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New Hole Center, FCl^-, in Mixed KCl-KF Crystals*

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By x-ray irradiation of a mixed KCl-KF crystal at liquid-nitrogen temperature, a molecule ion species identified as FCl^- can be formed oriented along a ⟨111⟩ axes of the crystal. The electron structure of this electron-deficient center has been investigated by electron spin resonance. The parameters of the appropriate spin Hamiltonian have been determined and are compared with those for F_2^- and Cl_2^-. A tentative assignment of signs for the isotropic parameter a is suggested.

I. INTRODUCTION

THE V_k or X_2^- center has been studied in considerable detail in both its optical and spin resonance spectra.[1,2] The essential feature of the X_2^- center is that it is a self-trapped hole associated with the formation of the molecular ion X_2^- which is oriented along a ⟨110⟩ direction. Furthermore, the spectrum of the center is determined almost entirely by the interaction of the hole with the two nuclei of the molecular ion and is only affected very slightly by other nuclei in the crystal lattice. Mixed halogen molecules such as FCl, BrCl, and ICl are well-known species. Since the series F_2, Cl_2, Br_2, and I_2 form stable X_2^- ions in alkali halide crystals,[1,2] it seemed reasonable that XY^- ions might also be produced in mixed alkali halide crystals.

In this paper we shall discuss only the properties of FCl^- in any detail. This is because FCl^- has several interesting or convenient features:

1. Its spectrum is fairly simple since F has only one stable isotope and a spin of $\frac{1}{2}$.
2. FCl^- is oriented along a ⟨111⟩ direction (see Sec. III.2).
3. Quadrupole effects should be small since F has no quadrupole moment and Cl has a relatively small one.

At least two other XY^- centers have been observed. These will be discussed briefly in Secs. IV and VI.

II. EXPERIMENTAL PROCEDURES

All crystals used in these experiments were grown in air by the Kyropoulus method. To the melt of KCl, amounts of KF and $PbCl_2$ were added so that if they completely dissolved, the single crystal formed would contain about 0.5 mole% of F^- and 0.1 mole% of Pb^{++}. Analysis of the prepared crystals indicated that there was less than 0.1 mole% of F^- present. The crystals used for the spin-resonance measurement were about 2.5 mm×2.5 mm in cross section and about 5 mm in length. Color centers were produced by x-ray irradiation from a Machlett tube with tungsten target operating at 50 kV and 50 mA and filtered through 1 mm of quartz backed with aluminum foil. All irradiations were performed at liquid-nitrogen temperature for about a half-hour on crystals that were first annealed for a few minutes at about 200°C.

The resonance measurements were performed with a Varian electron paramagnetic resonance spectrometer model V4500, with 100 kc/sec field modulation, and a 6-in. electromagnet V-4007-1. Through the use of a variable temperature device V-4547 (gas cryostat) and a Dewar vessel, measurements could be made from liquid nitrogen up to room temperature.

The magnetic field was measured by using a Harvey-Wells nuclear magnetic resonance Gaussmeter 6501 in conjunction with a Signal Corps Frequency Meter BC221AE. The frequency generated by the latter instrument was beat against the rf probe of the Gaussmeter. The microwave frequency was measured with a Hewlett Packard Cavity Wavemeter (X532B). Measurements of the klystron frequency and the magnetic field at the resonance of DPPH, which has a known g value, permitted calibration of the wavemeter. The crystal was mounted on the end of a Lucite rod, the axis of which could be tipped with respect to the magnetic field. The crystal could be further oriented by rotation about this axis as indicated by a pointer at the top of the rod.

Bleaching of samples was done while the crystal was mounted on a Lucite holder and was immersed in a Dewar flask. The bleaching light from an AH-6 mercury lamp passing through a Corning-3389 filter, entered the Dewar flask through quartz windows, and passed lengthwise through the crystal. Generally, a crystal was bleached about 16 min; 8 min on each end. The purpose of the bleaching was to remove the Cl_2^- centers also formed in the x-ray irradiation.

III. ELECTRON SPIN RESONANCE SPECTRA AND INTERPRETATION

A. Isotope Effect

Figure 1(A) shows the electron spin resonance spectrum of the FCl^- center in KCl with 0.5 mole% F^- and 0.1 mole% Pb^{++} added, taken with the dc magnetic field along the ⟨100⟩ axis. The most striking feature of the spectrum is the double set of four relatively equally

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[1] T. C. Castner and W. Känzig, J. Phys. Chem. Solids 3, 178 (1957); T. O. Woodruff and W. Känzig, *ibid.* 5, 268 (1958).

[2] C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **111**, 1235 (1958); C. J. Delbecq, W. Hayes, and P. H. Yuster, *ibid.* **121**, 1043 (1961).

