

$\langle 111 \rangle$ -Oriented FCl^- , FBr^- , and FI^- Centers in Mixed Alkali Halides*

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$\langle 111 \rangle$ -oriented FCl^- molecule ions occupying one negative ion vacancy are produced in F^- -doped KCl by x or γ irradiation at 77°K. At temperatures above 150°K these FCl^- centers decay by dissociating into a substitutional Cl^- ion and a F° atom which can migrate interstitially. If the crystal also contains substitutional Br^- or I^- ions, the F° atoms can be retrapped to form $\langle 111 \rangle$ -oriented FBr^- and FI^- . The ESR spectra of these centers have also been found and analyzed in the other alkali chlorides together with a $\langle 111 \rangle$ -oriented FBr^- in F^- -doped KBr. This analysis and comparison with the X_2^- centers indicates that for the fluorine hyperfine components in F_2^- and FX^- , $A_{\parallel}(\text{F}) > 0$ and $A_{\perp}(\text{F}) < 0$, while for X_2^- and FX^- , $A_{\parallel}(\text{X}) > 0$ and $A_{\perp}(\text{X}) > 0$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). The main optical absorption band of FCl^- is situated at 300 $m\mu$, while the approximate positions for the FBr^- and FI^- transitions are at 294 $m\mu$ and 275 $m\mu$, respectively.

I. INTRODUCTION

IN alkali halides, at sufficiently low temperatures, positive holes produced by x or γ irradiation are self-trapped and form $\langle 110 \rangle$ -oriented homonuclear X_2^- molecule ions ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) occupying two negative ion vacancies.¹⁻⁴ These centers are also called V_K centers. The possibility of forming XY^- and Y_2^- centers by doping AX with AY suggested itself and recent experiments⁵⁻⁹ have shown that these centers can indeed be produced. Most of these XY^- and Y_2^- centers in the mixed alkali halides are also $\langle 110 \rangle$ oriented and occupy two negative ion vacancies. Up to now three exceptions, which form an interesting class in itself, have been observed,^{6,9} namely, FCl^- , FBr^- , and FI^- , which are $\langle 111 \rangle$ oriented and occupy only one negative ion vacancy. The FCl^- center was discovered and analyzed by Wilkins and Gabriel in a F^- -doped KCl crystal.⁶ Because the KCl crystals they used contained the usual unintentional small amounts of Br^- impurity, they observed that thermal destruction of FCl^- resulted in the formation of a new center which was tentatively identified as a $\langle 111 \rangle$ -oriented FBr^- . Our analysis has verified this identification in KCl crystals intentionally doped with F^- and Br^- . The experiments with FBr^- immediately suggested the

method for producing $\langle 111 \rangle$ -oriented FI^- , namely, doping the KCl crystal with F^- and I^- . These centers are also found in the other alkali chlorides, and in addition a $\langle 111 \rangle$ -oriented FBr^- has been observed in F^- -doped KBr. This paper will be limited primarily to the analysis of the electron spin resonance data of these mixed molecule ions at and above 77°K, and only the more obvious optical and thermal properties will be touched upon. A detailed correlation study between the optical absorption and ESR spectra at lower temperatures will be the subject of a subsequent paper.

II. EXPERIMENTAL

The crystals used in these experiments were grown in air by the Kyropoulos method. The following crystals were grown: LiCl, NaCl, KCl, RbCl, and KBr doped with 0.5 mole % of the appropriate fluoride; NaCl, KCl, and RbCl doped with up to 0.5 mole % of the appropriate fluoride and bromide; and NaCl, KCl, and RbCl doped with up to 0.5 mole % of the appropriate fluoride and iodide. In general the appropriate lead halide was also added, since Pb^{++} ions act as efficient electron traps at 77°K.^{3,4}

The electron spin resonance measurements were performed with the Varian variable-temperature spectrometer used in the FCl^- investigation.⁶ The inner diameter of the Dewar was increased to 7 mm allowing the use of larger samples. The sample sizes were $4 \times 4 \times 16 \text{ mm}^3$ for angular variation studies around a $\langle 100 \rangle$ axis, and $4 \times 4 \times 4.5 \text{ mm}^3$ (or $4 \times 4 \times 16 \text{ mm}^3$ but cut along a $\langle 110 \rangle$ direction) for angular variation studies around a $\langle 110 \rangle$ axis. For the measurements the crystals were held in suitable Lucite holders. The magnetic field was measured using a Harvey Wells G-501 proton-resonance gaussmeter in conjunction with a Systron Donner 1037 frequency counter.

The color centers were produced by γ rays from a 2000 Ci Co^{60} source or by x irradiation from a tungsten target Machlett tube operating at 50 kV and 50 mA and filtered through 1 mm of quartz wrapped in a thin aluminum foil. All irradiations were performed at 77°K. The optical bleachings were done outside the cavity in

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

¹ T. G. Castner and W. Känzig, *J. Phys. Chem. Solids* **3**, 178 (1957).

² T. O. Woodruff and W. Känzig, *J. Phys. Chem. Solids* **5**, 268 (1958).

³ C. J. Delbecq, W. Hayes, and P. H. Yuster, *Phys. Rev.* **121**, 1043 (1961).

⁴ C. J. Delbecq, B. Smaller, and P. H. Yuster, *Phys. Rev.* **111**, 1235 (1958).

⁵ E. Boesman and D. Schoemaker, *J. Chem. Phys.* **37**, 671 (1962).

⁶ J. W. Wilkins and J. R. Gabriel, *Phys. Rev.* **132**, 1950 (1963).

⁷ D. Schoemaker, C. J. Delbecq, and P. H. Yuster, *Bull. Am. Phys. Soc.* **9**, 629 (1964).

⁸ D. Schoemaker, in *International Symposium on Color Centers*, Urbana, October 1965, Abstracts Nos. 167 and 168 (unpublished). In converting the experimental data a computational error was made: The $|\psi(0)|^2$ values given in these abstracts are too high by a factor of 2.5.

⁹ D. Schoemaker, C. J. Delbecq, and P. H. Yuster, *Bull. Am. Phys. Soc.* **10**, 1201 (1965).

TABLE I. Classification of $\langle 111 \rangle$ -oriented molecule ions for three important orientations of the static magnetic field \mathbf{H} with respect to the crystal axes.

Direction of \mathbf{H}	Angle θ	Degeneracy or relative intensity
$\langle 111 \rangle$	0°	1
	70.5°	3
$\langle 110 \rangle$	35.3°	2
	90°	2
$\langle 100 \rangle$	54.7°	4

a Dewar with quartz windows. The bleaching light source was an HBO-500 mercury lamp with appropriate combinations of Bausch and Lomb interference filters and Corning glass filters.

III. THE SPIN-RESONANCE SPECTRA

1. FCl^-

The FCl^- spin resonance spectrum in KCl has been described extensively by Wilkins and Gabriel,⁶ and only a brief description will be given here. The spin resonance spectrum of FCl^- is observed at 77°K in F^- -doped alkali chlorides after x or γ irradiation at this temperature. At the same time Cl_2^- and F centers are also formed. When Pb^{++} ions are also present the rate of formation, and the final concentration, of Cl_2^- centers that can be produced is strongly increased. At the same time the formation of F centers is somewhat suppressed. However, the presence of Pb^{++} ions does not seem to affect the formation characteristics of the FCl^- center. In both types of crystals the FCl^- concentration is dependent primarily upon the length of irradiation; it takes one to two hours to produce a high FCl^- concentration.

The Cl_2^- centers can easily be removed at 77°K by irradiating into the $365\text{ m}\mu$ absorption band of Cl_2^- , preferably on the long-wavelength side with $436\text{ m}\mu$ light. Practically all Cl_2^- centers are then destroyed, but this treatment does not change the FCl^- concentration.

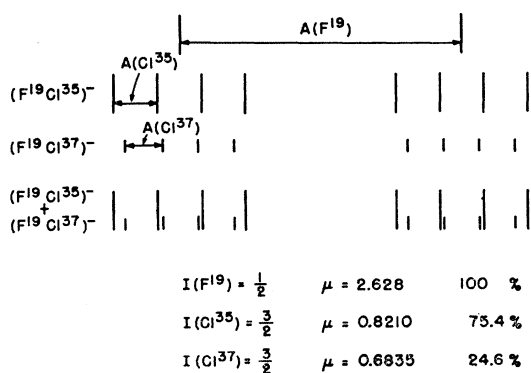


FIG. 1. The basic FCl^- pattern. The ratio of A_{Cl} to A_{F} is that of the experimental $\theta=0^\circ$ spectrum given in Ref. 6.

The basic FCl^- pattern is shown in Fig. 1. Fluorine has only one naturally occurring isotope, F^{19} , with a large nuclear moment and nuclear spin $\frac{1}{2}$. Chlorine has two naturally occurring isotopes, Cl^{35} and Cl^{37} , with relative abundance 3:1, both with nuclear spin $\frac{3}{2}$ and smaller nuclear moments. The interaction of the hole with the fluorine nucleus gives two lines, each of which is further split into two sets of four lines with intensity ratio 3:1 by the interaction with the nuclei of the two chlorine isotopes. The experimental FCl^- spectra, as reproduced in Ref. 6, agree very well with this pattern.

