isotropic interaction constant is to be unambiguously determined. Both sets of transitions have been observed in all of the spectra reported here. Theoretical values of the coupling constants[15] are also shown where available. In view of the difficulties encountered in such theoretical calculations the agreement is considered encouraging.

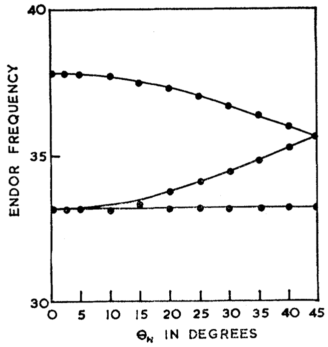

FIG. 5. Angular dependence of the first-shell ENDOR spectrum due to F centers in NaCl. Only the grosser features of the high-frequency transitions are shown. The expected quadrupole splitting was obscured by subsidiary splittings which have not yet been analyzed.

Most of the spectra showed resolved quadrupole splitting. In the first-shell spectrum of NaCl the splitting was more complex than the triplet expected for spin $\frac{3}{2}$ nuclei, and no analysis has been carried through for this splitting. The second-shell spectrum in KBr exhibited a normal triplet. The values quoted were obtained from the well-resolved splitting of the Br^{81} nuclei in position A (Feher's notation[4]) and from the ratio of the widths of the poorly-resolved triplets due to the nuclei in positions C and D. Because of the overlapping of the two bromine spectra this ratio was determined for the Br^{79} nuclei, with the assumption that it would be the same for Br^{81}. The second-shell quadrupole constants differ markedly from crystal to crystal. In KCl the quadrupole interaction was asymmetric with the major axis in the x_2 direction. In NaCl it is nearly axially asymmetric along the x_3 axis. KBr, like KCl, has a decidedly asymmetric interaction, but with the major axis along x_3. The quadrupole interaction is thus much more sensitive to the detailed crystalline environment than is the magnetic interaction. The sensitivity of the quadrupole interaction to strains and localized charges raise the hope that it may be possible to turn this complex and delicate interaction to the study of the ill-understood coagulation process of the electron excess centers.

Powder Spectra

Although single-crystal studies are certainly to be preferred, much useful information may be obtained by ENDOR experiments on powdered samples. This is fortunate since many interesting materials, in particular some of the alkali hydrides, will be difficult, or even impossible, to obtain in the form of single crystals. From Eqs. (3) and (8) it can be seen that both the anisotropic magnetic interaction and the electric quadrupole interaction will tend to smear out the ENDOR lines in powdered samples. To simplify the interpretation of the ENDOR powder patterns the small quadrupole term will be neglected. Moreover the magnetic interaction will be assumed to have axial symmetry about x_3. Both assumptions are quite justified for the relatively crude powder measurements. In a sample consisting of a large number of randomly oriented grains every nucleus in a shell may be considered as equivalent. The remaining angle-dependent term in Eq. (8) must simply be averaged over all angles, θ, weighting each θ appropriately. This same type of averaging occurs in crystalline powder spectra in nuclear magnetic resonance (NMR) in metal powders due to the anisotropy of the

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[14] N. W. Lord, Program of the International Symposium on Color Centers in Alkali Halides, Oregon State College, Corvallis, Oregon, 1959 (unpublished), p. 37.

[15] B. S. Gourary and F. J. Adrian, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 127.

TABLE I. Experimental values of the magnetic- and electronic-quadrupole-coupling constants in Mc/sec for F centers in NaCl, KBr, and NaH. Here a is the isotropic contact term and $B_{ii}/2h$ and $eQV_{ii}/2h$ are the principal values of the magnetic and electric quadrupolar tensors. Note that $B_{33}/2h=b/h$. The experimental uncertainty is in the last digit quoted. The values in parentheses, shown for comparison, are based upon other experimental results[a,b] and upon theory.[c]