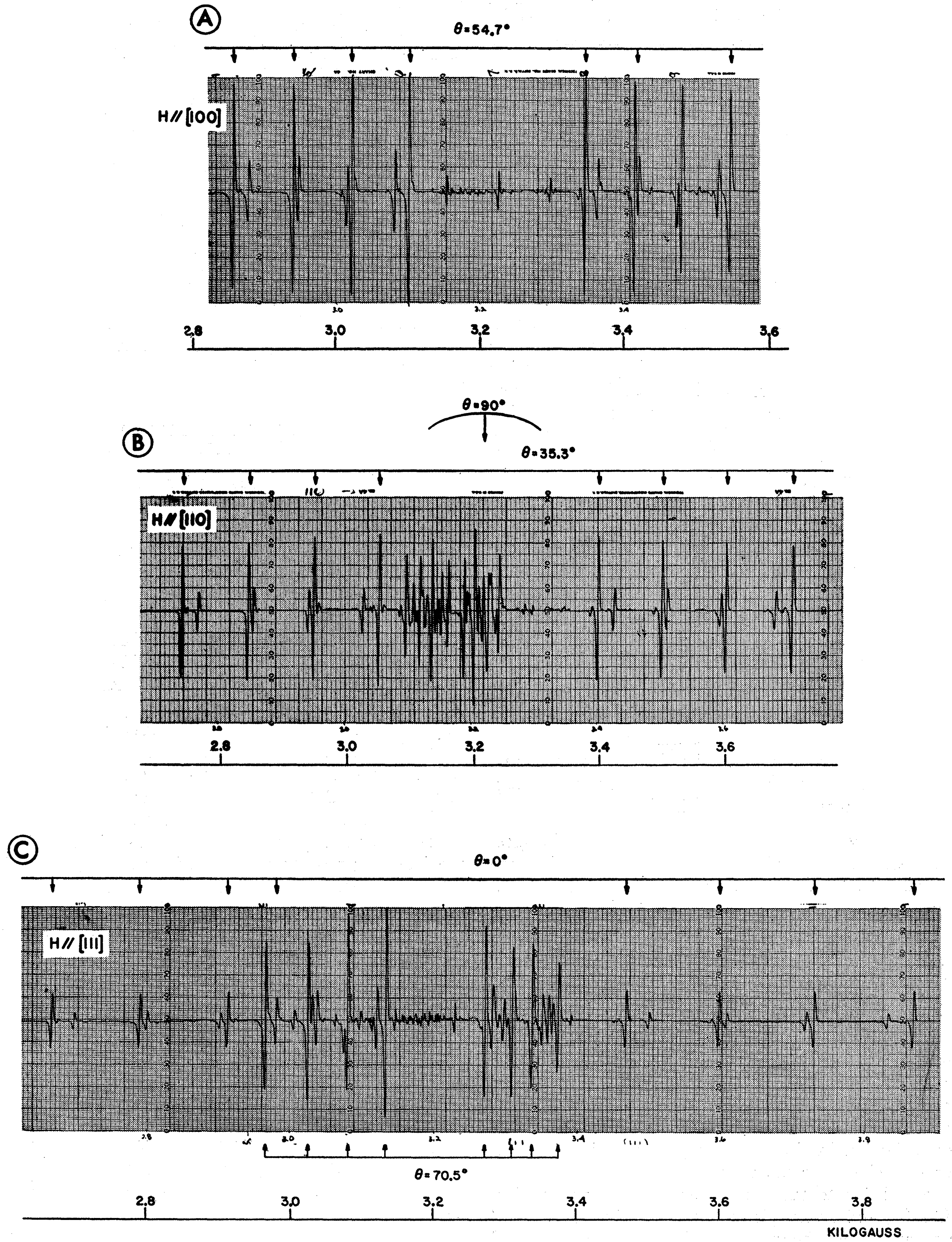

FIG. 1. (A), (B), and (C). Electron spin resonance absorption spectra of the FCl⁻ center observed at about 9.3 kMc/sec with the dc magnetic field along the [100], [110], and [111] axes, respectively. The arrows mark the $(\mathrm{Cl}^{35}-\mathrm{F}^{19})^-$ spectra. In all cases the microwave magnetic field is perpendicular to the dc magnetic field. The first derivative of the absorption is recorded.

TABLE I. Classification of molecular ions along ⟨111⟩ direction for simple orientations of the crystal in the dc magnetic field.

Direction of dc field	Angle θ	Abundance
[100]	54.7°	4
[110]	35.3°	2
[110]	90°	2
[111]	0°	1
[111]	70.5°	3

spaced lines. This can be explained by assuming that the hole interacts more or less equally with the F^- and Cl^- ions. The only isotope of fluorine F^{19} has a spin of $\frac{1}{2}$; while both isotopes of chlorine, Cl^{35} and Cl^{37}, have spins of $\frac{3}{2}$. Each set of four lines is the hyperfine splitting due to the chlorine nucleus. The separation of the two sets is the hyperfine splitting due to the fluorine nucleus. The hyperfine splitting of F is several times larger than that of Cl which is in agreement with Castner's and Känzig's observations on the spectra of Cl_2^- and F_2^-.[1]

That this center is a self-trapped hole associated with the molecular-ion FCl^- is further evidenced by the double set of four less intense lines which are displaced toward the center from the principal lines discussed above. The most obvious interpretation is that the principal lines are associated with the center $(F^{19}\text{–}Cl^{35})^-$ and the secondary lines with $(F^{19}\text{–}Cl^{37})^-$. This interpretation is supported by two observations:

1. The relative intensities of the two sets of lines are consistent with isotopic abundances.
2. The relative separations for the two adjacent sets of four lines are consistent with the relative magnetic moments of the chlorine isotopes.

[The fairly weak lines in the middle region of the spectrum are remnants of Cl_2^- which were left after the optical bleaching. They are present in the spectra in Figs. 1(B) and 1(C), as well as in 1(A).]

B. Orientation of Center

On the basis of the results for X_2^- centers and since it seemed reasonable that F^- would be present substitutionally in KCl, it was thought that the FCl^- molecular ion would be oriented along a ⟨110⟩ axis of the crystal. However, FCl^- is oriented along a ⟨111⟩ axis of the crystal. This can be seen by comparing Fig. 1(A), 1(B), 1(C) with Table I, which gives the angles θ which a molecular ion in the direction ⟨111⟩ would make with three specific orientations of the crystal.