The electron spin resonance spectrum of FCl^- is strongly anisotropic, has axial symmetry, and the molecular axis is oriented exactly along a $\langle 111 \rangle$ direction of the crystal.⁶ Since the same conclusion will be reached for the FBr^- and FI^- centers, it is convenient to review here the reasons for this statement. For a center with axial $\langle 111 \rangle$ symmetry one expects to see for an arbitrary direction of the external magnetic field \mathbf{H} four different basic spectra corresponding to four different angles between the symmetry (molecular) axis and \mathbf{H} . For special orientations of the magnetic field, some centers become geometrically equivalent (degenerate), and the number of spectra observed is reduced. Table I gives the classification of the spectra for three important orientations of \mathbf{H} . The properties listed in this table are faithfully reproduced by the experimental spectra in Ref. 6; consequently, the $\langle 111 \rangle$ symmetry of the FCl^- center is established. The FCl^- centers have also been found and analyzed in F^- -doped RbCl and NaCl after x or γ irradiation at 77°K . No convincing evidence was found for the presence of FCl^- in $\text{LiCl}:\text{LiF}$ at this temperature.

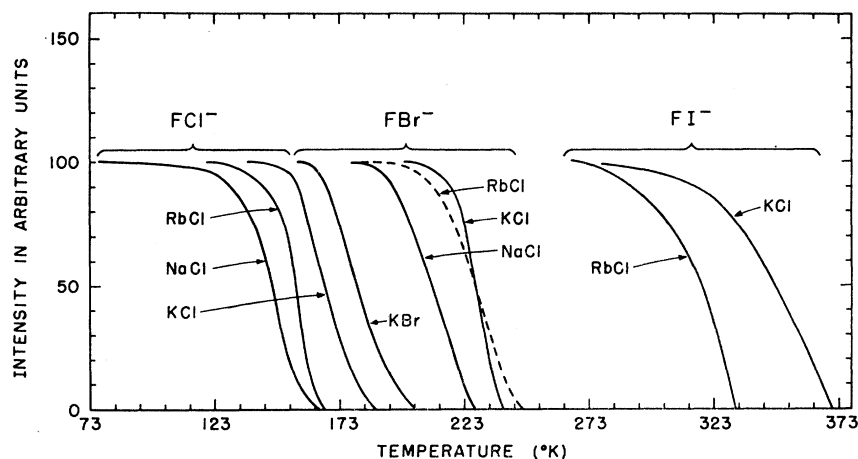
The FCl^- centers are less stable thermally than the Cl_2^- molecule ions. The pulse-annealing results in Fig. 2 show that in a $\text{KCl}:\text{KF}:\text{PbCl}_2$ crystal FCl^- decays at about 170°K while Cl_2^- decays at about 220°K . The decay of FCl^- does not result in the formation of any other center that can be seen with ESR at 77°K , except when Br^- or I^- ions are present in the lattice (see following paragraphs).

Besides this FCl^- center, which we will call FCl^- (1), another FCl^- (2) center has been observed with low intensity in KCl ⁶ and RbCl . A detailed study was not attempted, but the molecular axes of these FCl^- (2) centers appear to make a small angle ϵ with the $\langle 111 \rangle$ directions. In RbCl , $\epsilon \approx 1.5^\circ$.

2. FBr^-

$\langle 111 \rangle$ -oriented FBr^- molecule ions can be produced at 77°K by irradiating a $\text{KCl}:\text{KF}:\text{KBr}$ crystal with x or γ rays. The predominant species that are observed are FCl^- , Cl_2^- , and F centers, although $\langle 110 \rangle$ -oriented ClBr^- ^{7,8} is also produced in small quantities. A warmup to 170°K for a few minutes destroys FCl^- completely and a high concentration of FBr^- is produced. One could again remove the Cl_2^- by bleaching in the $365\text{ m}\mu$

Fig. 2. Pulse annealing results of FCl^- , FBr^- , and FI^- in various crystals. The successive temperature intervals were 10°K and at each temperature the crystal was held for two minutes and then cooled rapidly to 77°K where the changes were measured. The shape and position of the curves are approximate to within 10° and the experimental points are not shown.



absorption region, but this increases the concentration of the $\langle 110 \rangle$ -oriented ClBr^- centers. However, since the spin resonance signal of Cl_2^- partially saturates, while that of FBr^- does not, one can suppress the former by working at high microwave power.

The basic FBr^- spectrum is constructed in Fig. 3. Again each of two F hyperfine lines is split into two times four lines through the interaction with the Br nuclei. Naturally occurring bromine has two equally abundant isotopes, both with nuclear spin $\frac{3}{2}$ and with large nuclear moments. The result is a characteristic 16-line spectrum, which is easily recognized in the experimental spectra of Fig. 4. A study of the angular variation of the strongly anisotropic spectra and a comparison of Fig. 4 with Table I again shows that the molecular axis of the FBr^- center is oriented exactly along the $\langle 111 \rangle$ direction, just as was the case for the FCl^- center. In Fig. 4(c) relatively strong $|\Delta M_I| = 1$ transitions can be seen, especially at the high-field side of the spectrum. A detailed study of these weakly allowed transitions has not yet been performed.

The pulse-annealing experiments in Fig. 2 show that FBr^- is more thermally stable than either FCl^- or Cl_2^- . In KCl it decays at about 230°K .

The $\langle 111 \rangle$ -oriented FBr^- center in F^- -doped KBr can be observed immediately after x irradiation at 77°K , together with Br_2^- . Again the presence or absence of Pb^{++} ions does not seem to influence the FBr^- formation. The Br_2^- can be eliminated by bleaching into its absorption band at $385 \text{ m}\mu$. The FBr^- concentration does not change with this treatment. This FBr^- center decays at 180°K , and no other center is subsequently detected at 77°K with ESR. The $\langle 111 \rangle$ -oriented FBr^- center has also been found in RbCl and NaCl.

3. FI^-

The production of FI^- is analogous to the production of FBr^- . Immediately after x irradiation of e.g., a KCl:KF:KI crystal, the most predominant species are FCl^- , Cl_2^- , F centers and a new center which has been

identified as a $\langle 110 \rangle$ -oriented ICl^- center, weakly interacting with the nucleus of a F^- ion.¹⁰

After a warmup to about 170°K for a few minutes, FCl^- has disappeared completely and a strong FI^- spectrum appears. However, in most KCl crystals there is a sizeable Br^- impurity present, and after such a warmup one also observes a FBr^- spectrum. A crystal containing only FI^- may be obtained by warming the crystal to room temperature for a few minutes. This treatment completely destroys other centers such as Cl_2^- , FBr^- , and ClBr^- , but does not affect FI^- which is stable up to about $+50^\circ\text{C}$ (see Fig. 2). Keeping the crystal overnight at room temperature reduces the FI^- concentration by about 30%.

The basic FI^- spectrum is constructed in Fig. 5. Each of the two fluorine hyperfine lines is now split into six lines through the interaction with the I^{127} nucleus, the only stable isotope, with nuclear spin $\frac{5}{2}$ and a large nuclear moment. The characteristic twelve-line spectrum is easily recognized in the experimental spectrum of Fig. 6(a). Again a study of the angular variation and a comparison of the spectra of Fig. 6 with Table I shows that the molecular axis of FI^- is oriented along a

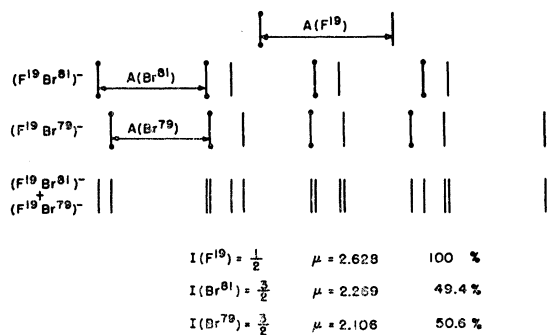


Fig. 3. The basic FBr^- pattern. The ratio of A_{Br} to A_{F} is taken from the experimental $\theta = 0^\circ$ spectrum in Fig. 4(a).

¹⁰ An analysis of this ICl^- (F^-) and other ICl^- centers will be given in another paper.