	a/h	$B_{11}/2h$	$B_{22}/2h$	$B_{33}/2h$	$eQV_{11}/2h$	$eQV_{22}/2h$	$eQV_{33}/2h$
NaCl							
Na^{23}[100]	60.9_4 $(71)^a$ $(110)^c$	axial		3.0_7 $(3.3)^a$ $(2.5)^c$	axial		···
Cl^{35}[110]	12.4_8 $(13)^a$	0.5_6	0.5_2	1.0_7 $(1.3)^a$	0.1_1	0.1_3	0.2_4
KBr							
K^{39}[100]	18.1_0	axial		0.7_8	axial		0.1_9
Br^{81}[110]	42.7_3	1.4_1	1.3_1	2.7_1	0.3_0	0.1_5	0.4_5
NaH							
Na^{23}[100]	71.5 $(74.3)^b$	axial		2.6	axial		···
H^1[110]	8.0 $(17.1)^b$	···	···	0.2		vanishes	

[a] See reference 2.
[b] See reference 3.
[c] See reference 15.

Knight shift.[16] The line shape, $g(\nu)$, as a function of frequency measured from its average value is

$$g(\nu)\propto(1+2\nu/b)^{-\frac{1}{2}} \tag{9}$$

within the range of resonant ENDOR frequencies covered as θ ranges from zero to $\pi/2$. Outside of this range $g(\nu)$ is zero. The expected line shape is shown by the broken line in Fig. 6. It is superimposed on the observed first-shell-powder spectrum for F centers in NaH. Of course the experimental curve does not become infinite as Eq. (9) predicts, because other sources of broadening are present.

Evidently two identical ENDOR powder patterns are expected here, corresponding to the two signs in Eq. (2). The separation between the two peaks should be twice the NMR frequency for sodium, as is observed. The curve shown was taken with a lightly colored sample at 77°K. The mean position of the two peaks occurs at $a(1)/2-b(1)/2$ and the width is $3b(1)/2$. Thus, from a powder spectrum one obtains a value for both the isotropic and anisotropic interactions. Experiments with powdered KCl were carried out to check the method and gave results consistent with the single crystal ENDOR spectra. The first-shell powder pattern results on NaH are tabulated in Table I. The contact term $a(1)$ is compared with the value recently obtained[3] from the well resolved EPR spectrum in this substance and the agreement is good. There are no corresponding values of $b(1)$ with which to make comparison.

The second-shell NaH powder spectrum is shown in Fig. 7. Here the interaction of the nuclei (protons) with the external field is stronger than their interaction with the center electron. This was expected in view of the exceptional resolution of the EPR spectrum. When the $g\mu_0H$ term is larger than the contact term, a two-line spectrum is observed, centered on the NMR frequency. The separation between the two peaks is equal to the contact term $a(2)$. In this case the two powder

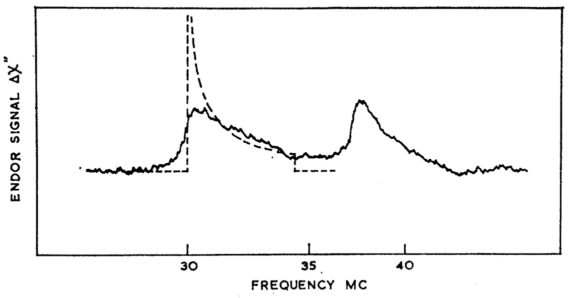

FIG. 6. First-shell ENDOR powder pattern due to F centers in NaH. The curve was obtained with a lightly colored sample at 77°K. The broken line shows the theoretical line shape. Both the high and low frequencies are shown, separated by twice the Na^{23} nuclear-resonance frequency.

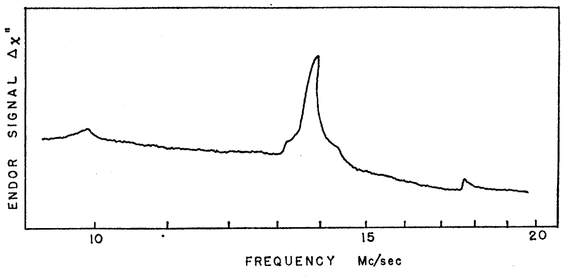

FIG. 7. Second-shell ENDOR powder pattern due to F centers in NaH. Here the contact interaction is smaller than the interaction of the protons with the external field. The ENDOR lines bracket the proton resonant frequency and "face inwards". The strong central line is due to weakly coupled protons. The shoulders are attributed to a shell with intermediate coupling, possibly shell 4.