In addition to the general agreement between Figs. 1(A)–(C) and Table I, it should be noted that the $\theta=0°$ spectrum shows the greatest splitting, while the $\theta=90°$ shows the least. This is in agreement with previous investigations on X_2^- centers[1,2] and with an analysis to be given in Sec. V. Furthermore, looking on the oscilloscope at one of the lines associated with $\theta=70.5°$, we could see the line break into three lines as the orientation was changed slightly. Similar effects were also observed on lines associated with the other θ values in Table I.

In Table II the experimental line positions (in G) for the $(F^{19}\text{–}C^{35})^-$ center are listed for several values of θ. We estimate that the errors in measuring the relative field strengths are within a few tenths of a gauss. The error in measuring a line may be greater than this because of the difficulty in determining the center of the line. This is particularly true of the $\theta=90°$ spectrum which is quite sensitive to orientation. An additional source of error is in measuring the absolute field strengths which is primarily reflected in the g values. This error may be expressed in terms of the kystron frequency, which we estimate may be in error by about ±1 Mc/sec.

IV. MODEL FOR FCl⁻ CENTER AND FORMATION MECHANISMS

As noted in the previous section, the FCl^- center is oriented along a ⟨111⟩ direction. This implies that the fluorine component of the center is located interstitially in the KCl lattice along a ⟨111⟩ direction. Using the values for the radii of K^+ and Cl^-, 1.331 and 1.806 Å, respectively, and the lattice parameter of KCl, 3.139 Å,[3] one can show that a spheroid with center at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ in the KCl lattice could fit in the available space with a semimajor axis of 1.325 Å in the (100) plane and a semiminor axis of 1.50 Å in the (110) plane. The radii of F and F^- are 0.68 and 1.341 Å, respectively. Consequently, the lattice could accommodate a FCl^- center with relatively little distortion. From the present work it is impossible to tell exactly where along the ⟨111⟩ direction the FCl^- molecular ion is oriented with respect to the position of the original undisturbed Cl^- ion.

From this model for the center one might suppose the following mechanism for its formation: The F^- is dissolved interstitially in the KCl; upon x-ray irradiation the F^- is ionized and FCl^- is formed, the F atom relaxing toward one of the adjacent Cl^- ions with

TABLE II. Experimental line positions (in G) for the $(F^{19}\text{–}Cl^{35})^-$ center at various orientations. Klystron frequency =9.128 kMc/sec.

θ	0°	35.3°	70.5°	90°
R_1	2664.5	2744.2	2969.5	3107.5
R_2	2790.3	2852.8	3030.2	3130.6
R_3	2916.2	2960.3	3085.5	3149.4
R_4	3042.7	3065.9	3139.4	3175.4
R_5	3470.5	3411.8	3277.0	3201.4
R_6	3596.3	3510.2	3315.2	3217.5
R_7	3722.5	3606.9	3342.7	3239.3
R_8	3848.9	3702.5	3378.4	3256.4

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[3] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945), Chap. 10, Table 44-2, p. 350.

which it shares a hole. This mechanism does not appear to be the dominant one. Another possible mechanism arises from the fact that KF dissolves substitutionally in KCl. The fluorine atoms formed upon x-ray irradiation are small (0.68 Å) and neutral in charge. Accordingly, they can easily migrate through the KCl lattice to interstitial positions where they are trapped by Cl^- ions, forming FCl^-.

The chief difference between these two possible mechanisms is that in the migration model the formation of a FCl^- center would also result in the formation of a negative-ion vacancy—i.e., an α center[4]—whereas in the interstitial dissolution model this would not be the case, assuming the K^+ also was present interstitially (which is consistent with observation that no α centers are seen in unirradiated KCl:KF). Experimentally, we do find α centers in irradiated KCl:KF, and, incidentally, none are seen in irradiated KCl. This we regard as evidence for the migration mechanism. In addition, some of the F atoms formed in x-ray irradiation might not migrate very far but be trapped by adjacent Cl^- ions. The orientation of such FCl^- centers would be affected by the presence of adjacent negative-ion vacancies. It is possible such centers may be the source of the very small lines associated with large lines (in the ⟨100⟩ spectrum) which could not be removed by more careful orientation of the crystal.

Finally, there is some evidence that F atoms move interstitially through the lattice. When the crystal is warmed to −100°C for a couple of minutes and then cooled again to liquid-nitrogen temperature, it is found that the FCl^- centers are no longer present but that a new center has been formed. This new center is oriented along a ⟨111⟩ direction and has tentatively been identified as BrF^-.[5] It is known that Br^- is an impurity in our KCl crystals. (For example, when Cl_2^- centers are formed in KCl:Pb, $BrCl^-$ is detected when the crystal is warmed to remove the Cl_2^-.) Furthermore, when this crystal containing the proposed BrF^- is warmed to 0°C and then cooled to liquid nitrogen, $BrCl^-$ was detected. The only way that BrF^- could be readily formed is if the F atom migrates interstitially through the crystal. At liquid nitrogen temperature, we can think of no other reasonable mechanism by which F or F^- could move through the crystal.

V. ANALYSIS OF SPIN-RESONANCE SPECTRA

In this section we shall fit a set of parameters for the spin Hamiltonian (1a) appropriate to the FCl^- center.

$$\frac{\mathcal{H}}{g_0\beta_0}=\frac{g}{g_0}HS_{z'}+\sum_{j=1}^{2} a_j\mathbf{I}_j\cdot\mathbf{S}+\sum_{j=1}^{2} b_jI_{j,z}S_z\,, \tag{1a}$$

where I_1 and I_2 are the nuclear spin operators of fluorine and chlorine nuclei, respectively, and S is the electron spin operator. The axis of the dc magnetic field H is designated by z' and the axis of the molecular ion by z; g_0 and g are the spectroscopic splitting factors of the free electron and of the molecular ion. β_0 is the Bohr magneton.