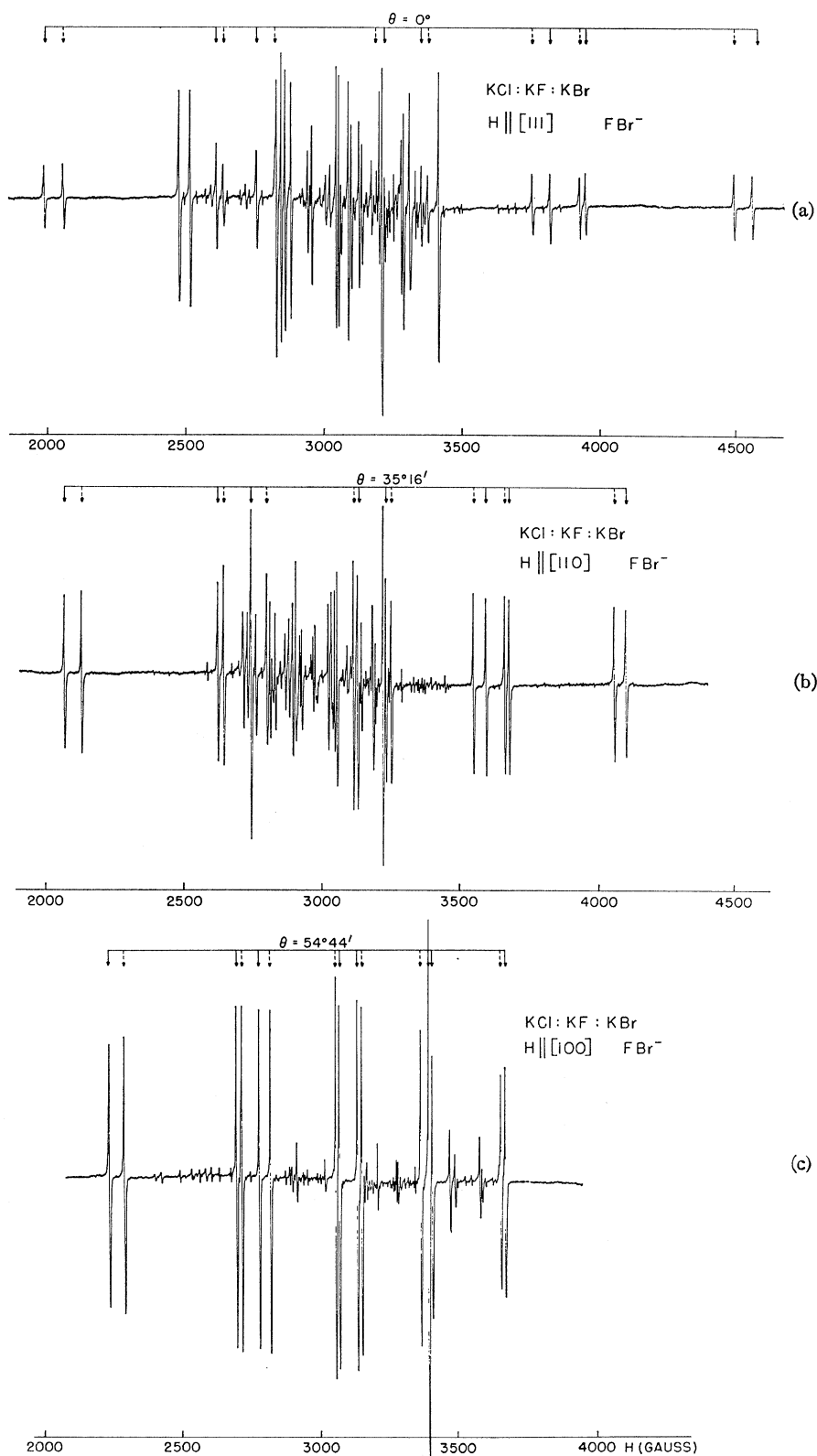


FIG. 4. Experimentally observed FBr^- spectra at 77°K in a F^- - and Br^- -doped KCl , for the three important orientations of the magnetic field. The gain is approximately the same for the three spectra. The $\theta = 70.5^\circ$ spectrum in (c) and $\theta = 90^\circ$ spectrum in (b) are not designated. Weak lines of Cl_2^- and ClBr^- are also seen. The microwave frequency is $\nu = 9.126 \text{ kMc/sec}$.

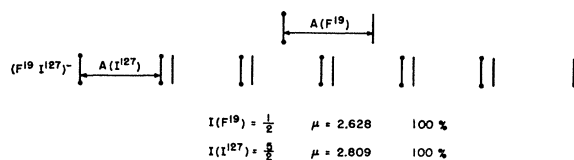


FIG. 5. The basic FI^- pattern. The ratio between A_F and A_I is that of the $\theta=0^\circ$ spectrum in Fig. 5(a).

$\langle 111 \rangle$ direction of the crystal. The $\langle 111 \rangle$ -oriented FI^- center has also been observed in RbCl . No attempt has, as yet, been made to detect FI^- in KI . The FI^- spectrum does not saturate at 77°K . The lines are temperature broadened at 77°K , and become increasingly more so as the temperature is raised. At 130°K , the ESR spectrum of FI^- can no longer be detected.

IV. QUANTITATIVE ANALYSIS

1. The Spin Hamiltonian

The spin Hamiltonian used to analyze the FX^- centers was taken as (in the usual notation):

$$\mathcal{H}/g_0\beta = (1/g_0)[g_{11}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] + \sum_{i=1}^2 [A_{11,i}S_zI_{z,i} + A_{\perp,i}(S_xI_{x,i} + S_yI_{y,i})] + P_2I_{z,2}^2, \quad (1)$$

where 1 stands for F and 2 for $X = \text{Cl}, \text{Br}, \text{I}$. Since the fluorine nucleus has no quadrupole moment, only the quadrupole term for the second nucleus X is included.

Wilkins and Gabriel in their analysis of FCl^- used (1), without the quadrupole term, and fitted it to the experimental results using a computer program. However, (1) can also be solved for an arbitrary direction θ of the magnetic field H with respect to the symmetry axis by means of second (or higher) order perturbation theory. The procedure is well known,^{11,1} and therefore details of the calculation will be omitted. The result can be put into a form which gives the line positions, in gauss, as a function of the nuclear quantum numbers, and the parameters occurring in (1). Up to second order the result is

$$H(M_1M_2) = \frac{g_0}{g}H_0 - \frac{g_0}{g} \sum_{i=1}^2 \left\{ K_i(1 + \epsilon_i)M_i + 2\epsilon_i H_0 [I_i(I_i + 1) - M_i^2] + \sum_{j=1}^2 \frac{D_i D_j}{2H_0} M_i M_j \right\} + \frac{g_0}{g} \left\{ \frac{R_2^2 S_2^2}{K_2} [4I_2(I_2 + 1) - 8M_2^2 - 1] M_2 - \frac{R_2^4}{2K_2} [2I_2(I_2 + 1) - 2M_2^2 - 1] M_2 \right\} \quad (2)$$

¹¹ B. Bleaney, Phil. Mag. 42, 441 (1951).

with

$$H_0 = h\nu/g_0\beta = \text{free electron field}$$

(ν = microwave frequency),

$$K_i^2 g^2 = A_{11,i}^2 g_{11}^2 \cos^2\theta + A_{\perp,i}^2 g_{\perp}^2 \sin^2\theta,$$

$$g^2 = g_{11}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta,$$

$$\epsilon_i = \frac{A_{\perp,i}^2 [A_{11,i}^2 + K_i^2]}{8[H_0^2 - \frac{1}{4}K_i^2]K_i^2}, \quad (3)$$

$$D_i = \frac{g_{11}g_{\perp}}{g^2} \frac{A_{11,i}^2 - A_{\perp,i}^2}{K_i} \sin\theta \cos\theta,$$

$$R_2 = P_2 \frac{A_{\perp,2}^2 g_{\perp}^2}{K_2^2 g^2} \sin^2\theta, \quad S_2 = P_2 \frac{A_{11,2}^2 g_{11}^2}{K_2^2 g^2} \cos^2\theta.$$

The distinguishing feature of (2) from the sum of two atomic cases is the occurrence of a term in M_1M_2 .

The procedure followed to determine the parameters was roughly as follows. From the $\theta=0^\circ$ spectrum, $A_{11}(\text{F})$, $A_{11}(\text{X})$, and g_{11} could be accurately determined. In the case of FBr^- and FI^- $A_{\perp}(\text{Br})$ and $A_{\perp}(\text{I})$ could also be calculated quite accurately from the already sizeable second-order shifts in the $\theta=0^\circ$ spectrum. This could not be done for $A_{\perp}(\text{F})$, because of the fact that $I = \frac{1}{2}$, and the appropriate second-order terms shift all the lines by exactly the same amount. It was found that for the three molecule ions the $\theta=0^\circ$ spectrum could be fitted quite accurately with the second-order expression (2). In addition, from the $\theta=35.3^\circ$ and $\theta=54.7^\circ$ spectra, $K_{35.3^\circ}(\text{X})$, $K_{35.3^\circ}(\text{F})$, $g_{35.3^\circ}$, etc. were determined, and then, using formulas (3), $A_{\perp}(\text{F})$, $A_{\perp}(\text{X})$, and g_{\perp} were calculated.

In the case of FCl^- , where all the spectra including $\theta=70.5^\circ$ and $\theta=90^\circ$ can be measured, it was found that all angles were reasonably well described by (2). In this case one can obtain A_{\perp} and g_{\perp} immediately from the $\theta=90^\circ$ spectrum. The results agree very well with those obtained by Wilkins and Gabriel.

For FBr^- , $\theta=90^\circ$ could not be measured. Though the second-order expression (2) was adequate, it appeared that for an accurate description of the $\theta=54.7^\circ$ spectrum it may be necessary to go to fourth order. The $\theta=35.3^\circ$ spectrum, however, can be described quite well by (2).