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[16] Reference 8, p. 206.

patterns should "face inwards" as observed. The measured separation between the two ENDOR peaks is much smaller than expected using the value of $a(2)$ computed from the apparent resolution of the EPR spectrum. The discrepancy arises because in the analysis of the resolved EPR spectrum the unknown-anisotropic first-shell interaction $b(1)$ had to be neglected and all of the apparent peak widths attributed to the isotropic-second-shell interaction $a(2)$. This led to an overestimate of $a(2)$ in the earlier work. The difference between the two estimates of $a(2)$ is consistent with the value of $b(1)$ deduced from the first shell ENDOR powder spectrum. It seems quite likely that Lord's value for $a(2)$ in[2] NaF may also be found to be too high for the same reason. The width of the second shell ENDOR peaks provides an estimate of the constant $b(2)$ as tabulated. Note that here the neglect of the quadrupolar interaction is rigorously correct since the quadrupole moment of the proton is zero.

An interesting feature of the ENDOR spectrum in this region is the occurrence of a very strong peak at the proton resonant frequency itself. It cannot be due to the usual distant ENDOR effect[17] since no relaxation effects in this peak were noted even at 1.25°K. Moreover, it gives a strong signal with AM ENDOR using a modulation frequency of 500 cps, and distant ENDOR effects are characterized by relatively long nuclear-relaxation times. It seems appropriate to attribute this peak to a group of protons lying within some radius of the center within which the relaxation time is still quite short, but for which the interactions are not strong enough to shift the frequency very much. The well-defined shoulders on this peak could then be attributed to the next-nearest proton shell after the second. From the separation between the two shoulders one gets an isotropic coupling constant a 1.11 Mc/sec. Although their position makes it clear that these partially resolved peaks are due to protons, the assignment to the fourth shell remains dubious. The contact terms do not always decrease monotonically with shell number.[5] In any event, it is clear that the more central portions of the central proton peak are due to still less tightly coupled protons and the strength of the central peak is remarkable. The more so since a comparable peak does not occur at the Na^{23} resonant frequency. The strength of the proton interaction suggests that *F* centers in alkali hydrides could be used very efficiently to produce polarized protons in the bulk material.

Similar pairs of ENDOR lines are observed bracketing Na^{23} NMR resonant frequency, but without, as has been said, the central lines. From the spacings one computes contact terms of 1.88, 0.91, and 0.25 Mc/sec. A monotonic decrease of coupling with shell number would assign these peaks to the next-three cation shells, respectively. One might feel confident in assigning the 1.88-Mc/sec line to the third shell, but not more. The absence of the central peak, in view of its occurrence for the protons, remains baffling.

V. CONCLUSION

The results of ENDOR experiments on *F* centers in a number of crystals have been presented and compared with independent measurements where possible. Single-crystal measurements indicate that the magnetic interaction of the second-shell nuclei is very nearly axially symmetric, and this is probably quite generally true. For the electric quadrupole interaction, however, both the degree of asymmetry and the major axis of the interaction varies from crystal to crystal. The sensitivity of the quadrupole interaction makes it a sensitive probe for further studies of the structure of the *F* centers themselves and, possibly, for coagulations studies as well. It has been shown that much useful information may be obtained from ENDOR powder studies, even when considerable anisotropic broadening occurs, the broadening itself providing some of the information. Earlier estimates of the second shell contact interaction have been shown to be substantially in error due to the neglect of the first-shell anisotropic interaction. In NaH containing *F* centers a strong AM ENDOR signal was observed at the proton resonant frequency, but not at the Na^{23} resonant frequency. Efficient polarization of the protons is expected in the inverse experiment.

Note added in proof. The single crystal results obtained here are in good agreement with the recently published work of W. C. Holton and H. Blum, Phys. Rev. **125**, 89 (1962); and H. Seidel, Z. Physik **165**, 218 (1961).

ACKNOWLEDGMENTS

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[17] J. Lambe, N. Laurance, E. C. McIrvine, and R. W. Terhune, Phys. Rev. **122**, 1161 (1961).