Equation (1a) is a simplified version of a Hamiltonian of the form

$$\frac{\mathcal{H}}{g_0\beta_0}=\frac{1}{g_0}(H_xg_{xx}S_x+H_yg_{yy}S_y+H_zg_{zz}S_z)+\sum_j(I_{j,x}A_{xx}{}^jS_x+I_{j,y}A_{yy}{}^jS_y+I_{j,z}A_{zz}{}^jS_z)\,. \tag{1b}$$

But the FCl^- molecular ion is oriented along the ⟨111⟩ axis of the crystal, and, as a very good first approximation, we may regard

$$A_{xx}{}^j=A_{yy}{}^j$$

and

$$g_{xx}=g_{yy}\,.$$

Then (1b) reduces to the form (1a) in which we write

$$g=(g_{\parallel}{}^2\cos^2\theta+g_{\perp}{}^2\sin^2\theta)^{1/2}\,, \tag{2}$$

where θ is the angle between the z and z' axes.

Writing $gS_{z'}=g_{\parallel}\cos\theta S_z+g\ \sin\theta S_x$, we can transform the Hamiltonian (1a) into the form

$$\frac{\mathcal{H}}{g_0\beta_0}=\gamma_{\parallel}S_z+\gamma_{\perp}S_x+\sum_{j=1}^{2} A_jI_{j,z}S_z+\sum_{j=1}^{2} a_j\{I_{j,x}S_x+I_{j,y}S_y\}\,, \tag{3}$$

where

$$\gamma_{\parallel}=(g_{\parallel}/g_0)H\cos\theta\,,$$
$$\gamma_{\perp}=(g_{\perp}/g_0)H\sin\theta\,, \tag{4}$$

and

$$A_j=a_j+b_j\,.$$

We observe that the x and y directions are not fixed. Consider the unitary transformation

$$U=\exp\{-i\textstyle\sum_j I_{j,z}\varphi\}\,.$$

The eigenvalues of $\mathcal{H}$ are identical with those of any equivalent Hamiltonian such as $U\mathcal{H}U^{-1}$. In particular, for the case $\varphi=\pi$, we find that

$$U\frac{\mathcal{H}}{g_0\beta_0}U^{-1}=\gamma_{\parallel}S_z+\gamma_{\perp}S_x+\sum_{j=1}^{2} A_jI_{j,z}S_z-\sum_{j=1}^{2} a_j\{I_{j,x}S_x+I_{j,y}S_y\}\,.$$

Thus, it is not possible to determine the sign of a_j relative to that of A_j for a system described by the Hamiltonian (1a). From this analysis it is clear why

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[4] C. J. Delbecq, P. Pringsheim, and P. H. Yuster, J. Chem. Phys. 19, 574 (1951).

[5] The number of lines, 8 plus isotope pairs, and their spacing together with the width of the spectrum, nearly 2600 G, is consistent with the assignment of the center as BrF^-.

TABLE III. Ordering of the basis states $|m_s;\, m_1 m_2\rangle$.

$|1\rangle=|\frac{1}{2};\,\frac{1}{2}\,\frac{3}{2}\rangle$	$|5\rangle=|\frac{1}{2};\,\frac{1}{2}\,\frac{1}{2}\rangle$	$|9\rangle=|\frac{1}{2};\,\frac{1}{2}-\frac{1}{2}\rangle$	$|13\rangle=|\frac{1}{2};\,\frac{1}{2}-\frac{3}{2}\rangle$
$|2\rangle=|-\frac{1}{2};\,\frac{1}{2}\,\frac{3}{2}\rangle$	$|6\rangle=|-\frac{1}{2};\,\frac{1}{2}\,\frac{1}{2}\rangle$	$|10\rangle=|-\frac{1}{2};\,\frac{1}{2}-\frac{1}{2}\rangle$	$|14\rangle=|-\frac{1}{2}-\frac{1}{2}-\frac{3}{2}\rangle$
$|3\rangle=|\frac{1}{2};\,-\frac{1}{2}\,\frac{3}{2}\rangle$	$|7\rangle=|\frac{1}{2};\,-\frac{1}{2}\,\frac{1}{2}\rangle$	$|11\rangle=|\frac{1}{2};\,-\frac{1}{2}-\frac{1}{2}\rangle$	$|15\rangle=|\frac{1}{2};\,-\frac{1}{2}-\frac{3}{2}\rangle$
$|4\rangle=|-\frac{1}{2};\,-\frac{1}{2}\,\frac{3}{2}\rangle$	$|8\rangle=|-\frac{1}{2};\,-\frac{1}{2}\,\frac{1}{2}\rangle$	$|12\rangle=|-\frac{1}{2};\,-\frac{1}{2}-\frac{1}{2}\rangle$	$|16\rangle=|-\frac{1}{2};\,-\frac{1}{2}-\frac{3}{2}\rangle$

previous investigators of X_2^- centers were unable to determine the sign of a relative to that of $(a+b)$.[1]

It should not be concluded that the sign of a can never be determined. One possibility, an *ab initio* calculation, is at present not feasible. Castner and Känzig[1] have stated that a positive sign of a is consistent with observed values of g_{zz} for Cl_2^- and Br_2^-. Looking at their data, we think a negative sign of a is equally consistent for Cl_2^-. Furthermore, we would remark that the theory[6] used, which predicts that $g_{zz}-g_0<0$, fails completely to explain the positive deviation of $g_{zz}-g_0$ for F_2^-. In Sec. VI we shall offer a possible sign assignment.