As for FI^- , only the $\theta=0^\circ$ spectrum was analyzed. The reason is that, because of the large hyperfine and quadrupole interactions, the weakly allowed $|\Delta M_I| = 1$ transitions become increasingly stronger as θ increases and it takes a careful study to assign the lines in Fig. 6(b) and 6(c). Furthermore, since $|P(\text{I})|$ is estimated to be of the order of 70 G, formula (2) may not be adequate for values of θ appreciably different from 0° .

The results of these calculations are given in Table II, together with some representative results on F_2^- , Cl_2^- ,

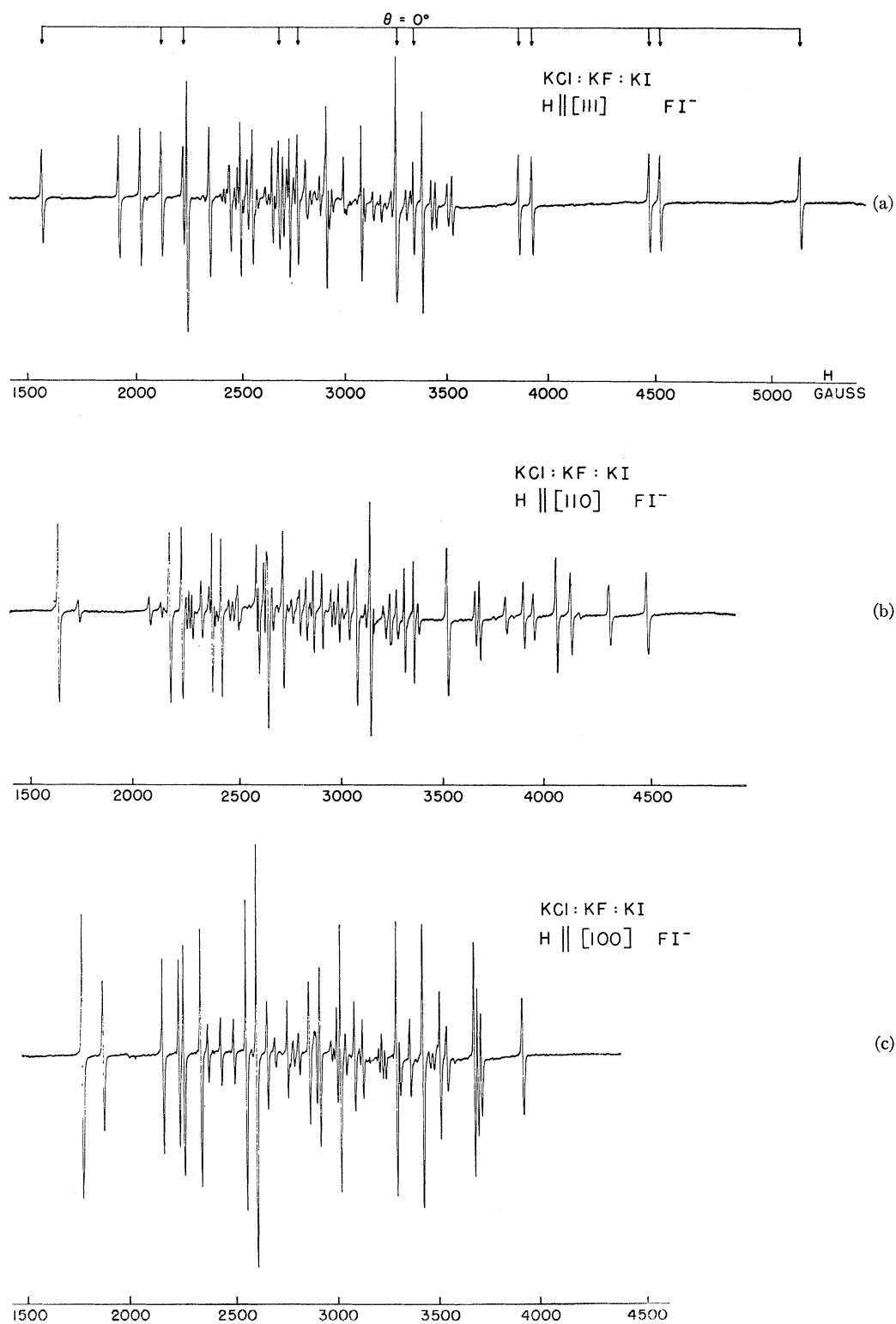


FIG. 6. Experimental spectra of FI^- at 77°K , in a F^- - and I^- -doped KCl crystal for the three important orientations of the magnetic field. The gain is approximately the same for the three spectra. The $\theta = 35.3^\circ, 54.7^\circ, 70.5^\circ$, and 90° spectra were not designated or studied. Strong $\Delta M_I = 1$ transitions are observable in the $\theta \neq 0$ spectra. The microwave frequency is $\nu = 9.124 \text{ kMc/sec}$.

TABLE II. Spin Hamiltonian parameters of $(\text{F}^{19}\text{Cl}^{35})^-$, $(\text{F}^{19}\text{Br}^{81})^-$, and $(\text{F}^{19}\text{I}^{127})^-$ together with some representative results of F_2^- , Cl_2^- , Br_2^- , and I_2^- . Data on FKr and FXe , which are isoelectronic with FBr^- and FI^- , are also included. A , P , and ΔH (linewidth between points of maximum slope) are in gauss. The errors quoted are average errors and are larger for centers with large linewidths.

Crystal	FX^- center	g_{11} (± 0.0005)	g_{\perp} (± 0.002)	$A_{11}(\text{F})$ (± 1)	$A_{\perp}(\text{F})$	$A_{11}(\text{X})$ (± 1)	$A_{\perp}(\text{X})$	$ P(\text{X}) $	ΔH (± 1)
RbCl	FCl^-	2.0020	2.029	+808.2	-77 \pm 5	+125.1	+18 \pm 5	...	8.8
KCl	FCl^-	2.0018	2.030	+805.6	-88 \pm 5	+126.1	+18 \pm 5	$\sim 5\pm 5$	6.5
NaCl	FCl^-	2.0018	2.030	+757.0	-113 \pm 10	+128.1	+16 \pm 5	...	9
RbCl	FBr^-	1.9898	2.123	+735.8	-50 \pm 20	+599.9	+125 \pm 10	...	7.4
KCl	FBr^-	1.9891	2.125	+735.2	-50 \pm 20	+600.9	+123 \pm 10	55 \pm 10	5.1
NaCl	FBr^-	1.9879	2.12	+687	-50 \pm 40	+597	+118 \pm 10	...	15
KBr	FBr^-	1.9903	2.12	+711	-50 \pm 30	+591	+115 \pm 10	...	15
KrF ₄	FKr^a	2.000	2.068	+1260	+271
RbCl	FI^-	1.9359	[2.26] ^b	+632	[~ 0] ^b	+565	+222 \pm 15	[~ 70] ^b	27
KCl	FI^-	1.9363	[2.26] ^b	+636	[~ 0] ^b	+561	+209 \pm 15	[~ 70] ^b	8.4
NaCl	FI^-	1.95	...	~ 600	...	~ 565	21
XeF ₄	FXe^c	1.9740	2.126	+946	+195	+845	+437
KF	F_2^- ^d	2.0020	2.0218	+908.1	-28 \pm 5	2.3
KCl	Cl_2^- ^d	2.0012	2.0426	+101.3	+12.5 \pm 1	9 \pm 1	1.4
KBr	Br_2^- ^d	1.9833	2.169	+450.0	+79 \pm 5	40 \pm 4	3.8
KI	I_2^- ^e	1.913	[2.34] ^b	+387	+100 \pm 15	[~ 50] ^b	11

^a From Ref. 13. ^b Estimated values. ^c From Ref. 12. ^d Recalculated values. ^e E. Boesman, thesis, University of Ghent, 1962 (unpublished).

Br_2^- , and I_2^- . The parameters of FKr^{12} and FXe^{13} which are isoelectronic with FBr^- and FI^- , are also included for comparison. The $H||\langle 111 \rangle$ spectrum of $\text{FCl}^-(2)$ in RbCl was also analyzed. Since $\epsilon \approx 1.5^\circ$ this analysis only gives approximate values of A_{11} and g_{11} ; i.e., $g_{11} = 2.0024$; $A_{11}(\text{F}) = 794$ G; $A_{11}(\text{Cl}) = 125$ G and $\Delta H = 4$ G. A simple analysis of the various parameters occurring in Table II will be given in the next paragraphs.

2. The g Components

The theory of the g components of the homonuclear X_2^- centers^{14,15} can readily be generalized for the heteronuclear XY^- centers. For the X_2^- center the calculation was based on the following part of the molecular configuration:

$$\cdots (\sigma_g)^2 (\pi_u)^4 (\pi_g)^4 (\sigma_u)^1,$$

the unpaired electron occupies the antibonding σ_u orbital and the ground state is ${}^2\Sigma_u^+$. Spin-orbit interaction mixes π_u , and only π_u , into σ_u and as a result the orbital angular momentum makes a nonzero contribution to the g components. In a one-hole description of the molecule ion, a hole occupies the σ_u orbital and π_g , π_u , and σ_g are unoccupied. A spin-orbit coupling constant with a negative sign must then be used.

¹² J. R. Morton and W. E. Falconer, *J. Chem. Phys.* **39**, 427 (1963).

¹³ W. E. Falconer, J. R. Morton, and A. G. Streng, *J. Chem. Phys.* **41**, 902 (1964).

¹⁴ M. L. Cohen, *Phys. Rev.* **101**, 1432 (1956); T. Inui, S. Harasawa, and Y. Obata, *J. Phys. Soc. Japan* **11**, 612 (1956).

¹⁵ For a detailed discussion of the calculation of the various approximations involved see: C. P. Schlichter, *Principles of Magnetic Resonance* (Harper & Row, New York, 1963), pp. 195-215. See also: T. N. Casselman and J. J. Markham, *J. Chem. Phys.* **42**, 4178 (1965).

The previous calculation implicitly assumes that the ground and excited states of the X_2^- molecule ions are well localized states in the crystal and can be described with molecular orbitals centered almost exclusively on the two X nuclei. The ESR results leave no doubt that at least the ${}^2\Sigma_u^+$ ground state is a very well localized state. One expects that the excited ${}^2\Pi_g$, ${}^2\Pi_u$, and ${}^2\Sigma_g^+$ will become progressively less well localized, but recent calculations by Gilbert¹⁶ seem to indicate that even the excited ${}^2\Sigma_g^+$ state of Cl_2^- still lies just above the valence band.

Assuming that approximately the same conclusions hold for the FX^- centers, then by analogy the part of the configuration to be used in the calculation of the g components of FX^- is

$$\cdots (\sigma_1)^2 (\pi_1)^4 (\pi_2)^4 (\sigma_2)^1.$$

The u and g classification does not apply since there is no inversion symmetry any longer and the indices 1 and 2 are for distinguishing between the orbitals.

Since the $\langle 111 \rangle$ -oriented FX^- occupies a single negative ion vacancy the symmetry group of FCl^- and its surroundings is C_{3v} . The degeneracy of the π orbitals is not lifted in such an environment and one expects a purely axial spin-resonance spectrum, which, within experimental error, is indeed observed. Take

$$\begin{aligned} \sigma_2 &= \alpha_F 2s(\text{F}) + \beta_F 2p_z(\text{F}) + \alpha_X ns(\text{X}) + \beta_X np_z(\text{X}), \\ \pi_2 &= \mu_2 2p_{x,y}(\text{F}) + \nu_2 np_{x,y}(\text{X}), \\ \pi_1 &= \mu_1 2p_{x,y}(\text{F}) - \nu_1 np_{x,y}(\text{X}). \end{aligned} \quad (4)$$

$2s(\text{F})$ and $2p(\text{F})$ are the s and p functions of a $2s$ and $2p$ electron of the fluorine atom (or ion), and $ns(\text{X})$

¹⁶ T. L. Gilbert, in International Symposium on Color Centers, Urbana, October 1965, Abstract No. 62 (unpublished).

and $n\dot{p}(X)$ have similar meanings for the ns and $n\dot{p}$ electrons ($n=3, 4, 5$) of $X=\text{Cl, Br, I}$.

The spin-orbit coupling not only mixes π_2 but also π_1 into σ_2 . Extending the theory one calculates

$$\Delta g_{11} = g_{11} - g_0 = - \sum_{k=1}^2 \frac{\lambda_k^2}{E_k^2}, \quad (5)$$

$$\Delta g_1 = g_1 - g_0 = \sum_{k=1}^2 \frac{2\lambda_k \delta_k}{E_k} - \sum_{k=1}^2 \frac{\lambda_k^2 + \lambda_k \lambda_k' \delta_k}{E_k^2}.$$

E_1 and E_2 are the energies of the $\pi_1 \rightarrow \sigma_2$ and $\pi_2 \rightarrow \sigma_2$ excitations, respectively, and

$$\begin{aligned} \lambda_k &= \mu_k \beta_F \lambda_F - (-1)^k \nu_k \beta_X \lambda_X, \\ \lambda_k' &= \mu_k^2 \lambda_F + \nu_k^2 \lambda_X, \\ \delta_k &= \mu_k \beta_F - (-1)^k \nu_k \beta_X, \end{aligned} \quad (6)$$

where λ_F and λ_X are the spin-orbit coupling constants of a $2p$ and $n\dot{p}$ electron of F and $X=\text{Cl, Br, I}$, respectively. From atomic data,^{17,1} one deduces: $\lambda_F = +269 \text{ cm}^{-1}$; $\lambda_{\text{Cl}} = +587 \text{ cm}^{-1}$, $\lambda_{\text{Br}} = +2456 \text{ cm}^{-1}$, and $\lambda_{\text{I}} = +5068 \text{ cm}^{-1}$.

Since formulas (5) and (6) contain too many unknown parameters, they are at this stage of limited quantitative value, but they agree at least qualitatively with the experimental results. For homonuclear X_2^- molecule ions, the terms in E_2 are zero and one expects therefore that in the FX^- case this contribution will be small compared to the terms in E_1 , though not necessarily negligible. Considering only the contribution in E_1 one can easily see that (5) predicts $\Delta g_1 = g_1 - g_0$ for the FX^- molecule ions to be about halfway in between the Δg_1 's of F_2^- and X_2^- . Inspection of Table II shows that this is indeed the case, so qualitatively at least, the g components contain no unusual features.

3. The Hyperfine Components

The hyperfine part of spin Hamiltonian (1) is given by $\langle \sigma_2 | \mathcal{H}_{\text{HFS}} | \sigma_2 \rangle$ where σ_2 is the orbital part of the ground-state wave function given in (4) and

$$\mathcal{H}_{\text{HFS}} = \sum_{i=1}^2 g_0 \beta \left[\frac{\mu_i \left[(\mathbf{L}_i - \mathbf{S}) \cdot \mathbf{I}_i \right]}{r_i^3} + 3 \frac{(\mathbf{r}_i \cdot \mathbf{S})(\mathbf{r}_i \cdot \mathbf{I}_i)}{r_i^5} + \frac{8\pi}{3} \delta(r_i) \right]. \quad (7)$$

Here, \mathbf{L}_i , \mathbf{S} , \mathbf{I}_i are, respectively, the orbital-angular-momentum-, the electron-spin, and the nuclear-spin operators; \mathbf{r}_i is the position vector of the unpaired electron, g_0 the free-electron g factor, β the Bohr magneton, and μ_i the nuclear moment. Since the ground state is an orbital singlet, this procedure yields only a zero-order approximation, since the term in $\mathbf{L}_i \cdot \mathbf{I}_i / r_i^3$ does not contribute anything. However the

calculation of the g components shows that mixing of excited states into the ground state, predominantly through spin-orbit interaction, leads to an appreciable nonzero contribution of the orbital angular momentum to the g shifts. Similarly, there should be a non-negligible contribution to the hyperfine components from $\mathbf{L}_i \cdot \mathbf{I}_i / r_i^3$ and consequently \mathcal{H}_{HFS} has to be computed between spin-orbit corrected wave function. The result of the calculation to first order can be put in the following somewhat simplified form:

$$A_{11,i} = A_i + 2\rho_i, \quad A_{1,i} = A_i - \rho_i + \frac{5}{2} \Delta g_1 \rho_i, \quad i = \text{F, X}, \quad (8)$$

where

$$\begin{aligned} A_i &= (8\pi/3) (\mu_i / I_i) \beta_i^2 |ns(0)|^2 \\ \rho_i &= \frac{2}{5} (\mu_i / I_i) \alpha_i^2 \langle r_i^{-3} \rangle_{np} \end{aligned} \quad (9)$$

and $n=2, 3, 4, 5$ for F, Cl, Br, I.

In order to analyze the experimental results of Table II with formulas (8) one needs to know the signs of $A_{11,i}$ and $A_{1,i}$. The spin-resonance data alone yield $|A_{11}|$ and $|A_1|$. Since $\mu_i > 0$ for the F and X nuclei, it is clear from (8) that $A_{11,i} > 0$. However, depending upon the relative magnitudes of A_i and ρ_i , $A_{1,i}$ may be either > 0 or < 0 .