In this section, we shall make a rough calculation of the parameters using perturbation theory. The results of this rough calculation are then used as initial values in an elaborate computer program described in the Appendix. We have included this calculation because (i) the results are quite close to those obtained on a computer, and (ii) the calculation indicates the power of ordinary perturbation theory even for certain relatively large matrices.

The following calculation scheme will be used here: 1. A complete set of states will be chosen and all the matrix elements of $\mathcal{H}$ with respect to those states will be calculated. 2. The resulting 16×16 matrix will be diagonalized for a certain orientation of the magnetic field with respect to the molecular axis. 3. The differences of appropriate energy levels evaluated at the magnetic field corresponding to resonance lines observed, i.e., the quantum sizes will be equated to the energy of the klystron frequency, and the parameters $|a_1|$, A_1, $|a_2|$, A_2, $g_\perp$, and $g_{\shortparallel}$ will be determined.

We can use the following complete set of states:

$$|Sm_s;\, I_1m_1;\, I_2m_2\rangle,$$

where

$$S=\tfrac{1}{2},\quad I_1=\tfrac{1}{2},\quad I_2=\tfrac{3}{2}$$

and

$$m_s=\pm\tfrac{1}{2},\quad m_1=\pm\tfrac{1}{2},\quad m_2=\pm\tfrac{3}{2},\quad \pm\tfrac{1}{2}.$$

Since all the matrix elements are diagonal in S, I_1, and I_2, we can represent the states by $|m_sm_1m_2\rangle$. Then, the 16×16 matrix, composed of entries of the form $\langle m_sm_1m_2|\mathcal{H}|m_s'm_1'm_2'\rangle$, must be diagonalized. It is convenient to order the 16 basis states as shown in Table III. (Observe that the states in Table III are ordered so that the electron spin resonance lines should roughly correspond to transitions between states 1 and 2, 3 and 4, etc.) Then the matrix can be broken up into 4×4 submatrices, those along the diagonal being diagonal in m_2. Now from the work of Känzig[1] we know that

$$(a+b)_1\sim 9(a+b)_2 \quad\text{and}\quad |a|_1\sim 6|a|_2. \tag{5}$$

Consequently, a reasonable approach would be to diagonalize exactly (or nearly so) the 4×4 submatrices diagonal in m_2 and treat those 4×4 submatrices not diagonal in m_2 as a perturbation. Accordingly we group the terms in the Hamiltonian in the following way:

$$\mathcal{H}/g_0\beta_0=\mathcal{H}_0+\mathcal{H}_1, \tag{6}$$

where

$$\mathcal{H}_0=\gamma_{\shortparallel}S_z+\gamma_\perp S_x+(A_1I_{1,z}+A_2I_{2,z})S_z+a_1(I_{1,x}+I_{1,y})S_y$$

and

$$\mathcal{H}_1=a_2(I_{2,x}+I_{2,y})S_y.$$

Then, the matrix elements of $\mathcal{H}_0$ are diagonal in m_2, while those of $\mathcal{H}_1$ are not. Let

$$D_{m_2}=\langle m_sm_1|\mathcal{H}_0|m_s'm_1'\rangle. \tag{7}$$

D_{m_2} is a 4×4 matrix diagonal in m_2. We call it a "diagonal block." Let

$$O_{m_2,m_2'}=\langle m_sm_1m_2|\mathcal{H}_1|m_s'm_1'm_2'\rangle. \tag{8}$$

We call these "off-diagonal blocks." Then we can write

$$\left\langle\frac{\mathcal{H}}{g_0\beta_0}\right\rangle=\begin{bmatrix} D_{3/2} & O_{3/2,1/2} & O_{3/2,-1/2} & O_{3/2,-3/2} \\ & D_{1/2} & O_{1/2,-1/2} & O_{1/2,-3/2} \\ & \text{transpose} & D_{-1/2} & O_{-1/2,-3/2} \\ & & & D_{-3/2} \end{bmatrix}. \tag{9}$$

The diagonal and off-diagonal blocks are readily calculated and are given by

$$D_{m_2}=\frac{1}{4}\begin{bmatrix} 2\gamma_{\shortparallel}+A_1+2m_2A_2 & 2\gamma_\perp & 0 & 0 \\ 2\gamma_\perp & -(2\gamma_{\shortparallel}+A_1+2m_2A_2) & 2a_1 & 0 \\ 0 & 2a_1 & 2\gamma_{\shortparallel}-A_1+2m_2A_2 & 2\gamma_\perp \\ 0 & 0 & 2\gamma_\perp & -(2\gamma_{\shortparallel}-A_1+2m_2A_2) \end{bmatrix},$$

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[6] T. Inui, S. Harasawa, and Y. Obata, J. Phys. Soc. Japan **11**, 612 (1956).

$$O_{3/2,1/2}=\tfrac{1}{2}\sqrt{3}\begin{bmatrix}0 & 0 & 0 & 0\\ a_2 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & a_2 & 0\end{bmatrix}, \tag{10}$$

and

$$O_{3/2,1/2}=O_{1/2,\,-3/2}=\tfrac{1}{2}\sqrt{3}O_{1/2,\,-1/2}.$$

Now the parameters can be calculated using the experimental data listed in Table II. Specifically, we consider the cases $\theta=0°$ and $\theta=90°$. For the case $\theta=0°$, $\gamma_\perp=0$, and for $\theta=90°$, $\gamma_\parallel=0$.