We will present some arguments supporting the fact that $A_{11}(\text{F}) > 0$ and $A_1(\text{F}) < 0$ for F_2^- and all FX^- while $A_{11}(X) > 0$ and $A_1(X) > 0$ for FX^- and all X_2^- . In the case of Cl_2^- , ClBr^- , and Br_2^- it has been established⁸ that A_{11} and A_1 are both > 0 . This conclusion was based first on the comparison of the experimentally determined value of ρ with the computed value of ρ [from (9)] using reliable $\langle r^{-3} \rangle_{np}$ values from atomic data, and second, on the study of the changes in A_{11} and A_1 going through the series of salts RbX to LiX . For instance, $(|A_{11}|, |A_1|)$ of Cl_2^- changes from $(|102|, |13|)$ in RbCl to $(|96|, |10|)$ in LiCl with the values in KCl and NaCl in between these.⁸ If A_{11} and A_1 are both taken to be > 0 one calculates from (8) that both ρ and A increase going from LiCl to RbCl . The value of A increases about 30% but ρ increases only about 1 or 2%. To a first approximation ρ may be considered to be constant with respect to A . These changes in ρ and A are physically acceptable and can be attributed to changes in the s - p hybridization of the ground-state wave function brought about by the changing crystal-line field going from RbCl to LiCl . Since ρ , through $\langle r^{-3} \rangle$, depends on the total radial part of the ground-state wave function, sizeable changes in this wave function must occur in order to change the value of ρ appreciably. A , on the other hand, depends only upon the amount of s character in the ground state. Since this amount is small to start with (see Table III), even a minor change of s character (with respect to the total wave function) will have a strong influence upon the hyperfine components. Quite likely it is primarily the change in A , not ρ , that determines the change of the hyperfine components.

If it is assumed that $A_{11} > 0$ and $A_1 < 0$, then A and ρ not only change in opposite directions, but the change

¹⁷ M. Blume and R. E. Watson, Proc. Roy. Soc. (London) A271, 565 (1963).

TABLE III. Result of the analysis of the hyperfine components occurring in Table II using formulas (8) and (9) and the data of Table IV

Crystal	FX ⁻ center	A _F	ρ _F	A _X	ρ _X	α _F ²	β _F ²	α _F ² +β _F ²	α _X ²	β _X ²	α _X ² +β _X ²	∑ _{i=F,X} (α _i ² +β _i ²)
RbCl	FCl ⁻	204	302	52.1	36.5	0.012	0.559	0.561	0.031	0.695	0.726	1.287
KCl	FCl ⁻	198	304	52.5	36.8	0.011	0.562	0.573	0.032	0.700	0.732	1.305
NaCl	FCl ⁻	163	297	51.7	38.2	0.009	0.549	0.558	0.031	0.727	0.758	1.316
RbCl	FBr ⁻	154	291	248	176	0.009	0.538	0.547	0.030	0.716	0.746	1.293
KCl	FBr ⁻	153	291	247	177	0.009	0.538	0.547	0.030	0.720	0.750	1.297
NaCl	FBr ⁻	141	273	243	177	0.008	0.505	0.513	0.027	0.720	0.747	1.260
KBr	FBr ⁻	145	283	239	176	0.008	0.523	0.536	0.027	0.716	0.743	1.279
KrF ₄	FKr	564	348	0.033	0.644	0.677
RbCl	FI ^{-a}	94	269	273	146	0.005	0.498	0.503	0.037	0.684	0.721	1.224
KCl	FI ^{-a}	98	269	261	150	0.006	0.498	0.504	0.035	0.703	0.738	1.242
XeF ₄	FXe	388	279	541	152	0.022	0.516	0.538
KF	F ₂ ⁻	274	317	0.016	0.586	0.602	1.204
KCl	Cl ₂ ⁻	39.9	30.6	0.024	0.582	0.606	1.212
KBr	Br ₂ ⁻	162	144	0.019	0.586	0.605	1.210
KI	I ₂ ^{-a}	147	120	0.020	0.563	0.583	1.166

^a Analysis partly based on estimated parameters (see Table II).

of ρ is actually bigger than*the change of A . Such a behavior cannot be easily understood, and furthermore the value of ρ obtained in this way shows a strong discrepancy with the theoretical computed value. Exactly the same behavior has been observed experimentally for ClBr⁻, Br₂⁻, and I₂⁻, where it was also established that $A_{11} > 0$ and $A_1 > 0$. Keeping in mind the near constancy of ρ with respect to A and looking at (8), one can formulate the following rule: *If for the same molecule ion (X₂⁻ or XY⁻) in different crystals $|A_{11,i}|$ and $|A_{1,i}|$ vary in the same sense (i.e., they both decrease or increase together) then $A_{11,i}$ and $A_{1,i}$ have the same sign; if, however, $|A_{11,i}|$ and $|A_{1,i}|$ vary in the opposite sense, then $A_{11,i}$ and $A_{1,i}$ have opposite signs.* The changes, of course, have to be distinct and outside experimental error, and allowance has to be made for the higher order corrections.

The last case is observed for the fluorine hyperfine components of F₂⁻ and FX⁻. Bailey¹⁸ has determined, and we have verified, that ($|A_{11}|$, $|A_1|$) for F₂⁻ varies from ($|887|$, $|58|$) to ($|908|$, $|28|$) going from LiF to KF. Applying the rule one concludes that $A_{11} > 0$ and $A_1 < 0$ considering also that $\mu_F > 0$. This trend continues for the fluorine hyperfine components of FX⁻ (see Table II), so that also in these cases $A_{11}(F) > 0$ and $A_1(F) < 0$. Furthermore, this choice of signs gives the best continuity between F₂⁻ and FX⁻. Similar arguments show that $A_{11}(X) > 0$ and $A_1(X) > 0$ for the X = Cl, Br, I hyperfine components of FX⁻.

In the case of FI⁻, $A_1(F)$ and g_1 could not be determined experimentally, but looking at the trends in Table II, one can make a rough estimate which has been included in the table. Knowing the signs of $A_{11,i}$ and $A_{1,i}$ and using the experimental g shifts, one can solve Eq. (8) for A_i and ρ_i . The results are summarized in Table III. From the knowledge of A_i and ρ_i and using

¹⁸ C. E. Bailey, Phys. Rev. **136**, A1311 (1964).

(9) one can calculate the amount of s and p character, i.e., α_i^2 and β_i^2 , ($i = F, X$) at each atom of the molecule ions if one knows $\langle r_i^{-3} \rangle_{np}$ and $|ns(0)|^2$. There are two main sources for $\langle r_i^{-3} \rangle_{np}$ values. One can either calculate them with Hartree-Fock functions or extract them from experimental atomic data.

For Cl, Br, and I, experimental values of $\langle r_i^{-3} \rangle_{np}$ can be obtained from the atomic-beam results. These values are given in the first column of Table IV. The second and third columns give $\langle r_i^{-3} \rangle_{np}$ and $|ns(0)|^2$ values calculated from atomic wave functions. The results derived from the various analytical Hartree-Fock functions obtained by Bagus, Mayers, and Watson and Freeman are quite consistent and the computed $\langle r_i^{-3} \rangle_{np}$ agree very well with the experimental $\langle r_i^{-3} \rangle_{np}$. However, $\langle r_i^{-3} \rangle_{np}$ and $|ns(0)|^2$ values calculated from the somewhat less accurate Hartree-Fock-Slater functions, obtained by Herman and Skillman, are systematically

TABLE IV. Compilation of $\langle r_i^{-3} \rangle_{np}$ and $|ns(0)|^2$ values of the halogen atoms (in 10²⁴ cm⁻³).

	$\langle r_i^{-3} \rangle_{np}$ (expt.)	$\langle r_i^{-3} \rangle_{np}$ (calc.)	$ ns(0) ^2$ (calc.)	$\langle r_i^{-3} \rangle_{np}$ Values used in this paper	$ ns(0) ^2$
F	...	50.9 ^d 50.9 ^e 57 ^h	75.0 ^d 80.8 ^e 85 ^h	50.9	78.0
Cl	49.5 ^a	45.6 ^d 45.5 ^f 50 ^h	71.7 ^d 71.8 ^f 86 ^h	47.5	71.8
Br	80.5 ^b	80.0 ^g 92 ^h	131.0 ^g 163 ^h	80.2	131
I	94.0 ^c	113 ^h	200 ^h	94.0	155

^a V. Jaccarino and J. G. King, Phys. Rev. **83**, 471 (1951); **84**, 852 (1951).
^b J. G. King and V. Jaccarino, Phys. Rev. **94**, 1610 (1954); H. H. Brown and J. G. King, *ibid.* **142**, 53 (1966).

^c V. Jaccarino, J. G. King, and R. A. Satten, Phys. Rev. **94**, 1798 (1954).
^d P. S. Bagus, Phys. Rev. **139**, A615 (1965).

^e D. F. Mayers, as quoted in Ref. 12.
^f R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961).
^g R. E. Watson and A. J. Freeman, Phys. Rev. **124**, 1117 (1961).

^h F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

TABLE V. Experimental $\langle r_i^{-3} \rangle$ and $|\psi_i(0)|^2$ values for the molecular ground state of the FX^- and X_2^- molecule ions (in 10^{24} cm^{-3}).

FX^- or X_2^-	$\langle r_F^{-3} \rangle$	$\langle r_X^{-3} \rangle$	$ \psi_F(0) ^2$	$ \psi_X(0) ^2$
F_2^-	29.9	...	1.23	...
FCl^-	28.3	33.6	0.85	2.25
FBr^-	26.8	57.9	0.67	3.81
FI^-^a	25.3	65.2	0.43	5.62
Cl_2^-	...	27.8	...	1.73
Br_2^-	...	47.1	...	2.53
$I_2^-^a$...	52.9	...	3.09

^a Results partly based on estimated parameters (see Table II).