The approximation we initially suggested was to diagonalize D_{m_2} exactly and use perturbation theory to calculate the effect of the off-diagonal block matrix elements on the energy levels. However, we shall assume that the values of the parameters a_j and A_j will be about the same as their values in the X_2^- centers.[1] For reference, their values in G are

$$\begin{aligned} A_1&=887, & |a_1|&=59,\\ A_2&=101, & |a_2|&=9, \end{aligned} \tag{11}$$

also

$$\gamma_\parallel\sim 3000.$$

Since $a_1/\gamma_\parallel\sim 0.02$, even the off-diagonal elements of D_{m_2} can be treated by perturbation theory. Finally, the effects of the off-diagonal blocks could be calculated by perturbation theory. The value of a_2 is so small compared with that of $\gamma_\parallel$ that the off-diagonal blocks can be neglected for the case $\theta=0°$. The calculated energy shifts (in G) are less than 0.1. This is not true for the case $\theta=90°$. It should be noted that in the $\theta=0°$ case, shifts in the energy levels due to off-diagonal matrix elements in the diagonal blocks are very small. Hence, the eigenvectors are essentially unchanged and the matrix elements in the off-diagonal blocks can be used directly in perturbation theory. If the shifts were larger, then a unitary transformation connecting the old and new eigenvectors would have to be calculated, and the off-diagonal blocks transformed into the new representation. In the $\theta=90°$ case where $\gamma_\parallel=0$, it would be convenient to make a unitary transformation on D_{m_2} which more nearly diagonalizes it before using perturbation theory. In point of fact we transformed the I's into a coordinate system where the z axis was parallel to the applied field H. In this coordinate system the remark above about the size of the energy shifts due to off-diagonal matrix elements in the diagonal blocks was applicable.

The details of the calculation will not be presented; only a few of the results will be given together with the fitted parameters. For example, for the case $\theta=0°$ $(\gamma=g_\parallel H/g_0)$

$$\begin{aligned} E_1&\simeq\tfrac{1}{2}\gamma+\tfrac{1}{4}A_1+\tfrac{1}{2}(\tfrac{3}{2})A_2,\\ E_2&\simeq-\tfrac{1}{2}\gamma-\tfrac{1}{4}A_1-\tfrac{1}{2}(\tfrac{3}{2})A_2-a_1^2/(4\gamma),\\ E_3&\simeq\tfrac{1}{2}\gamma-\tfrac{1}{4}A_1+\tfrac{1}{2}(\tfrac{3}{2})A_2+a_1^2/(4\gamma),\\ E_4&\simeq-\tfrac{1}{2}\gamma+\tfrac{1}{4}A_1-\tfrac{1}{2}(\tfrac{3}{2})A_2. \end{aligned} \tag{12}$$

For the other energy levels, the number in the parenthesis in front of A_2 changes appropriately to $\frac{1}{2}$, $-\frac{1}{2}$, and $-\frac{3}{2}$. The energy difference associated with electron spin resonances can be labeled by nuclear spin levels. In this case

$$\Delta E_{m_1,m_2}=\gamma+m_1A_1+m_2A_2+a_1^2/(4\gamma). \tag{13}$$

Experimentally the transition frequency $(\Delta E_{m_1,m_2}/h)$ is fixed (by the klystron),[1] and the magnetic field is varied until the separation (in frequency) between, e.g., E_5 and E_6 is equal to the klystron frequency. If we use the value of a_1 that is gotten from fitting the 90° spectrum, viz., $a_1\sim 80$ G, then we find that $g_\parallel\simeq 2.0023$, $A_1=806$ G, and $A_2=126$ G. Finally, from the 90° spectrum, the approximate values $a_1\sim 80$ and $a_2\sim 20$ G are determined. This rough treatment does not allow one to calculate a delicate number like $g_\perp$ which for the purposes of the calculation was taken as the average of the values of $g_\perp$ for Cl_2^- and F_2^-. These estimates of the parameters were then used in a computer calculation which is described in the Appendix.

TABLE IV. Fitted parameters for FCl^- center and F_2^- and Cl_2^- centers.

	FCl^-	$F_2^{-(1)}$	$Cl_2^{-(1)}$
$(a+b)_F$	806	887	...
$\|a_F\|$	81	59	...
$(a+b)_{Cl}$	126	...	101
$\|a_{Cl}\|$	21	...	9
$g_\parallel$	2.0023	2.003	2.00010
$g_\perp$	2.030	2.023	2.0438

VI. DISCUSSION OF RESULTS

The results of fitting the parameters of the spin Hamiltonian (1a) to the experimentally observed spectra for FCl^- are summarized in Table IV along with values appropriate to F_2^- and Cl_2^-. For a discussion of the errors in the calculations, see the Appendix. As for the error arising from experimental factors we estimate that $\Delta g_\parallel/g_0=\pm 0.001$ and $|\Delta A|<1$ G. It should be noted that all values for chlorine refer to the chlorine-35 isotope.

Following the treatment of Castner and Känzig,[1] we suppose the FCl^- molecule ion can be thought of in the simplest approximation as an unpaired electron shared more or less equally by a fluorine and a chlorine atom. We write the molecular orbital ground-state wave function as a linear combination of atomic wave functions for the two atoms. Due to the mutual polarization of the two atoms, the atomic wave functions will be hybrids of s and p orbitals. Using such wave functions, if we average over the dipole-dipole interaction term, neglecting overlap terms, we generate the spin Hamiltonian (1a) minus the Zeeman term. Then the values

TABLE V. The results of calculating $\Delta a/\Delta b$ (i) from Eqs. (14) for different s orbitals and (ii) from the experimentally determined parameters for different sign choices of a and a'. The primed quantities refer to FCl^- and the unprimed to X_2^-.