10 to 20% higher than the previous values. Therefore, in the final choice of $\langle r^{-3} \rangle_{np}$ and $|ns(0)|^2$, as given in the last two columns of Table IV, these values were not taken into consideration. However, they did permit one to make an estimate of $|5s(0)|^2$ of the I atom.

In the original treatment of the X_2^- center,¹ $|\psi(0)|^2$ values were used halfway between $|ns(0)|^2$ and $|(n+1)s(0)|^2$. Since $|ns(0)|^2/|(n+1)s(0)|^2 \approx 10$, such a procedure leads to values of the s character α_i^2 that are too large. It appears that using only $|ns(0)|^2$ is preferable. This in turn may underestimate the s character somewhat but probably to a lesser extent than the original procedure overestimates it. With these $\langle r^{-3} \rangle_{np}$ and $|ns(0)|^2$ values, α_i^2 and β_i^2 are easily calculated. The results are summarized in Table III together with $\alpha_i^2 + \beta_i^2$. If overlap is neglected, $\sum_{i=F,X}(\alpha_i^2 + \beta_i^2)$ should equal 1. However, this is a crude approximation and if overlap in normalization is included then: $\sum(\alpha_i^2 + \beta_i^2) \cong 1 - 2\alpha_F\alpha_X S$ where $S = \int p_z(F)p_z(X)d\tau$ is the overlap integral. Since on the average $\sum(\alpha_i^2 + \beta_i^2) = 1.28$, one calculates that $S = -0.23$ which is the right sign and about the right magnitude for the antibonding ground orbital.

The α_i^2 and β_i^2 values show two definite trends. First, the hole density $\alpha_i^2 + \beta_i^2$ shifts progressively away from F towards X in FX^- with $X = Cl, Br, I$ in that order. The greater part of this shift is undoubtedly caused by the increasing difference in electronegativity between F and X, which results in a progressively higher hole density on X in FX^- . The electronegativities of the halogens are¹⁹ $\chi_F = 11.4$ eV, $\chi_{Cl} = 8.9$ eV, $\chi_{Br} = 8.2$ eV, and $\chi_I = 7.5$ eV. Within certain limits the ionicity i of a bond is proportional to the difference in electronegativity of the two atoms involved.^{20,21} For the FX^- centers $i \cong (\alpha_X^2 + \beta_X^2) - (\alpha_F^2 + \beta_F^2)$ and one should have

$$i \cong C(\chi_F - \chi_X).$$

Using the values of χ given above and the results of Table III, one easily verifies that this relation is reasonably obeyed, probably somewhat fortuitously, by the three molecule ions with $C = 0.067 \text{ eV}^{-1} \pm 0.010 \text{ eV}^{-1}$.

¹⁹ G. Klopman, J. Chem. Phys. **43**, 124 (1965).

²⁰ M. A. Whitehead and H. H. Jaffe, Theoret. Chim. Acta **1**, 209 (1963).

²¹ O. C. Hoffer and R. Ferreira, J. Phys. Chem. **70**, 85 (1966).

The second trend one observes in Table III is that the s character on F decreases going from F_2^- to FCl^- to FBr^- to FI^- , while the s/p ratio on X increases going from Cl_2^- to FCl^- or from Br_2^- to FBr^- or from I_2^- to FI^- . These trends are also evident from Table V where the experimental $\langle r_i^{-3} \rangle$ and $|\psi_i(0)|^2$ values [for which $\beta_i^2 \langle r^{-3} \rangle_{np}$ and $\alpha_i^2 |ns(0)|^2$ in (9) are only approximations] for the molecular ground state of the FX^- and X_2^- molecule ions are presented. The numbers for FCl^- , FBr^- , and FI^- in this table are average values.

These effects have also been observed in the Cl_2^- , $ClBr^-$, Br_2^- series³ and the following rules can be formulated: if the electronegativity of X is greater than Y, then (1) the hole density is greater on Y than on X in XY^- , and (2) the s/p ratio on X decreases going from X_2^- to XY^- while the s/p ratio on Y increases going from Y_2^- to XY^- .

Expressions (4) represent only the lowest approximation to the molecular orbitals and should be supplemented in a more accurate quantitative treatment with other s -, p -, and even d -type wave functions. Furthermore, exchange polarization contributions were neglected. Nevertheless, the results of the foregoing hyperfine analysis appear to be quite reasonable and should give at least a good qualitative idea of the behavior of these molecule ions.

The hyperfine components of these molecule ions are temperature-dependent. It was observed that they decrease with increasing temperature. For instance at 110°K, where the linewidth has increased to about 15 G, the values for FI^- are

$$\begin{aligned} A_{11}(F) &= 628 \text{ G}, \\ A_{11}(I) &= 558 \text{ G}, \\ A_{12}(I) &= 210 \text{ G}. \end{aligned}$$

This temperature dependence is a general property which has been observed for all the X_2^- and XY^- centers, and is probably connected with the increasing internuclear distance of the X_2^- and XY^- molecule ions brought about by the expansion of the lattice as the temperature is raised. Recently, Dreybodt²² has made a study of this effect for FCl^- in KCl .

The heteronuclear FX^- molecule ions possess an electric dipole moment $\mu(FX^-)$ and the results of Table III leave no doubt that the sign of this dipole moment corresponds to $(F^{(-)}X^{(+)})^-$. The knowledge of the ionicity i permits one to make a crude estimate of $\mu(FX^-)$ provided the internuclear distance r is also known. The relation is $\mu(FX^-) = i|e|r$ in which e is the electronic charge. Person²³ has made an estimate of r for Cl_2^- , Br_2^- , and I_2^- . By comparing these with the internuclear distances of the neutral F_2 , Cl_2 , Br_2 , and I_2 molecules²⁴ an extrapolation can be made to estimate

²² W. Dreybodt, Phys. Letters **19**, 274 (1965).

²³ W. B. Person, J. Chem. Phys. **38**, 109 (1963).

²⁴ G. Herzberg, *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules* (D. Van Nostrand, Inc., Princeton, New Jersey, 1950).

r for F₂⁻ and it is found that $r=2.2$ Å, 2.6 Å, 2.8 Å, and 3.1 Å for F₂⁻, Cl₂⁻, Br₂⁻, and I₂⁻ in that order. If it is assumed that r of FX⁻ should be an average of the r 's of F₂⁻ and X₂⁻ one obtains $r=2.4$ Å, 2.5 Å, and 2.7 Å for FCl⁻, FBr⁻, and FI⁻, respectively. In the same order, the average ionicities in Table III are $i=0.18$, 0.20, 0.23. Consequently $\mu(\text{FCl}^-)=2.1$ D, $\mu(\text{FBr}^-)=2.4$ D, and $\mu(\text{FI}^-)=3.0$ D. In view of the various approximations and uncertainties, these values represent only crude estimates of the electric dipole moments. The order of magnitude appears to be reasonable since for the neutral molecules²⁵: $\mu(\text{FCl})=0.88$ D and $\mu(\text{FBr})=1.29$ D. Primarily because of the difference in internuclear distance one does indeed expect $\mu(\text{FX}^-) > \mu(\text{FX})$.

4. The Quadrupole Term

In previous work on the electron spin resonance of the FCl⁻ and X₂⁻ centers,^{6,1} quadrupole effects were not analyzed. They are, however, quite measurable especially for the Br nuclei. The Cl₂⁻ and Br₂⁻ spectra were reanalyzed with the specific purpose of obtaining $|P(\text{Cl})|$ and $|P(\text{Br})|$ so that they could be compared with the same quantities for FCl⁻ and FBr⁻. The experimental results distilled out of the second-order shifts are given in Table II.

It is interesting to compare these $P(X)$'s with the theoretically computed values. The term $P_2 I_{2,2}^2$ in spin Hamiltonian (1) is obtained to a first approximation by averaging

$$\mathcal{H}_Q = \frac{e^2 Q_2}{2I_2(2I_2-1)} \left[\frac{I_2(I_2+1)}{r_2^3} - 3 \frac{(\mathbf{r}_2 \cdot \mathbf{I}_2)^2}{r_2^5} \right]$$

over the ground orbital σ_2 of the unpaired hole. Q_2 is the quadrupole moment of nucleus $X=\text{Cl, Br, I}$. One finds that

$$P_2 \text{ or } P(X) = \frac{12}{5} \frac{e^2 Q_2}{2I_2(2I_2-1)} \frac{\alpha_2^2 \langle r_2^{-3} \rangle_{np}}{g_0 \beta},$$

where $P(X)$ is expressed in gauss. Using $Q(\text{Br}^{81})=0.25 \times 10^{-24}$ cm² and $Q(\text{Cl}^{35})=-0.08 \times 10^{-24}$ cm² and the results of Tables III and IV, one calculates that $P(\text{Cl})=-11.3$ G for Cl₂⁻ and $P(\text{Cl})=-13.9$ G for FCl⁻. Similarly $P(\text{Br})=+65.1$ G for Br₂⁻ and $P(\text{Br})=+81.1$ G for FBr⁻. The absolute values are somewhat larger than the experimental ones as given in Table II, but the agreement is probably not so bad considering the fact that Sternheimer effects²⁶ were neglected. This modest agreement suggests that one can make a rough estimate of $P(\text{I})$ which so far has not been experimentally determined. Using $Q_{\text{I}}=-0.59 \times 10^{-24}$ cm² one estimates that the experimental $|P(\text{I})|$ values of I₂⁻ and FI⁻ should be in the range of 50 to 70 G. This

rough estimate has been included in Table II, and should provide useful starting values in a more complete quantitative analysis of the I₂⁻ and FI⁻ spin-resonance spectra for which up to now only the $\theta=0^\circ$ spectra have been analyzed.⁵

V. DISCUSSION

The fact that the molecular axes of the FCl⁻, FBr⁻, and FI⁻ centers are oriented exactly along a (111) direction leaves little doubt that these molecule ions occupy only one single negative-ion vacancy, i.e., the FX⁻ centers involve an interstitial. They may be thought of as the heteronuclear equivalents of the H center, a homonuclear X₂⁻ molecule ion occupying a single negative-ion vacancy²⁷; however, there are two important differences. First, an H center is (110) oriented, while the FX⁻ centers are (111) oriented. Second, an H center also interacts weakly with two other X nuclei in the (110) direction, but no analogous effect is observed for the FX⁻ centers.