X	s admixture	Calc. from (14)	Calc. from experiment (Table IV)				
			Sign a'	+		−	
			Sign a	+	−	+	−
F	$2s$	−8.9		−0.21	−0.63	**−2.4**	+0.37
	$3s$	−0.72					
Cl	$3s$	−9.0		0.92	**−6.0**	−0.55	−0.32
	$4s$	−1.05					

a and b are given approximately by

$$a_j=\frac{\mu_{I_j}}{2I_j}\left[\frac{8\pi}{3}\beta^2{}_j|\psi_j(0)|^2-\tfrac{2}{5}\alpha^2{}_j\left\langle\frac{1}{r^3}\right\rangle_j\right],$$
$$b_j=\frac{\mu_{I_j}}{2I_j}\left[\frac{6}{5}\alpha^2{}_j\left\langle\frac{1}{r^3}\right\rangle_j\right], \tag{14}$$

where μ_{I_j} is the magnetic moment of the halogen nucleus j with spin I_j. α^2 and β^2 are the fraction of p and s orbitals in the hybrid atomic wave function. $\langle 1/r^3\rangle_j$ is an average of $1/r^3$ taken over the np orbital centered at the nucleus, and $|\psi_j(0)|^2$ is the amplitude of the s orbital at the nucleus. As Känzig and Woodruff[7] have pointed out, the appropriate value for $|\psi(0)|^2$ should be intermediate to those for the ns and $(n+1)s$ orbitals. We shall use the same values of $|\psi(0)|^2$ and $\langle 1/r^3\rangle$ which are compiled in Känzig's and Woodruff's paper.[7] For convenience we shall use the following notation: a_x, b_x and a_x', b_x' are the appropriate values for X in X_2^- and FCl^-, respectively; $\Delta a=a'-a$ and $\Delta b=b'-b$. Observing that $\Delta\alpha^2+\Delta\beta^2=0$, we are thus able to calculate $\Delta a/\Delta b$ from (14) without ever calculating α^2 or β^2; this ratio is found for both s-orbital possibilities. Also $\Delta a/\Delta b$ is calculated from the fitted parameters in Table IV for all possible sign choices of a and a'. The results of these calculations are displayed in Table V. If we believe that the correct value of $\Delta a/\Delta b$ should lie between the values for the ns and $(n+1)s$ orbitals, then we should look for those experimental values of $\Delta a/\Delta b$ which lie in this range. Incredibly there is only one choice of signs for a and a' for which $\Delta a/\Delta b$ is in that range for each nucleus. According to this analysis,

$$\text{in } F_2^-,\ a_F=+59,\quad \text{in } Cl_2^-,\ a_{Cl}=-9,$$

and

$$\text{in } FCl^-,\ a_F'=-81\quad\text{and}\quad a_{Cl}'=+21.$$

Surprising as this result may be, we do not think too much faith should be put in it. Many items have been neglected in this analysis, for example, heteronuclear effects, the overlap of the wave functions, and core polarization. A detailed analysis, if and when it can be carried out, may completely upset these results. With respect to the g values we only remark that they are intermediate to those of F_2^- and Cl_2^-.

As is of course obvious, this paper is but a small beginning step in the field of XY^- centers. In conclusion we should like to mention at least a few topics which present themselves most immediately.

1. The systematic discovery and investigation of other XY^- centers is of course an obvious goal. Already the $BrCl^-$ center has been positively identified. The center lies along a ⟨110⟩ direction, and the spectrum contains 64 lines, 16 for each isotope combination. As noted earlier in the paper, the center BrF^-, along a ⟨111⟩ direction, has been tentatively identified in KCl:KF.
2. The optical spectra of these centers should be investigated and correlated with the spin-resonance spectra especially by means of polarized light experiments.
3. Finally, it should be noted that the XY^- and X_2^- centers may prove a valuable tool in studying the mobility, stability, and other properties of atoms and vacancies in the alkali halides.

Experiments are presently in progress at Argonne National Laboratory concerning these items.

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APPENDIX

The eigenvalues and eigenstates of the Hamiltonian should be found exactly. However, if perturbation methods in reasonably low order can be used without serious loss of accuracy, machine time can be saved.

As was suggested in Sec. V, ordinary perturbation procedures do not work well at angles between 0° and 90° because matrix elements which contribute only in second order may be so large that they invalidate the first-order calculation.

A procedure due to Pryce[8] based on a suggestion by Van Vleck[9] is used. This generates a nuclear spin Hamiltonian H which is a polynomial in the nuclear

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[7] W. Känzig and T. O. Woodruff, J. Phys. Chem. Solids **9**, 70 (1959).

[8] M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950).

[9] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

spin operators with coefficients that depend only on the electronic energy and wave functions, and whose eigenvalues give the splittings of the nuclear manifold correct to second order. H is the sum of the ordinary first-order perturbation operator which is the interaction of the nuclear moment with the expectation of the electron spin coupled to the nuclear site by the dipole-dipole interaction, and a second-order operator which allows for the effect on the nuclei of matrix elements in the hyperfine interaction which couple to other electronic states, i.e., the second-order terms in cases where ordinary perturbation theory applies. Because of time-reversal symmetry, the first nonzero corrections to this method are fourth order in the perturbation parameter (nuclear hyperfine splitting/electronic Zeeman splitting).

In addition to the nuclear levels, the program calculates the differential coefficients of the energy of each level with regard to the following parameters: $g_\perp$, $g_{\parallel}$, a_1, A_1, a_2, and A_2. It then goes on to examine the intensities of each of the transitions which might occur. If the intensity is large enough to be of interest, the corresponding quantum size is calculated together with the differential coefficients of the quantum size with respect to the six parameters.

The program is used in the following way: When a spectrum has been observed and rough values of the parameters have been found by hand calculation, these are used together with the magnetic-field values and orientations to calculate all of the possible quantum sizes which would cause transitions at each magnetic field. It is then possible to see which transitions have quantum sizes near the microwave quantum for each magnetic resonance absorption line. Usually there is just one calculated quantum size which looks reasonable for each line observed.

When the transitions have been assigned, the corresponding differential coefficients with regard to the parameters are taken from the results of the perturbation program and used in a least-squares fitting program to calculate changes in the parameters which reduce the discrepancies between the true quantum size and the calculated transition energies.

The new parameters may then be used as input to the perturbation program to obtain corrected quantum sizes and differential coefficients. The resulting changes in the differential coefficients can then be used to judge whether the results of a second least-squares fit would alter the coefficients enough to necessitate another iteration of the energy level calculation. If the first estimate is reasonable this is not usually needed and was not necessary for FCl$^-$.

The least-squares program includes a calculation of the estimated reliability or standard error of the fitted results. When the parameter values have been determined the four spectra may be divided into two pairs, e.g., 0° and 70° as one pair and 35° and 90° as the other. Each pair may then be used to fit a set of parameters. If the differences between the two sets of parameters are significantly larger than would be expected from the standard errors, it is probable that there are systematic discrepancies between the observed line positions and the predictions of the assumed Hamiltonian.

Such disagreements have been found in the FCl$^-$ results and are believed to come from experimental error, mainly in the 90° spectrum. Systematic displacements of the observed line centers by 2 or 3 G could account for these discrepancies.

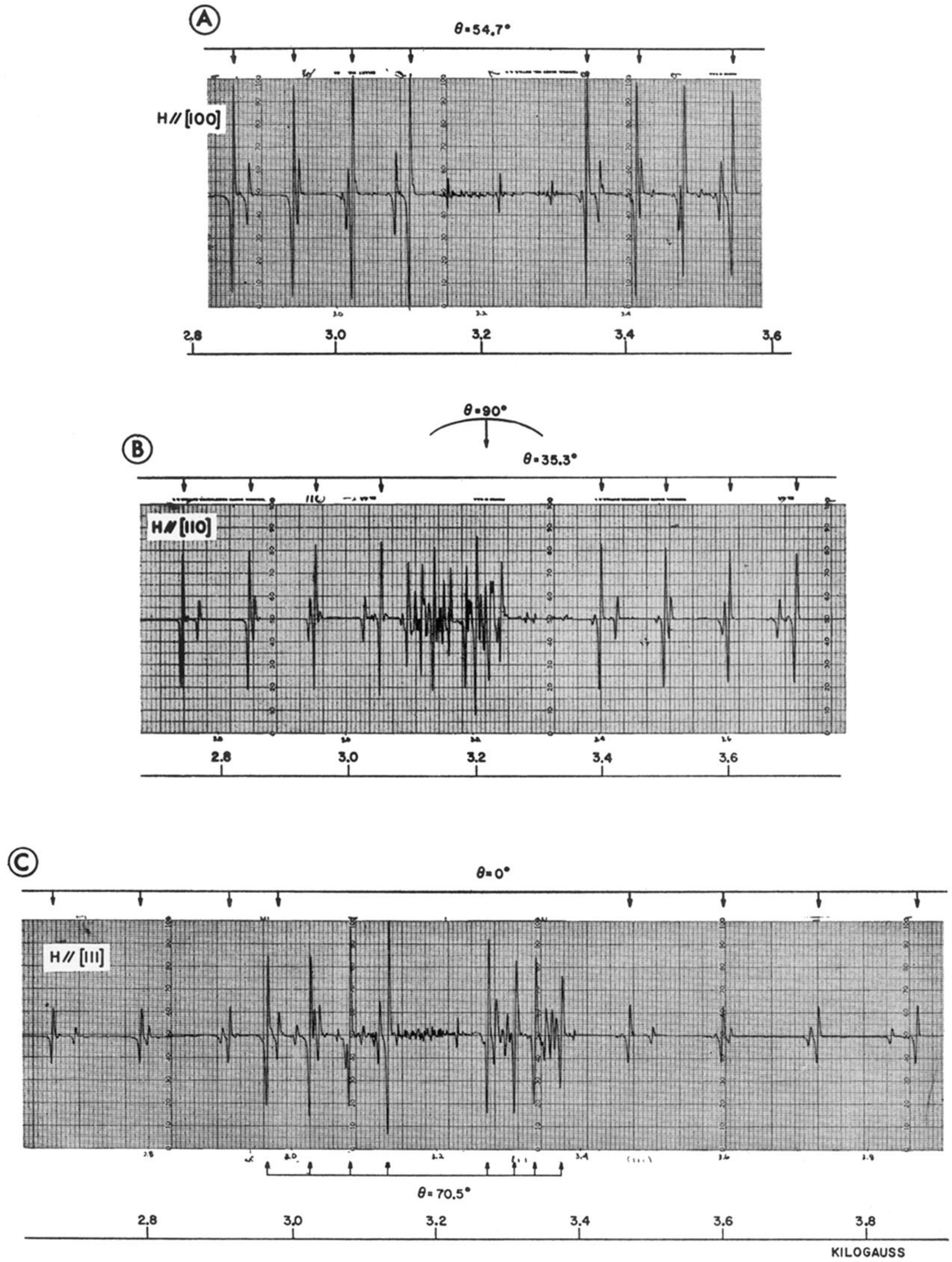

FIG. 1. (A), (B), and (C). Electron spin resonance absorption spectra of the FCl⁻ center observed at about 9.3 kMc/sec with the dc magnetic field along the [100], [110], and [111] axes, respectively. The arrows mark the $(Cl^{35}-F^{19})^-$ spectra. In all cases the microwave magnetic field is perpendicular to the dc magnetic field. The first derivative of the absorption is recorded.