The differences in orientation and interaction may be associated with the difference between a homonuclear and heteronuclear molecule ion. By sharing its hole somewhat with two other X⁻ ions in the (110) direction, the crowding is reduced. Obviously, this can only occur with the X₂⁻ molecule ion is (110) oriented. For the heteronuclear FX⁻ molecule ions, on the other hand, it is conceivable that the crowding can be reduced by a redistribution of the hole density within the molecule ion itself, i.e., by a shift to X, the larger component, and away from F, the smaller component. Quite possibly the most favorable condition for this to occur is when the molecular axes are oriented along (111). The analysis of the hyperfine components shows that the shift in hole density was indeed away from F towards X. Also this shift is more pronounced in NaCl where presumably the FX⁻ has less room than in KCl or RbCl.

The spin-resonance results do not indicate where the F and X nuclei lie with respect to the center of the negative-ion vacancy. Intuitively, because of its initial smaller size, one would expect the fluorine to be the more interstitial.

A posteriori the (111) orientation of the FX⁻ centers may not seem so unusual, but *a priori*, by comparison with the (110)-oriented ClBr⁻,^{7,8} one would have expected the formation of (110)-oriented FCl⁻ molecule ions, occupying two negative-ion vacancies. The temperature of irradiation, which was always 77°K in this work, may be important in this connection. It is planned to investigate whether or not (110)-oriented FCl⁻ can be produced by x irradiation at lower temperatures. It should be mentioned that the FCl⁻, after having been produced at 77°K, keeps its (111) orientation when cooled to 4.2°K; there is no change in orientation or symmetry.

²⁵ A. L. McClellan, *Tables of Electric Dipole Moments* (W. H. Freeman and Company, San Francisco, 1963).

²⁶ R. M. Sternheimer, *Phys. Rev.* **95**, 736 (1954).

²⁷ W. Känzig and T. O. Woodruff, *J. Phys. Chem. Solids* **9**, 70 (1958).

All the $\langle 111 \rangle$ -oriented centers described here involve a fluorine component. It is conceivable, however, that at suitably low temperatures other $\langle 111 \rangle$ -oriented molecule ions may be produced, e.g., $\langle 111 \rangle$ -oriented ICl^- might be formed in Cl^- -doped KI or RbI . The spin-resonance spectrum of $\langle 111 \rangle$ -oriented ClBr^- has not been detected at 77°K in Cl^- -doped KBr , but recent optical absorption measurements on this type of crystal at temperatures around 4.2°K have indicated the presence of interstitial Cl^- ions after x irradiation.²⁸ Thus, by a suitable treatment it may be possible to form $\langle 111 \rangle$ -oriented ClBr^- .

Two production mechanisms for FCl^- in F^- -doped KCl have been discussed by Wilkins and Gabriel.⁶ They were based on the following two possibilities. The F^- ions are dissolved either interstitially or substitutionally in the lattice. In the first mechanism they suggested that the x rays ionize the interstitial F^- ion, forming an interstitial fluorine atom F_i^0 which combines with an adjacent Cl^- ion producing a $\langle 111 \rangle$ -oriented FCl^- . In the second mechanism the substitutional F^- ion F_s^- is ionized and moves from its substitutional into an interstitial position. This F_i^0 atom might move a few lattice spacings and form FCl^- , leaving behind a negative-ion vacancy (α center). The very weak $\text{FCl}^-(2)$ center observable in KCl and RbCl has been ascribed⁶ to an FCl^- molecule ion formed close to the negative-ion vacancy. There is however a third possible mechanism and a potentially important one: Cl_i^0 may be produced by ionization of a Cl_s^- . The Cl_i^0 may migrate until it encounters an F_s^- and forms $\langle 111 \rangle$ -oriented FCl^- . Also in this case negative-ion vacancies or α centers are formed. Since optical absorption measurements show that FCl^- and the α band are formed together,⁶ the second and/or third mechanisms do occur to a sizeable extent. In fact they are probably the only possible mechanisms, since there is strong experimental evidence that the first one cannot take place. Indeed if F_i^- were present to any measurable extent, optical bleaching of Cl_2^- in $\text{KCl}:\text{KF}$, or Br_2^- in $\text{KBr}:\text{KF}$ should increase the FCl^- or FBr^- concentration, since F_i^- is negatively charged with respect to the lattice and is therefore expected to have a strong attraction for holes. It is observed that optical bleaching of Cl_2^- or Br_2^- does not increase the FCl^- or FBr^- concentration. Consequently the first mechanism, it seems, cannot occur, but the experimental evidence to date does not permit one to make a choice between the second and third mechanism. It is conceivable that they both contribute to the FCl^- formation.

The formation of FBr^- and FI^- in KCl is intimately connected with the decay of FCl^- . The FCl^- center decays rapidly and irreversibly at 170°K in KCl , and no other center is formed except when Br^- or I^- ions

are present. If Br^- or I^- is present in the crystal, $\langle 111 \rangle$ -oriented FBr^- or FI^- centers are produced. The conditions under which FBr^- and FI^- are formed strongly point to the fact that FCl^- dissociates according to the reaction $\text{FCl}^- \rightarrow \text{Cl}_s^- + \text{F}_i^0$ after which the fluorine atom moves interstitially through the lattice. F_i^0 can combine with an F^- center to form a substitutional F^- ion again or be trapped by a substitutional Br^- or I^- ion to form $\langle 111 \rangle$ -oriented FBr^- or FI^- . This explanation for the formation of FBr^- and FI^- appears by far to be the most acceptable one. One could also assume that there is a large preferential association of F^- and Br^- or I^- ions in a single negative-ion vacancy. In this case the FCl^- must decay by losing its hole, leaving behind an interstitial F^- ion. The hole would move through the crystal as Cl_2^- until it encounters the $(\text{F}^-, \text{Br}^-)$ or (F^-, I^-) pairs, producing FBr^- or FI^- . However, such a mechanism appears to be impossible, since at the temperature where FCl^- starts to decay slowly, i.e., 150°K , the Cl_2^- center is still completely immobile. Even at 170°K where FCl^- decays very rapidly (\sim two minutes) the Cl_2^- barely starts to move.^{3,4}

A third decay mechanism which one could devise is $\text{FCl}^- \rightarrow \text{F}_s^- + \text{Cl}_i^0$. In this case there would have to be a large preferential association of F^- and Br^- or I^- ions in two neighboring substitutional sites. The Cl_i^0 would then exchange its hole with the F_s^- , take its place, and the resulting F_i^0 would then combine with the neighboring Br^- or I^- to form FBr^- or FI^- . This possibility cannot be excluded, but the first suggested decay mechanism for FCl^- seems to be the most appealing one if only because of its simplicity.

The decay mechanisms for FBr^- and FI^- can be inferred from the previous considerations. First it should be remarked that the fact that FBr^- and FI^- are progressively more stable thermally than FCl^- (see Fig. 2) is probably connected with the progressive increase of the electronegativity difference between F and Cl , Br , or I . The decay of FBr^- probably proceeds as follows: $\text{FBr}^- \rightarrow \text{Br}_s^- + \text{F}_i^0$ and similarly for FI^- : $\text{FI}^- \rightarrow \text{I}_s^- + \text{F}_i^0$. Again the moving F_i^0 may combine with an F^- center to form F_s^- .

Finally a word should be said about the optical absorption bands of the FX^- centers. Preliminary optical measurements have shown that FCl^- , FBr^- , and FI^- in KCl have absorption bands whose peaks lie at 300, 294, and 275 $\mu\mu$, respectively.⁹ By analogy with the X_2^- centers,^{3,4} these bands arise undoubtedly from the ${}^2\Sigma_2 \rightarrow {}^2\Sigma_1$ charge-transfer transitions within the molecule ions.

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²⁸ N. Itoh, B. S. H. Royce, and R. Smoluchowski, in International Symposium on Color Centers, Urbana, October 1965, Abstract No. 94 (unpublished).